



## **BIOOIL UPGRADING MODELLING**

Lappeenranta–Lahti University of Technology LUT

Master's thesis

Erasmus Mundus Joint Master's in Sustainable Biomass and Bioproduct Engineering

2024

Diseye Deborah Egberike

Examiner(s): Professor, Kristian Melin

Professor, Toumas Koironen

## ABSTRACT

Lappeenranta–Lahti University of Technology LUT  
LUT School of Engineering Sciences  
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In co-operation with partner university/universities: Wroclaw University of Science and Technology (WUST) and Universidad de Castilla - La Mancha

Diseye Deborah Egberike

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### Abstract

The ever-increasing demand for energy on a global scale, in conjunction with the negative impact that fossil fuels have on the environment, has prompted the investigation of possible sustainable alternatives. The introduction of bio-oils, which are produced through pyrolysis and hydrothermal liquefaction from biomass, is an intriguing potential resolution. In order to improve the usefulness of bio-oils as renewable energy sources, this thesis investigates the upgrading and modelling of bio-oils to enhance their utility as renewable energy sources.

Bio-oils possess complex compositions, including high oxygen content, which affects their stability and energy density. The study focuses on optimizing pyrolysis processes and upgrading techniques to improve bio-oil quality. Through detailed process simulations using Aspen Plus, key parameters such as temperature and pressure usage are analysed to maximize yield and quality. The findings indicate that specific operating conditions can significantly reduce undesirable by-products and enhance bio-oil properties, making it a viable alternative to conventional fossil fuels. This research contributes to the development of efficient bio-oil production and upgrading methods, promoting a sustainable energy future.

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## **List of Abbreviations**

HTL – Hydrothermal Liquefaction

HTT – Hydrotreating

HDO – Hydrodeoxygenation

HPH – High-Pressure Homogenization

NREL – National Renewable Energy Laboratory

HHV – High Heating Value

EOS – Equation of State

GHG – Green House Gas

LTLP – Low Temperature and Low Pressure

HTHP – High Temperature and High Pressure

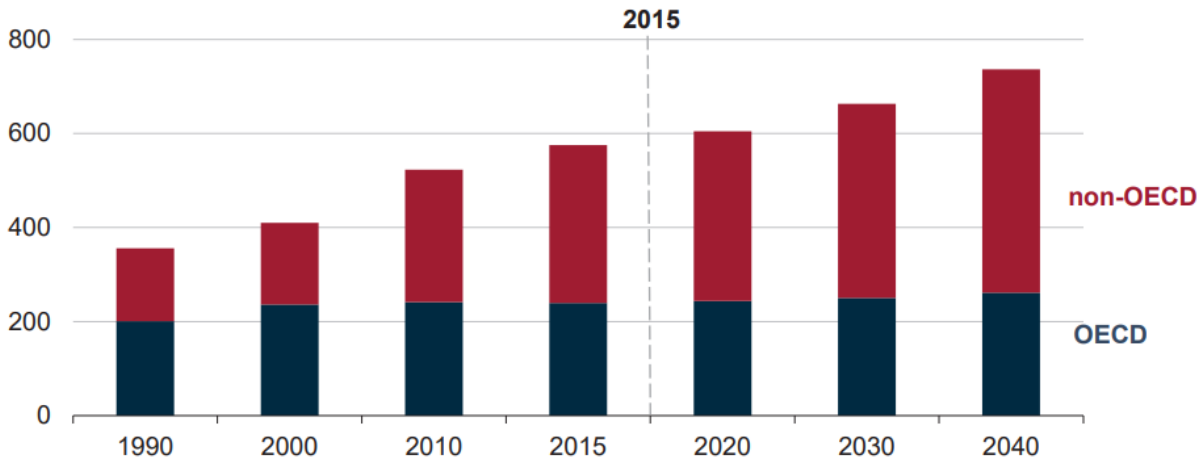
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## 1.0 Introduction

The globe is in need of energy, and this demand is growing every day due to population demands. Although fossil fuels are still one of the key sources of energy, they are not the most demanded. Petrol and diesel are two examples of traditional fossil fuels that are extensively relied upon by the transportation industry [1]. In accordance with the International Energy Outlook for the year 2017, usage of energy on a global scale is expected to increase by 28% between 2015 and 2040 [59].



**Figure 1:** World energy consumption

A significant portion of the world's overall energy consumption is attributed to the wide variety of fossil fuels, which include coal, natural gas, and crude oil, among others [2]. It's important to note that fossil fuels are finite, and their use has detrimental effects on the environment, such as the progressive rise in atmospheric carbon dioxide concentrations. It is imperative that the globe transition to renewable energy sources in order to preserve fossil fuels and reduce the harmful impact that they have on the environment.

Due to the increased demand for energy, renewable energy sources are becoming increasingly significant. In order to address this issue, the applications of energy research that are currently being conducted concentrates on sustainable energy conversion technologies and renewable energy sources [3]. For a number of reasons, including the limited supply of non-renewable energy sources and the negative impacts on the environment that are brought about by the combustion of fossil fuels, there has been a surge in the demand for renewable energy sources. Biofuels, and more specifically bio-oils obtained from biomass pyrolysis processes, have emerged as a significant source of renewable energy due to their renewable nature, non-toxic nature, biodegradable nature, and the possibility that they may be derived from biological waste processes [4–9].

Biomass is a versatile source of feedstock, depending on the technical method that is selected, can be converted into a variety of different types of energy, including bio-oils. The properties of the raw material and the intended energy form have a significantly influenced by the characteristics of the raw material as well as the form of energy that is desired to be produced. [10]. Numerous conversion methods have evolved in response to the desire for alternate fuels. Pyrolysis and hydrothermal liquefaction are two kinds of thermochemical conversion processes which provide a feasible way to manufacture liquid fuel from biomass. Bio-oils generated using this kind of technology are thought to be a feasible replacement for regular petroleum fuels

these bio-oils have the potential to be utilised for the generation of electricity, the heating of homes, and the extraction of chemical compounds. Hydrothermal liquefaction and flash pyrolysis are the two essential processes that are being utilised in converting biomass into bio-oil (Xiu & Shahbazi, 2012).

The phenomenon of flash pyrolysis involves rapidly heating organic compounds to high temperatures without oxygen, resulting in their swift disintegration. This procedure produces liquids, gases, and char. In contrast, HTL is a method that involves subjecting biomass to high pressures and temperatures in water, with or without a catalyst [12]. It is better suited to biomass of aquatic origin as it can withstand high moisture levels. Although there have been extensive efforts to develop pyrolysis processes to produce bio-oil in the past decade [13,14], HTL technology is still in its preliminary stages of development. The comprehensive analysis of HTL, which includes the development of processes, the study of mechanisms, the application of bio-oil, and other topics, is only partially covered by current studies. Despite their relative novelty, both flash pyrolysis and HTL are promising technologies for generating biofuels and bioproducts. The different approaches have their own set of benefits and drawbacks, and it is important to understand their differences for their effective and efficient utilization.

Bio-oil, a renewable and low-emission fuel, offers numerous environmental benefits compared to fossil fuels. As bio-oils are carbon-neutral, they release a reduced amount of CO<sub>2</sub> and greenhouse gases. Due to the low sulphur content in plant biomass, the emissions of SO<sub>x</sub> are negligible. Consequently, polluting emissions would not be subject to taxation for bio-oil. Bio-oil fuels in a diesel-powered turbine emit over 50% less NO<sub>x</sub> compared to petroleum products. Bio-oil, a sustainable energy source, can be produced domestically in nations with abundant organic waste [10]. This means bio-oils are greener and are less likely to pollute the environment. However, the capacity of bio-oil to be a direct substitute of petroleum fuels and chemical feedstocks is hindered by its high viscosity, high water and ash content, low heating value, instability, and corrosivity. In order to make bio-oil suitable for use as a source of fuel or chemical feedstock in a variety of applications, it is necessary to improve its existing properties by upgrading it [10].

## 2.0 Overview of Pyrolysis

### 2.1 Pyrolysis

Pyrolysis, alternatively referred to as thermolysis, is a thermochemical phenomenon wherein intricate chemical constituents of solids or fluids undergo irreversible treatment at elevated temperatures within an oxygen-deprived or inert environment. The rate of pyrolysis is temperature-dependent and exhibits an upward trend as the temperature increases. Pyrolysis is a term used to describe the process of subjecting molecules to temperatures that are exceedingly high, which leads to severe chemical vibrations that cause the molecules to stretch and shake. This process leads to the fragmentation of the molecules into smaller ones [15].

Pyrolysis reactions can be valuable for a wide range of industries as they occur at moderate temperatures of 400 to 800°C [15], this process is mostly applied to organic matter, there are different types of pyrolysis and pyrolysis produces three major products biochar, bio-oils and synthesis gas.

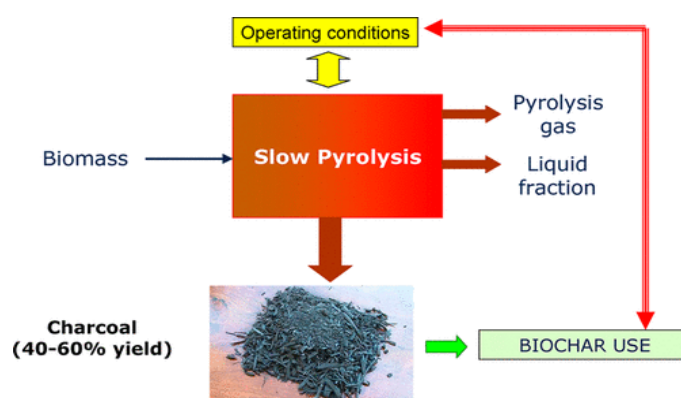
### 2.2 Types of Pyrolysis

There are different types of pyrolysis namely.

- Slow Pyrolysis
- Fast Pyrolysis
- Flash Pyrolysis

#### 2.2.1 Slow Pyrolysis

The technique known as slow pyrolysis, or conventional pyrolysis, is employed to thermally decompose organic materials in an oxygen-starved environment. This procedure entails subjecting the material to incremental increases in temperature, maintaining low temperatures, and allowing for prolonged periods of time within an atmosphere devoid of reactive substances. The pyrolysis process produces significant amounts of solid, liquid, and gaseous by-products [16].



**Figure 2:** Diagram of Slow Pyrolysis with Biochar as Main Product [17].

For several decades, the use of slow pyrolysis has successfully achieved an increase in char formation at reduced heating rates and temperatures. The residence time during which the vapour remains in this process is significantly prolonged, ranging from 5 to 30 minutes. Consequently, the constituents present in the vapour phase persistently engage in chemical

reactions, leading to the production of substantial amount of solid biochar, as well as a smaller quantity of liquid bio-oils and synthesis gas [16]. The process of converting biomass feedstock into char involves several distinct phases. The first stage of the degradation of biomass, which is known as pre-pyrolysis, occurs within a temperature range of 122°C to 202°C. There are a number of internal transformations that take place during this phase. These transformations encompass processes such as removal of water, bond cleavage, generation of free radicals, and the synthesis of hydroperoxide, carbonyl, and carboxyl functional groups. The subsequent phase of solid decomposition is connected to the fundamental pyrolysis process. This process is characterised by a high rate of occurrence and results in the generation of by-products through the process of pyrolysis. The char goes through a process of degradation during the third step of the formation process characterised by a very slow rate, leading to the creation of a carbonaceous solid residue.

This kind of pyrolysis, however, has several technological drawbacks that make it unlikely to be appropriate for producing high-quality bio-oil. Cracking occurs in the primary product as a result of the prolonged residence time that occurs during the slow pyrolysis process. This can have a negative effect on both the quality and quantity of the bio-oil that is produced during the process. Additionally, a prolonged duration of stay and limited heat movement necessitates additional energy input [18].

### **2.2.2 Fast Pyrolysis**

The term "fast pyrolysis", is a thermally intense procedure in which biomass is heated quickly at very high temperatures in an atmosphere devoid of oxygen. Consequently, it undergoes decomposition, producing primarily vapours and aerosols, along with a smaller amount of biochar. In the synthesis of bio-oils, It is essential to maintain a brief residence time in order to decrease the occurrence of secondary reactions [19]. Typically, this time period is around 1 second, although it is possible to get a satisfactory yield by extending the residence time to up to 5 seconds, as long as the temperature of the vapours remains below 400C. Upon undergoing the processes of cooling and condensation, a fluid substance that is dark brown in colour is formed. The product has a heating value that is approximately 50% which is a bit more than that found in standard conventional fuel oil. The fast pyrolytic process can yield around 60-75 wt % of liquid bio-oil, 15-25 wt % of biochar, and 10-20 wt % of synthetic gases, along with additional by-products, depending on the feedstock employed [20]. Fast pyrolysis achieves rapid heating rates by utilizing elevated operating temperatures, very short contact time frames, and finely broken down particles [21].

### **2.2.3 Flash Pyrolysis**

The term "Flash pyrolysis" refers to the rapid thermal decomposition of biomass at extremely high temperatures, typically ranging from 750°C to 1000°C. This process involves a rapid heating rate of over 1000°C/s and the use of very small particles, measuring less than 0.2 mm. The residence time, or the time it takes for the biomass to be exposed to these conditions, is less than 0.5 seconds [20]. Flash pyrolysis and slow pyrolysis are distinct in their approach. Slow pyrolysis involves converting large quantities of woody feedstock, in large sizes, into biochar. On the other hand, fast pyrolysis utilises small to medium-sized feedstock, in particle sizes ranging from 0.1mm to 0.2mm, within a controlled environment to primarily produce biooils. There are three primary protocols that can be utilised to carry out rapid pyrolysis [13].

- Ablative pyrolysis: This process involves the compression of biomass against a heated surface resulting in rapid displacement. During this process, the biomass. In this process, the biomass experiences a process of melting at the elevated temperature, resulting in the formation of a thin layer of oil that then undergoes evaporation [13].
- Fluidized bed and circulating fluidized bed pyrolysis system utilizes a combination of convection and conduction to transfer heat from a heat source to the biomass.
- Vacuum pyrolysis involves a gradual heating process that eliminates pyrolysis products as quickly as they are formed in the pre-liquid product.

Pyrolysis oil, also known as bio-oil, exhibits significant disparities compared to petroleum-based fuels, which consequently give rise to certain challenges when considering its substitution for petroleum fuels. The primary concerns that need to be addressed include elevated levels of water, oxygen, viscosity, and acidity [22].

**Table 1:** Pyrolysis process overview, operating parameters, ranges, and primary products [19]

Parameters	Conventional Pyrolysis	Fast Pyrolysis	Flash Pyrolysis
Pyrolysis Temperature (C)	277 - 677	576 - 977	776 - 1026
Heating rate (C/s)	0.1 - 1	10 - 200	>1000
Particle size (mm)	5 - 50	<1	<0.2
Solid residence time (s)	450 - 550	0.5 - 10	<0.5
Main Products	Biochar	Biooils	Biooils

### 2.3 Advantages of Pyrolysis

- Pyrolysis can be used in breaking down hazardous components and pathogens into more beneficial chemicals or fractions using high temperatures. Additionally, the high working temperature results in a decrease in water volume. By utilising the generated gases as a source of fuel, one can effectively reduce the need for external fuel.
- Pyrolysis can be used to subjecting hazardous components and pathogens to high temperatures in order to break them down into more useful compounds or fractions. In addition, the elevated operating temperature leads to a reduction in the volume of water. By using the produced gases as a fuel source, one can successfully decrease the need on external fuel.
- Pyrolysis can be performed as a batch process under low-pressure conditions, with minimal pre-treatment of the feedstock being necessary.
- Pyrolysis is a versatile process that may be used for a wide range of solid and liquid materials. It can be easily adapted to handle different compositions of the raw materials.
- The pyrolysis technology can be engineered to generate negligible quantities of non-utilizable by-products.
- Pyrolysis is a treatment method when compared to other procedures like gasification. The process results in reduced air emissions, with lower levels of nitrogen and sulphur oxides, and a decrease in the generation of CO<sub>2</sub> making it a greener process.

### 2.4 Disadvantages of Pyrolysis

Pyrolysis is a complex process that demands a substantial operating and investment expenditure. Installation of air purifiers is necessary in pyrolytic plants to treat flue gases generated during combustion. Pyrolysis generates ashes with high levels of heavy metals, which must be appropriately disposed of to prevent environmental harm.

## 2.5 Industrial Applications of Pyrolysis

- I. Pyrolysis is a viable method for treating waste streams characterised by a significant caloric content and high concentrations, as well as flows that provide complex processing challenges due to the inclusion of various substances.
- II. Pyrolysis has the potential to decrease the amount of sludge following the process of physio-chemical water purification.
- III. Pyrolysis is applicable for degradation complex oil-based flows.
- IV. Pyrolysis has the potential to be utilised in biorefineries as a means of producing a diverse array of products and materials that can serve as the foundation for a sustainable society in the future. These include various types of carbon, fuels, and other chemical feedstocks that hold significant value. Additionally, it has the capability to convert biomass into bio-oil [15].
- V. Pyrolysis encompasses a diverse range of processes that facilitate the generation of chemicals and biofuels. These processes exhibit variations in terms of their type, catalyst selection, feedstock composition and pre-treatment, as well as the resulting end product.
  - i. Rice straw and other biomass materials can undergo hydrous pyrolysis to produce bio-oils and fuels. [23].
  - ii. Catalytic fast pyrolysis is viable for synthesising aromatic chemicals from lignocellulosic feedstocks. Catalytic fast pyrolysis uses cost-effective aluminosilicate catalysts to perform pyrolysis reactions in a single reactor, making it a better biomass conversion method(Foster et al., 2012).
  - iii. Pyrolysis finds relevance in various industrial applications, including carbon-14 dating, thermal decomposition, thermal cleaning, and contamination removal, as well as analysis and identification needs. Pyrolysis can serve as a preliminary treatment for traditional methods, like incineration, gasification, or steam reforming [15].

### 3.0 Overview of Bio-oils

#### 3.1 Bio-oil

There are two main techniques for producing bio-oils: Flash pyrolysis and Hydrothermal liquefaction (HTL) are two distinct techniques employed for converting biomass into biofuels. Flash pyrolysis is a rapid thermal decomposition technique for decomposing biomass, as thoroughly elaborated upon in section 2.3.3. However, hydrothermal liquefaction (HTL) is a process that involves the interaction of biomass in water under high pressures and temperatures, with or without the use of a catalyst [24]. To carry out flash pyrolysis, the biomass needs to be exceptionally dry. Due to its high tolerance for moisture-rich biomass, HTL is an ideal option for biomass sourced from aquatic environments [10,24].

Biooil is a viscous fluid that has a dark brown colour and it also emits a smokey odour. It is made up of a varied and intricate combination of polymer fragments and reactive compounds that come from cellulose, hemicellulose, and lignin [10,25].

Bio-oil has a high degree of oxygenation, resulting in an elevated polarity and enhanced hydrophilicity, hence facilitating the retention of water within a solution. When the moisture content exceeds around 40 weight percent, the bio-oil undergoes heterogeneity and undergoes phase separation. The uppermost layer, known as the aqueous phase, consists of alcohols, sugars, water and organic acids,. On the other hand, the non-aqueous phase, also referred to as the tar layer, consists of various oxygenated chemicals and pyrolytic lignin [26].

#### 3.2 Properties of Bio-oil

When determining the quality of bio-oil, the composition of the biomass is a crucial component to consider [27]. Certain characteristics, such as a low pH level, high viscosity, increased density, large water content, higher oxygen content, a dark brown hue, a smoky aroma, and a moderate heating value, are what distinguish bio-oil from other types of oils. The distinct physical qualities exhibited by bio-oils can be attributed to their unique chemical composition, which differs greatly from those oils generated from petroleum. A complex mixture of a number of distinct organic compounds is referred to as "bio-oil." The bulk of these organic chemicals are acids, alcohols, aldehydes, esters, ketones, phenols, and oligomers. The phrase "bio-oil" refers to this complicated mixture [19,28]. In order to facilitate a comparison between the two types of oil, Table 3 compiles the characteristics that distinguish bio-oil from heavy fossil oil. These characteristics are given in the table alongside the characteristics of heavy fossil oil.

**Table 2:** Properties of bio-oil and their impact on their utilisation quality [25].

Properties	Biooil	Fossil oil (Crude oil)	Impact on fuel utilisation quality
HHV (MJkg <sup>-1</sup> )	14-20	40	Large volumes are needed
Water content (wt%)	15 - 30	0.1	Reduces heating, viscosity, density, and ignition.
pH	2.5	-	Compounding at high temperatures corrodes pipes and vessels.
Solids (wt%)	0.2 - 1	1	May increase bio-oil ageing, corrosion and equipment clogs.
Inorganics	0 – 0.2	0.1	Thermal corrosion, hard deposits, and bio-oil ageing
Viscosity (cP_50°C)	40 - 100	180	High-pressure drop increases equipment expenses, leaks, and ruptures.

Density	1.2	0.85	High density can affect pumping.
Oxygen content (wt%)	30 - 48	-	Immiscible with petroleum-based products

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### 3.3 Challenges in Biooil Utilization and the Imperative for Upgrading

Biooil possesses a range of unfavourable attributes and obstacles that require enhancement prior to its practical application. One of the primary obstacles lies in the elevated oxygen concentration. The physicochemical features of the substance are greatly influenced by the abundance of oxygenated molecules. The presence of certain compounds in bio-oil this makes it inappropriate for direct transportation usage, which result in combustion delays in automobiles and other modes of transportation this study was reviewed by Shihadeh *et al.* In order to utilise bio-oil as a transportation fuel, it is necessary to subject it to preheating in order to reduce its viscosity and enhance atomization, hence mitigating the risk of ignition delays this study was done by Boucher *et al.*, 2000. The composition of the bio-oil may undergo changes through intensified ageing reactions when subjected to elevated temperatures. Adding a cetane improver to the bio-oil can enhance its ignition problem, but this can be expensive, and the polarity of the bio-oil makes it challenging to combine without emulsifiers [25].

Furthermore, bio-oil exhibits corrosive properties and a low heating value as a result of its elevated acidity and water content. These properties fail to meet the requirements imposed for direct fuel utilisation, emphasising the need for upgrading processes. Stability is another issue associated with bio-oil. Because of oxygenated compounds, biooil becomes unstable when stored at room temperature this study was done by Oasmaa *et al.* The instability is evident in the form of oxidative and thermal degradation mechanisms that occur during the storage period, hence presenting difficulties in terms of its sustained viability and practicality.

In addition, bio-oil encounters difficulties relating to viscosity and the loss of volatile compounds. The phenomenon of oxidation-induced polymerization plays a significant role in the elevation of bio-oil viscosity, hence impeding its flow characteristics and introducing complexities in its handling and transportation. Moreover, the process of thermal degradation leads to the incomplete breakdown of bio-oil, resulting in the depletion of volatile molecules that are crucial for its energy content. This further amplifies the unsuitability of bio-oil for direct utilisation as a fuel source.

### 3.4 Biooil Upgrading Techniques

Various methodologies exist for the enhancement of bio-oil, sometimes employing a mix of two or more upgrading techniques.

#### 3.4.1 Hydrotreating (HTT)

Hydrotreatment offers the prospect to enhance both the quality of bio-oils and their use, the correlation between increasing hydrogen content in petroleum-based products leads to improved quality[10] Hydrotreating is a widely employed method for transforming petroleum and petroleum-derived goods into higher quality alternatives, HDT, or hydrothermal treatment, is a non-destructive process utilised to enhance product quality without modifying the boiling range. The process of hydrogenation, without concurrent cracking, is employed for saturating olefins and converting aromatic compounds into naphthene species.

Hydrotreating can be accomplished by two methods: either by introducing hydrogen into the reactor simultaneously as pyrolysis is taking place in the pyrolysis reactor, or by treating the

pyrolysis oil with hydrogen in a separate stage. The treatment of pyrolysis oil with hydrogen is contingent upon the degree of temperature severity. When pyrolysis oil is treated with hydrogen at a low temperature and high pressure, it is referred to as mild hydrodeoxygenation (HDO), which is also known as stabilisation. Mild-hydrodeoxygenation (MHDO) is a process designed to enhance the stability and storage of bio-oil by eliminating reactive components included in the bio-oil. When mild HDO is carried out, it consumes a relatively small amount of hydrogen[30]. The bio-oil obtained from this technique has excellent stability over time, making it suitable for long-term storage. Furthermore, it may be easily transported and directly utilised as a fuel source.

Stabilisation is achieved within a reactor through the reaction of hydrogen under high pressures ranging from 80 to 200 bars and moderate temperatures ranging from 180°C to 250°C. A broad range of chemical reactions and changes in physical properties take place during the process of stabilisation.

- i. Hydrodeoxygenation (HDO): While the process of stabilisation is taking place, oxygen-containing functional groups like hydroxyl (-OH) and carbonyl (-C=O) are transformed into molecules that are less reactive, such as water and carbon dioxide. During this process, the amount of oxygen that is present in the biooil is decreased, which results in a decrease in its corrosiveness and an increase in its heating value.
- ii. Hydrogenation: Concurrently with the process of hydrodeoxygenation, the process of hydrogenation takes place, which ultimately leads to the reduction of unsaturated molecules found in bio-oil and the saturation of double bonds. The oxidative breakdown of bio-oil is halted as a consequence of this.
- iii. Dehydration: This occurs when the water molecules in bio-oil is subjected to high pressure above their boiling point resulting to the removal of water molecules present in bio-oil. This reaction minimizes the risk of corrosion when and increases its energy density.
- iv. Decomposition of reactive species: The decomposition or conversion of reactive specie such as aldehydes and ketones occur during stabilization resulting to the formation of stable compounds. This reduces the acidity and reactivity of biooil.
- v. Polymerisation inhibition: This reaction occurs when bio-oil is stabilized at mild temperature and high pressure this reduces the formation of polymers thereby inhibiting the formation of products like coke and tar which would increase the viscosity of bio-oil, making it more fluid.
- vi. Hydrodeoxygenation (HDO): During stabilization the oxygen-containing functional group such hydroxyl (-OH) and carbonyl (-C=O) are converted to less reactive compounds like water and CO<sub>2</sub>. This process reduces the oxygen content in the biooil thereby decreasing its corrosiveness and enhancing its heating value.
- vii. Hydrogenation: The process of hydrogenation takes place simultaneously with hydrodeoxygenation, resulting in the saturation of double bonds and the reduction of unsaturated compounds found in bio-oil. As a result, this oxidative degradation of bio-oil is prevented.
- viii. Dehydration: This occurs when the water molecules in bio-oil is subjected to high pressure above their boiling point resulting to the removal of water molecules present in bio-oil. This reaction minimizes the risk of corrosion when and increases its energy density.

- ix. Decomposition of reactive species: The decomposition or conversion of reactive species such as aldehydes and ketones occur during stabilization resulting to the formation of stable compounds. This reduces the acidity and reactivity of biooil.
- x. Polymerisation inhibition: This reaction occurs when bio-oil is stabilized at mild temperature and high pressure this reduces the formation of polymers thereby inhibiting the formation of products like coke and tar which would increase the viscosity of bio-oil, making it more fluid.

An in-depth investigation on the process of mild hydrodeoxygenation (HDO) using a Parr reactor was carried out by Ardiyanti et al. In this study, hydrogen was subjected to a pressure of 110 bar and heated alongside the bio-oil at a temperature of 150°C for a period of one hour. The bio-oil upgrades produced a product that was dark brown in colour and had a viscosity that was rather low. When compared to the density of the aqueous phase, the improved bio-oil has a higher density. The oxygen concentration of the bio-oil reduced after it was subjected to mild hydrodeoxygenation (HDO), which ranged from 5.4 to 16.1 weight percent. This is a considerable decrease from the bio-oil that was initially present. During this process, a catalyst was utilised, and more specifically, NiCu was used as the catalyst component [31].

The enhancement of bio-oil through the utilisation of low-temperature and low-pressure hydrogen (LTLP) technology was the subject of a study investigation that was carried out by Rover et al. This work extracted the phenolic components of bio-oil from two distinct biomass sources: corn stover and red oak. The phenolic compounds obtained from the pyrolysis of corn stover biomass were preserved at a temperature of 5°C for a period of 6 months before undergoing hydrogenation. The phenolic components of red oak were promptly hydrogenated upon their extraction from the bio-oil. The phenolic compounds from both biomass samples were introduced into a reactor and subjected to hydrogenation under low pressure and low temperature conditions. The reaction took place at a temperature of 21°C and a pressure of 1 bar, Pd/C was the utilized catalyst for this study. The hydrogenation process lasted for a duration of 16 hours. As a result, the product exhibited an exceptionally high carbon yield of over 98% and a significant decrease in viscosity. Additional examination of the enhanced bio-oil utilising the different technique reveals heightened aliphatic constituents. This indicates that even under these moderate applications, the process of enhancing the quality of bio-oil continues. The phenolic fractions of the bio-oils, which include carbonyl groups, were transformed into alcohols, while the saturated compounds were turned into aliphatic groups [32].

Venderbosch conducted a study regarding the enhancement of bio-oil through the utilisation of high-temperature and high-pressure hydrogen (HTHP). In this experiment, bio-oil was injected into the reactor under a pressure of 300 bar and at a temperature of 350°C. Concurrently, hydrogen was introduced into the reactor using Ru/C as a catalyst, at an operating pressure of 300 bar and an operating temperature of 350°C, for a period of 2 minutes. The enhanced bio-oil possesses a carbon content of 60 wt %, and the constituents of the pyrolyzed bio-oil were transformed into viscous organics, aqueous, and gaseous phases. A little amount of tar was produced during this procedure, resulting in a slight decrease in the yield of upgraded bio-oil. This is attributed to the elevated temperature of the hydrotreating process [33].

An examination of the capacity of the bio-oil that was produced by the pyrolysis of miscanthus biomass was carried out by Oh et al., for the purpose of exploring its storage capacity. The

research study was conducted both before and after the bio-oil was subjected to HDO treatment. The hydrodeoxygenation (HDO) process of the bio-oil was conducted in this research by making use of three distinct noble metal catalysts, which are Pd/C, Ru/C, and Pt/C, at an operating temperature of 300°C and an operating pressure of 3MPa. Two non-mixable liquid products were obtained: an aqueous phase containing light oil, and an organic phase containing heavy oil. The heavy oil and pyrolyzed oil underwent a 12-week ageing test. The outcome of the ageing test for both pyrolyzed oil and HDO bio-oil exhibited notable disparities. Moreover, the physical characteristics of pyrolyzed bio-oil underwent unfavourable alterations over the course of storage. The HDO process enhanced the quality of the bio-oil by reducing its viscosity, acidity, and water content. Based on a prior investigation, bio-oil undergoes phase separation into two distinct phases during storage: a water phase and a viscous slurry phase. This investigation found no observable alteration in the appearance of the HDO treated bio-oil before and after storage [34].

### 3.4.2 Hydrocracking

Hydrocracking is less popular in the petrochemical (oil and gas) sector than hydrotreating, it is a thermal process that occurs at temperatures greater than 350°C and high pressures ranging from 10 – 200 bars. This change affects the overall quality of the end product, producing an extensive selection of distinct products. Hydrocracking is a process that involves the simultaneous occurrence of catalytic cracking and hydrogenation reactions. Typically, a dual-function catalyst is employed to simultaneously carry out both the cracking and hydrogenation processes. Hydrocracking is highly efficient for producing a significant quantity of light products. However, the process is hindered by its demanding conditions, including intense temperatures and pressures, which render it economically and energetically impractical [10].

The mechanism behind catalytic cracking this involves the decomposition of two bio-oil compounds namely guaiacol and acetic acid. The catalysts employed in this reaction are  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/HZSM-5 and Zn/HZSM-5. The above-mentioned research was carried out by Zhang *et al.* The individual model components undergo separate cracking processes they were fed into the reactor. The reaction is then conducted at a temperature of 600°C for a duration of 30 minutes. The products were obtained using a three-stage condenser with the assistance of ethanol. The results of the catalytic cracking experiment indicate that, in the absence of a catalyst, the majority of the acetic acid did not undergo decomposition at high temperatures. It was observed after the experimentation that just a small fraction of the acetic acid decomposed, yielding ethyl acetate and acetic anhydride. When the catalyst HZSM-5 was employed for cracking, just a negligible quantity of acetic acid remained undecomposed. The catalyst Zn/HZSM-5 enhances the breakdown of acetic acid, resulting in an improved selectivity towards ethyl acetate. Specifically, when catalyst Zn/HZSM-5 is employed, acetic acid is entirely converted into ethyl acetate and benzene.

During the process of cracking, guaiacol yielded phenolic compounds such as phenol and salicylaldehyde as the main products, in the absence of a catalyst. When HZSM-5 was utilised as the catalyst, the formation of non-phenolic compounds, such as toluene and coumarone, were found but its amount was minimal, while the production of phenol products increased by 20.34% to 30.89%. When Zn/HZSM-5 was employed as a catalyst, a new compound was discovered in a little quantity. The study's findings indicate that the utilisation of Zn/HZSM-5 as a catalyst enhances the rate of aromatization and increases the yield of aromatic compounds [35].

### 3.4.3 Hybrid Bio-oil Upgrading

Hybrid bio-oil upgrading can be defined as the combination of two or more upgrading techniques or refining processes of biomass for the purpose of enhancing the quality, stability, and practicality of bio-oil

IH2, is a US-based corporation, conducted research on the pyrolysis of biomass using hydrogen gas, which they referred to as "hydro-pyrolysis". The wood biomass underwent pyrolysis within a temperature range of 380°C to 450°C and a pressure range of 21 to 36 bars. The working condition of IH2 company for the pyrolysis of woody biomass is notably less intense compared to the operating conditions of typical fast pyrolysis of woody biomass. The temperatures for regular fast pyrolysis range from 450°C to 700°C, while the air pressure is maintained at 1 bar. Typical fast pyrolysis entails the thermal decomposition of biomass in an inert environment, sometimes with the assistance of nitrogen gas to facilitate the process. Nevertheless, IH2 implemented the use of hydrogen gas to enhance their pyrolysis process in order to achieve a higher yield of bio-oil. The fluidized bed reactor is supplied with hydrogen, which then undergoes pyrolysis together with the biomass. The bio-oil yield produced under these operating circumstances is 86%, which is considerably higher than that achieved through conventional flash pyrolysis. Furthermore, the attributes of the bio-oil, such as density and viscosity, closely resemble those of typical diesel fuel. Additionally, it was claimed that the bio-oil had a superior cetane number, surpassing that of petroleum-based diesel [36].

The process of esterification can be combined with other methods to develop a hybrid approach that improves the overall quality of bio-oil. Hu *et al* conducted a comprehensive research based on the examination of many researchers' work. An acid catalyst is usually required for the esterification of carboxylic acids in bio-oil. In addition to esterification, the process also involves several other processes including transesterification, acetalization, and aldol condensation reactions. The combination of these reactions results in a highly intricate network of esterification reactions in bio-oil [37].

A research investigation was done by Milina *et al.*, on the esterification of carboxylic acid in phenolics. The proposed esterification of acetic acid with o-cresol is significant due to the abundance of phenolic chemicals in bio-oil. The use of phenolic compounds for the esterification of carboxylic acids in bio-oil eliminates the need for additional alcohol from external sources, resulting in a significant cost reduction for the esterification process. When acetic acid was subjected to esterification with o-cresol at a temperature of 200°C, only 60% of the acetic acid was converted into ester. Additionally, polymerization occurred at this temperature. However, when the catalyst ZSM-5, mordenite was employed, there was a little enhancement in the esterification of acetic acid [38].

A research was done by Qin *et al* on the process of esterification combined with online extraction and distillation of acetic acid and aldehyde, which are constituents of bio-oil. This process aims to convert these components into different compounds throughout the esterification process. This approach aims to minimise the negative effects of water on the carboxylic acid conversion in bio-oil. During the experiment, bio-oil was put into a trap that was sealed with water, and 1-butanol and sulphuric acid were put into a flask with a circular bottom. Sulphuric acid serves as the catalyst in the esterification process, while 1-butanol acts as the alcohol component that reacts with the carboxylic acid in the bio-oil to produce water and

esters. The flask was subjected to heat, causing the vapours of 1-butanol to undergo condensation within the water-locked trap, facilitating the extraction of acids and aldehydes. Through this technique, all water was successfully removed from the bio-oil, resulting in a conversion rate of 97% for acetic acid and 100% for aldehyde. This demonstrates the high efficiency and effectiveness of this technology [39].

Sundqvist et al. studied the application of azeotropic distillation for the purpose of eliminating water from bio-oil before and during the process of esterification. In order to obtain efficient water removal, it was necessary to use a hydrocarbon entrainer such as n-heptane or petroleum ether. Following the process of esterification, the pH of the resulting products was elevated to a range of 4.0 – 5.6 [40]. Mahfud et al employed a comparable configuration to carry out reactive distillation. However, they utilised a higher boiling point alcohol, specifically n-butanol, and a solid acid catalyst. The reactions were conducted at temperatures ranging from 50 to 80°C under reduced pressure. This approach facilitated the continuous removal of water and ensured the completion of the desired reactions[41].

Wen Chen et al undertook a study on the utilisation of a physical mixture of Ru/C and sulphated catalyst. The transformation of an experimental feed comprising phenol, n-butanol, and acidic acids converted to alcohols and esters was effectively accomplished, yielding a 95% output s[42].

Reddy et al. investigated the transfer of hydrogenation processes using supported mono and bimetallic catalysts including nickel (Ni) and copper (Cu), using p-cresol and furfural as model components of bio-oil. The solvent employed for hydrogen donation was hydrogen, resulting in a product that was 95% hydrogenated and deoxygenated. Furthermore, it was shown that the catalysts remained active even in the presence of water, albeit their activity diminished as the concentration grew [43].

#### **3.4.4 Supercritical Fluid (SCF)**

Supercritical fluids refer to fluids that possess temperature and pressure values beyond their critical point. The transportation properties of supercritical fluids are distinct and unparalleled. They possess the ability to disperse through solids in a gaseous manner and dissolve substances in a liquid manner. This characteristic allows them to dissolve compounds that are often insoluble in both liquid and gaseous states [44]. In the present day, the utilisation of SCF has been employed to enhance both the yield and quantity of oil. Furthermore, it has demonstrated substantial potential in the production of bio-oil distinguished by a notably increased calorific value and decreased viscosity. Water is often utilised as a solvent in hydrothermal processing due to its cost-effectiveness and widespread application. Nevertheless, employing water as a solvent entails notable drawbacks, such as: (1) diminished generation of oil products that lack solubility in water; (2) the creation of a remarkably viscous bio-oil with a substantial oxygen concentration.

A research investigation carried out by the researcher Ramon *et al* to examine how the operating parameters of subcritical and supercritical water affect the enhancement of lignocellulosic bio-oil that is derived from pinewood (biomass). The experimental temperature range is 310°C to 450°C, and the pressure range is 200 to 260 bar. The catalyst employed in this method is Ni-Co/Al-Mg, and the reaction is carried out in a batch reactor. The temperatures and pressures were manipulated to achieve subcritical and supercritical states. The bio-oil utilised in this investigation was acquired from the Biomass Technology Group (BTG). The ratio of catalyst to bio-oil ranged from 0 to 0.25, and the duration of the complete reaction was varied from 0 to 60 minutes. The findings of this investigation indicated that oxygen was reduced by 70%, and the concentration of carboxylic acid was substantially reduced by the production of light gases during the experimental process[45].

Hermawan et al and Qing Zhang et al conducted a study on the enhancement of fast pyrolysis bio-oil using supercritical ethanol, without the need of any catalyst. At a temperature of 400°C and for a duration of 30 minutes in the experiment. The majority of organic compounds in the bio-oil were transformed, leading to a significant increase in the upgraded bio-oil, with a yield 83 wt%. Moreover, the high heating value (HHV) of the upgraded bio-oil was enhanced to 34.1MJ/kg, compared to the original pyrolysis oil's HHV of 24.3MJ/kg. The primary chemical constituents of the enhanced bio-oil consisted of alcohols, esters, phenols, and aromatics. The stability of the bio-oil was also assessed after being subjected to ageing at a temperature of 80°C for a duration of 7 days. It was observed that there was a slight rise in the viscosity of the improved bio-oil in comparison to the previous pyrolysis oil. An additional experiment was conducted utilising supercritical methanol instead of ethanol in order to observe any differences. This decision was made due to the higher cost of ethanol compared to methanol. Nevertheless, the yield achieved from supercritical methanol was inferior to that of ethanol, likely due to the absence of a carbon chain in methanol. This implies that methanol has much fewer carbon-carbon links compared to ethanol [46,47].

#### **3.4.5 High-Pressure Homogenization (HPH)**

The process of high-pressure homogenisation involves applying high pressure to a liquid in order to force it through a very small nozzle. The pressure that is applied typically falls somewhere between 15 and 40 bars. A considerable shear stress is produced as a result of this operation. This approach has the potential to be used in the stabilisation of bio-oil as an emulsion. Applying significant pressure can break the relatively fragile connections in macromolecules, allowing for control over both physical and chemical changes in bio-oil. The pressure and the size of the nozzle can be adjusted. A research investigation was done by Ronghai et al on the approach using bio-oil that was gotten from switchgrass. The study revealed a decrease in the ethanol-insoluble fractions and average molecular weight. The bio-oil underwent changes in its chemical composition characterised by a reduction in acetic acid and 1,2-ethanediol, and an increase in furfural and levoglucosan. A stability test indicates that HPH (high-pressure homogenization) has a substantial beneficial impact on the enhancement of bio-oil. After conducting the study, the researchers came to the conclusion that additional research is necessary in order to optimise the working conditions of HPH in order to get a high bio-oil output. In addition, it proposes conducting research into the possibility of utilising catalysts in the studies in order to have the process go more smoothly [48].

#### **3.4.6 Esterification**

The introduction of polar solvents including methanol, ethanol, and furfurals is one method that can be utilised to accomplish the esterification of bio-oil. A decrease in the viscosity of pyrolysed oil has been achieved by the utilisation of this technique. The incorporation of polar solvents into bio-oil results in a rapid reduction in viscosity and an increase in the heating value [29]. Recent research has revealed that the utilisation of reactive distillation, wherein oil is combined with alcohol and an acid catalyst under mild conditions, yields bio-oil of superior quality [49,50].

#### **3.4.7 Emulsification**

Biooil can be enhanced through emulsion processing to serve as a fuel for combustion, transportation, or as a heat source in boilers. This is achieved by combining biooil with other petroleum-based substances to create an emulsion. An inherent limitation of this approach is

the incompatibility between pyrolyzed oil and petroleum products. However, by utilising a surfactant, it is possible to generate an emulsion.

Bo-Jhih Lin et al did a study on the process of creating an emulsion of biodiesel using different combinations of emulsifiers. The emulsifiers utilised for this study can be located in his research report. For the purpose of this experiment, the bio-oil that was utilised was obtained by the pyrolysis of waste wood.. The findings of this study demonstrate that bio-diesel can be enhanced through the process of emulsification, resulting in highly stable emulsified bio-diesel. In addition to that, it is essential to take into consideration that the selection of the emulsifier that is utilised for this process is a limiting factor. Additionally, the emulsifiers employed in this method are moderately costly and may also be utilised as additives in food products, thereby creating competition and potentially driving up the price[48].

### **3.4.8 Steam Reforming**

The process of steam reforming is a highly effective way for improving the quality of pyrolysed oil. In order to successfully manufacture hydrogen from bio-oil, this method involves the quick pyrolysis of biomass, which is then followed by the catalytic steam and shift conversion of specific fractions. Together, these steps are necessary to get the desired result. The process of steam reforming has been utilised extensively with natural gas and other fossil fuels as reactants. Additionally, it has been utilised in industrial settings to produce synthetic gas or hydrocarbons. For example, the Haber-Bosch process is used to produce ammonia, and the Fischer-Tropsch process is used to produce synthetic hydrocarbons. A research conducted by Anastasia *et al* on the new developments in the steam reforming of bio-oil for the purpose of producing hydrogen. The study explored on the mechanism of steam reforming, which is an endothermic process that demands extremely high temperatures ranging from 400°C to 900°C. This process yields hydrogen and carbon dioxide, with an efficiency of 70% in hydrogen production. The main disadvantage of utilising steam reforming for hydrogen production from bio-oil is its high energy demand due to the endothermic nature of the process and the requirement for extremely high temperatures. This requires a continuous supply of heat, making the operation costly. Additionally, the production of tar poses a significant challenge in the steam reforming of bio-oil. While theoretically, steam reforming of bio-oil holds promise in generating substantial amounts of hydrogen, practical implementation is hindered by technological issues that necessitate further investigation and significant improvement before commercialization can be achieved [51].

The National Renewable Energy Laboratory (NREL) undertook a comprehensive examination into the creation of hydrogen by the reformation of bio-oil. Studies on the catalytic steam reformation of bio-oil were conducted by Trane *et al*.

There are many different chemicals that may be extracted from bio-oil. Some of these chemicals include volatile organic acids and phenols, which are chemicals that are frequently used in the resins industry in particular. The hydrothermal liquefaction (HTL) process yields biooils that consist of around 50 weight percent asphalt, making them suitable for extraction and use within the asphalt industry. Fini *et al* conducted a study where they separated and chemically altered bio-oil into a highly efficient asphalt bio-binder. This bio-binder shows great promise as a substitute or addition to asphalt made from petroleum. Presently, chemicals are commercially extracted for the purpose of manufacturing wood flavours or liquid smoke.

### **3.4.9 Biological Upgrading**

Biological upgrading is a potentially effective method compared to traditional upgrading processes. It involves selecting certain strains of microorganisms that can withstand and break down the components of bio-oil. This microorganism possesses metabolic pathways that can transform oxygenated molecules into hydrocarbons that are less complicated but have a higher energy density. Three important enzymes used for biological upgrading are laccases, peroxidases, and hydrolases. An investigation into the enhancement of bio-oil through the utilisation of microorganisms for the purpose of producing valuable biofuels and biochemicals under benign conditions through the utilisation of microbial conversions was carried out by a researcher named Doddapaneni [52].

There are multiple difficulties associated with this method of upgrading, with one of the main issues being the sluggish rate of reaction. This is in contrast to conventional upgrading procedures, which rely on high temperature and pressure to accomplish the desired results. Biological enzymes function at a slower rate, which negatively impacts the overall efficiency of the upgrading process, rendering them commercially unfavourable due to their extended time frame. One of the most important of the several difficulties in using bacteria to enhance bio-oil is its complicated character itself. Due to the fact that bio-oil is an intricate mixture that contains a large number of oxygenated compounds and acids, it is challenging to create specialised microbes that are capable of successfully converting these compounds into products that can be utilised.

### **3.5 Industrial applications of Biooil**

- I. Companies such as Chevron, Ensyn, and Vyttera are now engaged in the manufacture of bio oil and its application in makings of granulated activated carbon (GAC). Biooil is utilised in the creation of binders, which is a component of the GAC manufacturing process [53].
- II. Biooil has the potential to serve as a wood tar softener in the manufacturing process of industrial charcoal briquettes. These briquettes find application in many industrial applications such as cooking, heating, and other related uses. Ensyn and BTG bio-liquid are presently making significant contributions to this particular application.
- III. Bio-oil is utilised as a treatment for wooden materials in the wooden industry, specifically for housing construction. The application of this substance improves the durability, resistance to decay, and pest resistance of wood. Green fuel Nordic Oy and Secil are engaged in the manufacturing of biooil with this specific objective.
- IV. Biooil functions as a multifaceted additive in the composition of road construction materials, augmenting the characteristics of asphalt and bitumen, hence enhancing the overall quality of road construction. The Brazilian company Petrobas is now investigating the co-processing of biooil at refineries for this specific objective.
- V. The utilisation of biooil in the synthesis of anhydro-sugars, like levoglucosan, holds potential for the creation of biodegradable polymers and therapeutic surfactants.

## **4.0 Aim & Scope**

### **4.1 Aim**

This thesis is designed to investigate and establish an effective methodology for the upgrading and modelling of bio-oil that is derived from pine biomass feedstock. The objective is to improve the properties of bio-oil following pyrolysis and to establish them as a viable alternative to traditional fossil fuels. This entails the examination of the pyrolysis process of pine biomass, the optimisation of conditions to achieve the highest possible yield and quality of bio-oil, and the modelling of the refining process to enhance and stabilise the characteristics of bio-oils. The ultimate objective is to facilitate the advancement of sustainable and renewable energy sources that can reduce reliance on fossil fuels and mitigate environmental consequences.

### **4.2 Scope**

The scope of this thesis encompasses the following key areas:

- Pyrolysis process optimization.
- Stabilization and upgrading of bio-oils.
- Simulation and Modelling with Aspen Plus.

## 5.0 Plant Design Basis

The study utilised Aspen Plus® version 14 simulation software to build the process design model. Three types of components were employed: conventional, non-conventional, and solids. The analysis presented in this study is derived from the proximate and ultimate analyses reported by (Lyu et al., 2015) Table 1 Pine is employed as a biomass material in the simulation of this process.

**Table 3.** Ultimate, Proximate and Component Analysis of Biomass Feedstock

Ultimate Analysis	W <sub>daf</sub> %	Proximate Analysis	W <sub>ad</sub> %	Component Analysis	W <sub>ad</sub> %
C	49.18	Volatiles	86.10	Hemicellulose	21.66
H	5.83			Cellulose	46.97
O <sup>a</sup>	44.95	Fixed Carbon	12.60	Lignin	27.65
N	0.02				
S	0.02	Ash	1.30	Extractive	2.70

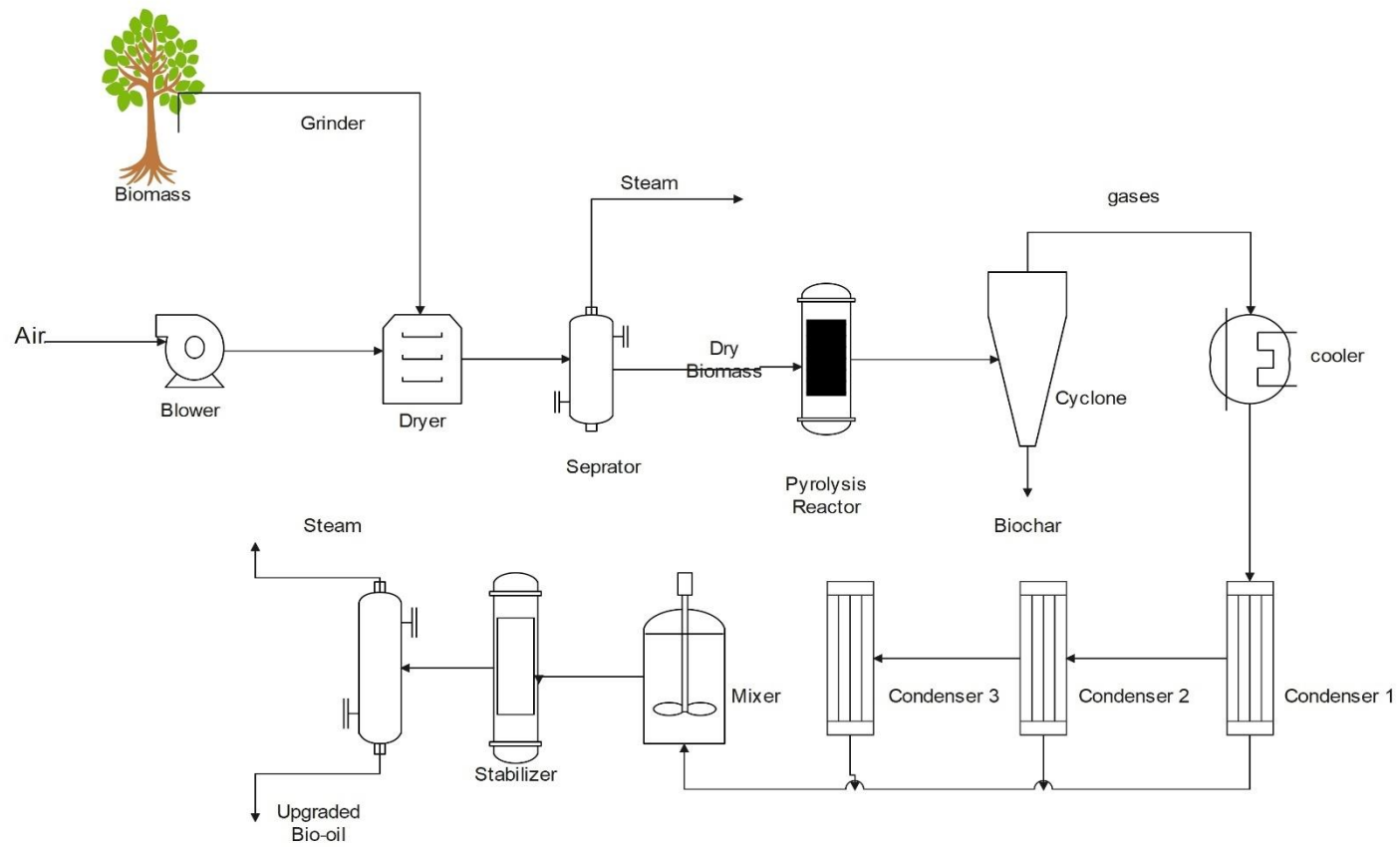
daf = dry and ash-free basis  
ad = air dry basis  
a = Calculated by difference

A comprehensive block diagram is presented in Figure 3, which illustrates the process by which pine biomass is transformed into bio-oil, which is a form of sustainable energy. Fast pyrolysis is combined with a stabilisation process in order to accomplish this conversion, which is necessary for the upgrading of bio-oil. During this procedure, the pine biomass feedstock is first ground to achieve a particle size range of 2-6 mm, which enhances the material's suitability for effective pyrolysis. The entire simulation, which included both the pyrolysis and upgrading phases of the bio-oil, was meticulously simulated with the help of the Aspen Plus® software. The Peng-Robinson equation of state was utilised to precisely forecast phase behaviour and thermodynamic parameters. The designated capacity of the plant for this study has been set at 1000 kg/hr, which corresponds to a throughput of roughly 24 dry tonnes per day. This capacity guarantees a consistent and expandable functioning that is well-suited for industrial applications. The fast pyrolysis unit is specifically engineered to quickly raise the temperature of the biomass in an environment without oxygen, which encourages the organic material to break down into vapours, aerosols, and a small amount of biochar.

Pyrolysis results in the production of vapours, which are then rapidly cooled and condensed in order to generate bio-oil. Bio-oil is a complex mixture of hydrocarbons that additionally contains oxygen among its constituents. For the purpose of enhancing the quality of bio-oil and extending its shelf life, it would be subjected to stabilisation, which is a mixture of various reactions such as hydrogenation and the breakdown of reactive species. This process goals to decrease the quantity of oxygen, viscosity, and water in the bio-oil. Bio-oil is a green alternative to traditional petroleum products as a consequence of the upgrading of bio-oil, which is highly critical to the fuel qualities of the bio-oil.

The modelling of the plant considers the incorporation of heat integration and energy recovery systems, this is aimed to enhance the efficiency of the operations. The design take into account

environmental factors, such as minimizing greenhouse gases and managing by product like biochar and non-condensable gases.



**Figure 3:** Flow diagram of the plant design

## 6.0 Process simulation

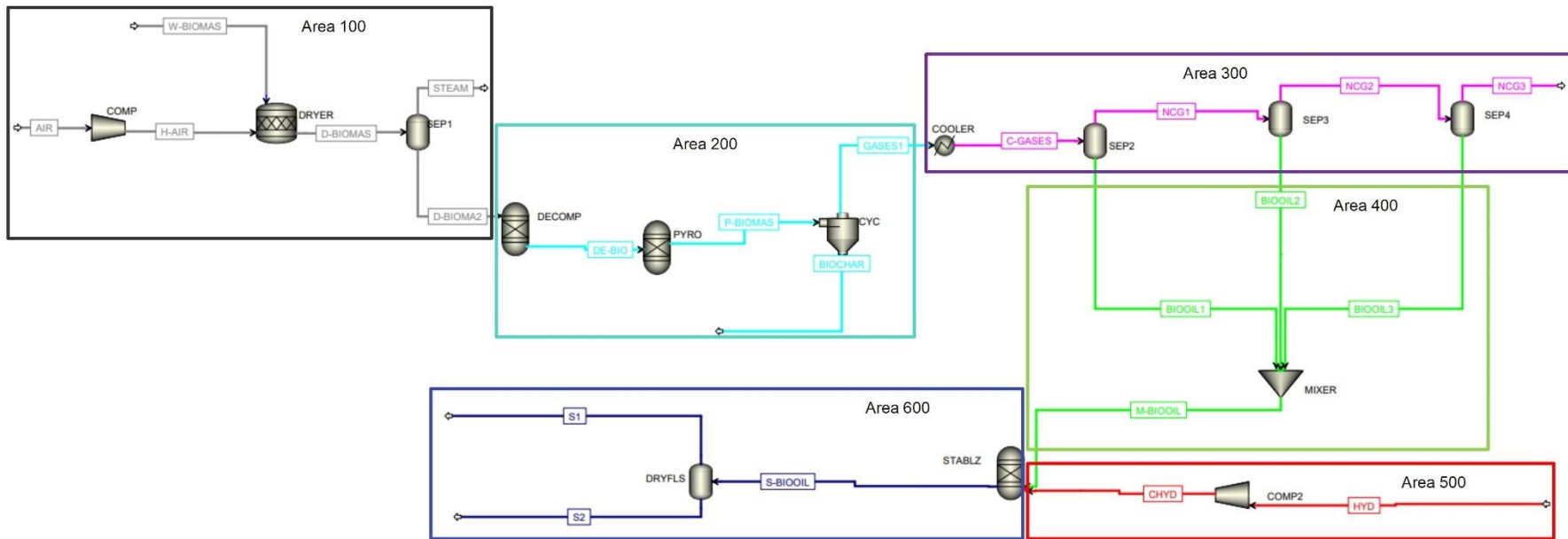
Pine feedstock is the biomass material that has been selected for fast pyrolysis for the production and stabilisation of bio-oil. This decision was made due to the availability of pine feedstock, the locations where it can be found, and the rate at which it grows. The pine feedstock was specified in Aspen Plus by applying the comprehensive analysis, which is presented in Table 4. The pine feedstock (biomass) and ash were modelled as non-conventional solids in Aspen Plus. In Aspen Plus®, non-conventional components such as biomass can be modelled using methodologies originally developed for other non-conventional materials like coal. This approach leverages the similarities in the thermal decomposition and combustion processes of these materials. This is because biomass and coal share complex organic structures and exhibit similar thermal decomposition behaviours. The coal enthalpy model offers a robust framework adaptable to biomass due to these similarities.

Pine biomass requires a specific property model that is tailored to its unique characteristics. The HCOALGEN model is selected for calculating the enthalpy of the biomass. This model is specifically designed to handle complex heat formation and heat capacity essential for accurately representing the thermal properties of biomass. The justification for using HCOALGEN lies in the organic composition of both biomass and coal, which primarily includes carbon, hydrogen, oxygen and traces of nitrogen and sulphur these similarities makes the HCOALGEN model suitable for both materials

The pyrolysis and combustion processes of coal and pine biomass involve thermal decomposition of complex organic matter into simpler compounds, realising energy. Therefore, the thermal behaviour modelled by 'HCOALGEN' for coal can be used to effectively represent biomass as well. The only difference between the combustion of coal and the pyrolysis of biomass is the presence of oxygen during thermal degradation for coal while pyrolysis occurs in an oxygen free environment. The 'DCOALIGT' model is used to determine the density of the biomass, this is very important for the calculation of accurate mass and energy balance calculations. Similar to coal biomass exhibits variability in physical properties because this depends on the composition and moisture content of the biomass being modelled. DCOALIGT accounts for these variations by providing a reliable estimation of density.

The characterisation of feedstock requires component attributes such as PROXANAL (Proximate analysis), ULTANAL (Ultimate analysis) and SULFANAL (Sulphur analysis) these components provide essential data on moisture content, volatile matter, fixed carbon, ash, elemental composition and sulphur content. These components are very essential for accurately defining the biomass feedstock. 'HCOALGEN' and 'DCOALIGT' model provide a reliable framework for calculating the thermodynamic properties necessary for detailed process simulation.

The choice of pine feedstock for the production and stabilization of bio-oil through fast pyrolysis is driven by several factors: its availability, its widespread distribution, and its rapid growth rate. In the simulation environment of Aspen Plus, pine feedstock (biomass) and ash are represented as non-conventional solids, employing methodologies initially developed for coal. This decision leverages the similarities between biomass and coal in their thermal decomposition and combustion behaviours.



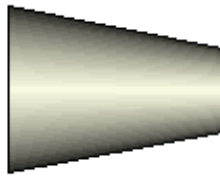
**Figure 4:** Aspen Plus simulation of Bio-oil Modelling and Upgrading

## 6.1 Model Components used in this Aspen Plus Simulation

The model components used for this simulation of bio-oil modelling and upgrading are:

- i. Compr
- ii. Rstoic
- iii. Flash2
- iv. Ryield
- v. RGibbs
- vi. SSplit
- vii. Cooler
- viii. Mixer

### 6.1.1 Compr

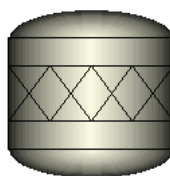


**Figure 5:** Aspen Plus model component representation of a Compr

The "Compr" model components in Aspen Plus are specifically designed to replicate the characteristics and operational efficiency of a compressor or turbine. This device symbolises a compressor or turbine that operates in a single stage and has the capability to accommodate different types of compressors, such as centrifugal, reciprocating, and screw compressors. The Compr model component is utilised in industries that necessitate the transportation, processing, or storage of gases at elevated pressures. It calculates the amount of work needed to compress a gas from an initial pressure to a desired higher pressure, taking into account the thermodynamic properties of the gas and the efficiency of the compressor. The operating parameters can be calculated by considering the discharge pressure circumstances or referring to the compressor's performance curve when it is used as a compressor, or by evaluating the work yield during expansion when it is used as a turbine.

This model component is primarily intended for simulating a compressor or turbine, although it can also be utilised for modelling a blower. This equipment is akin to a compressor but is mostly employed for transporting gases at modest pressure. Unlike a compressor, it does not cause significant compression, resulting in lesser energy consumption. The difference in energy use comes from the pressure ratio; blowers typically operate at lower pressure ratios in contrast to compressors.

### 6.1.2 Rstoic



**Figure 6:** Aspen Plus model component representation of a Rstoic

The “RStoic” model component in Aspen Plus is specifically designed to simulate stoichiometric reactions. These kinetic reactions may be known or unknown, unlike kinetic bases model reactors that require a detailed mechanism and rate laws the RStoic model component uses stoichiometric relationships to define the reactions it allows the user to specify stoichiometric coefficients of reactants for a given reaction or a set of reactions, it calculates the conversion of reactants based on user-defined extents or fractional conversions this makes it very useful for defining reactions of unknown stoichiometry like biomass pyrolysis or drying where reactions are not the primary concern.

The RStoic model component is versatile and can be used in a large range of industrial and research applications in cases where stoichiometric data is sufficient for process simulation. Common examples where RStoic model components have been used in process simulation.

- Styrene production
- Biomass pyrolysis
- Coal drying
- Waste treatment

### 6.1.3 Flash2



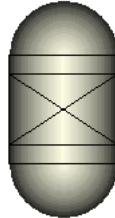
**Figure 7:** Aspen Plus model component representation of Flash2

The "Flash2" model component is especially intended to replicate a process of separating a substance into two distinct phases. It determines the state of balance between. The system determines the balance between two distinct states, usually liquid and vapour, by considering certain parameters of temperature and pressure. This model component attains a state of equilibrium by adhering to the principles of thermodynamics. The Aspen Plus software utilises the vapor-liquid equilibrium (VLE) equations to calculate the equilibrium temperature, pressure, composition, and quantity of each phase. This is based on three primary parameters.

- **Phase Equilibrium Calculations:** The Flash2 model components utilise the equation of state (EOS) or activity coefficient models to reliably determine the equilibrium between the vapour and liquid phases in phase equilibrium calculations. The most often used EOS models include the Peng-Robinson and Soave-Redlich-Kwong equations. As for activity coefficient models, examples include the NRTL and Wilson equations.
- **Energy Balance:** The Flash2 model maintains energy balance by accounting for heat exchange during phase separation processes, ensuring that the enthalpy of the system remains balanced. This also involved performing calculations for isothermal, isobaric, and adiabatic flash processes.
- **Material Balance:** The Flash2 model components ensure that the accumulation of the masses of all of the constituent components is maintained during the phase separation that takes place.

The Flash2 model components are extensively utilised in diverse industrial contexts due to their adaptability and precision in simulating phase separations. Distillation and refining are two instances of how this process is utilised in the business. They are employed to separate crude oil into different fractions, such as petrol, diesel, and kerosene. Additionally, this method is used to eliminate hydrocarbons and water from natural gas.

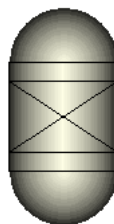
#### 6.1.4 RYield



**Figure 8:** Aspen Plus model components representation of RYield.

The "RYield" model components are specifically developed to replicate processes in which the precise paths and mechanisms of a reaction are either not well-defined or too intricate to be explicitly modelled. The RYield model utilises empirical yield data to forecast the product distribution from a particular feedstock under specific conditions, rather than relying on specific stoichiometric equations and kinetic characteristics. This approach streamlines the process of representing intricate processes, rendering the model highly valuable in many businesses, particularly those involved in biomass and waste treatment as raw materials for conversions. The RYield model is extensively utilised in many industries due to its capacity to manage intricate and ambiguously specified reactions. These are instances where it is employed: biomass decomposition, which involves breaking down complex polymers found in biomass. Modelling the precise decomposition pathways is difficult, but RYield simplifies this task by utilising empirical data to forecast the production of gases, bio-oil, and char during pyrolysis processes. Additionally, it is employed to replicate the process of converting biomass into biofuels, such as bioethanol or biodiesel, as well as to model coal decomposition.

#### 6.1.5 RGibbs

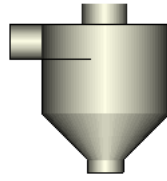


**Figure 9:** Aspen plus model components representation of RGibbs

The "RGibbs" model components in Aspen Plus are utilised for simulating chemical processes that assume reactions reach equilibrium. Unlike kinetic-based models that require specific information about reaction rates and mechanisms, the RGibbs model minimises the system's Gibbs free energy to calculate stoichiometric balance and VLE.

The RGibb model components are applied in many sectors for different purposes, including the Haber-Bosch ammonia production process where they are utilised to model equilibrium between nitrogen, hydrogen and ammonia optimising conditions for maximum yields and also use to model the combustion to fuel.

### 6.1.6 SSplit

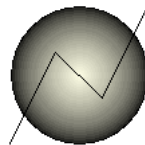


**Figure 10:** Aspen Plus model components representation of SSplit

The "SSplit" (Steam Splitter) model component is specifically developed to partition a singular input stream into two or more output streams, in accordance with the designated split fractions. The capacity to recreate physical stream-splitting procedures makes process simulation crucial.

The SSplit is a highly adaptable and extensively employed device in diverse industries. Specifically, in the chemical and petrochemical sector, it is utilised to disperse feedstock to numerous reactors or processing units. In the pharmaceutical and biotechnology industry, batches of intermediate or final products were traditionally divided into several processing streams for additional purification or formulation purposes. Environmental engineering employs the use of wastewater treatment to divide wastewater streams into separate treatment units, enabling customised treatment of different contaminants. In the food and beverage business, the concept for ingredient distribution involves dividing raw ingredients into different processing lines, such as mixing and packaging units. In the energy sector, the fuel stream is divided into various boilers or turbines to optimise the energy process.

### 6.1.7 Cooler

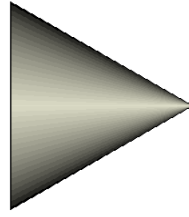


**Figure 11:** Aspen Plus model components representation of a cooler

The "cooler" or "heater" model component in Aspen Plus is intended to be used as a heat exchanger. Its primary function is to ease the transfer of heat between a process stream and a utility stream. The amount of heat that must be removed or introduced in a process stream in order to achieve the specified temperature is calculated by this machine. Maintaining temperature in a variety of industrial processes is extremely important, and it is accomplished through the use of the heat exchange concept.

It is utilised for heat exchange in a variety of industries, including the food business, the energy industry, and the pharmaceutical industry.

### 6.1.8 Mixer



**Figure 12:** Aspen Plus model components representation of a mixer.

The "mixer" model component in Aspen Plus is intended to make it possible to merge various process streams into a single stream that is consistent throughout. The blending of raw materials or finished products is a vital operation in many different industries, as it allows for the achievement of the necessary composition and process conditions. The mixer functions according to the principle of mass and energy balance, which guarantees that the collective output stream appropriately represents the characteristics of the streams that are being fed into it.

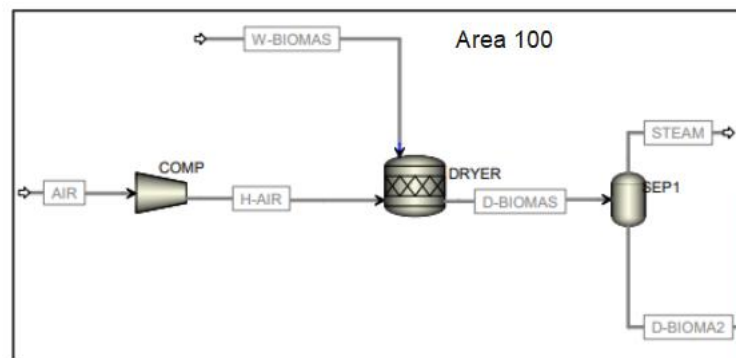
## 7.0 Process Design

The process design primarily comprises of the following areas.

- Area 100: Feed handling and drying of feed materials.
- Area 200: Decomposition, Fast pyrolysis and separation of gases and solids
- Area 300: Pyrolysis vapour cooling and recovery of products
- Area 400: Combination and collection of products recovered.
- Area 500: Hydrogen production
- Area 600: Stabilization of bio-oil

These sections present the process overview and design basis for each process area of the plant.

### 7.1 Area 100: Feed Handling and Drying of Feed Materials



**Figure 13:** Feed Handling and Drying

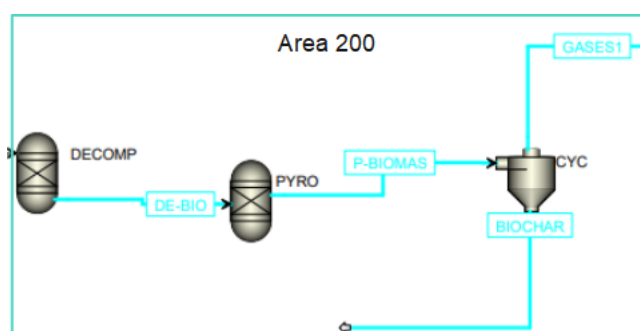
In ASPEN PLUS<sup>®</sup> version 14, A blower which is an adept model of a compressor is used to extract air from the surroundings at a rate of 2000 kg/hr. The blower is employed to guarantee a consistent and uninterrupted stream of air at a stable pressure into the drier (RSTOIC). A blower was chosen over a compressor because to its ability to provide a constant stream of air at ambient temperature and pressure, while consuming less electricity. In contrast, a compressor would raise the pressure and hence raise the temperature of the compressed air. The blower is well-suited for situations that do not require high levels of pressure and also helps prevent unnecessary thermal strain on the system.

The pine biomass feed does not exist in the Aspen Plus database the feed characterization was obtained from a study done by Lyu *et al*, the biomass feed is pre-processed before sent to the drier by grinding to a particle size between 0.5 and 1.4mm according to Aguilar *et al* [55]. The size range is critical for various reasons. The larger surface area facilitates more efficient heat and mass movement during the drying process. An optimal moisture removal from the biomass is achieved, resulting in improved efficiency and uniformity. Additionally, a specific particle size range is necessary for the subsequent pyrolysis process to produce a significant amount of bio-oil, as indicated by Aguilar *et al* [55] the biomass is then transferred to the RSTOIC drier. The RSTOIC model component is modelled to be used as a drier for this simulation the operating conditions were based on duty and pressure. It is programmed using a FORTRAN code written in the CALCULATOR block under the Flowsheeting options. This code is specifically written to control the dryer's operations and ensures after drying that the biomass achieves a final moisture content of precisely 10%. What determines the quality of dried biomass and whether or not it is suitable for pyrolysis, The amount of moisture that is present in the biomass is greatly considered. If the moisture content of the biomass is high. As a result

during pyrolysis, the heating value of the fuel is decreased when there is a high moisture content, and the temperature at which ignition takes place is raised. This makes it more difficult for the temperature to rise within the biomass particles and for the conversion reaction to take place [56]. When water is present in the reactor, it has a negative influence on the reactor, which has a catalytic effect on volatile cracking. Additionally, when the biomass feedstock that is used in pyrolysis has a high moisture content, it results in a reduced activation energy. This, in turn, facilitates the production of char, non-condensable gases, and more water according to Rezaei *et al.* To enhance the quality of fuel produced, it is recommended to reduce the moisture content of biomass to less than 10%.

After drying the mixture of the dried biomass is sent to a separator which is modelled using Flash2 model component in Aspen Plus simulation environment, to separate the biomass into two different phases dried biomass and steam. The unit operations model RStoic and Flash2 is used to simulate a single piece of plant equipment for drying and it is operated under two conditions isobaric and adiabatic conditions. This means that the pressure within the dryer remains constant throughout the drying process and this consistency is very important in maintaining the boiling point of water within the biomass (pine) ensuring that the moisture contained in the biomass is removed effectively, the system is insulated preventing any heat loss to the surroundings, all the energy required and used for drying comes from the internal energy of the system this maximises efficiency and control. This process does not only enhance the efficiency of biomass drying but also ensures the final product meets the specific moisture content requirement for pyrolysis.

## 7.2 Decomposition, Fast pyrolysis and separation of gases and solids



**Figure 14:** Decomposition, fast pyrolysis and phase separation

The dried biomass, which underwent processing in Area 100 to reduce its moisture content to 10%, is transferred to the decomposer. The decomposer is simulated using the RYield model component and it operates at room temperature (25°C) and pressure of 1 bar. During this process, the biomass (Pine) undergoes decomposition. The RYield model components simplify the pyrolysis of biomass by breaking down the complex heterogeneous structures such as cellulose, hemicellulose and lignin into simpler predefined components like carbon, hydrogen and oxygen by breaking the biomass into simpler basic elements the RYield model components convert this complex feedstock into manageable components. The precise decomposition process of biomass is highly complex and variable, dependent upon the particular feedstock and its features, the RYield model component is suitable for decomposition because it runs the simulation without the need for stoichiometric equations or kinetics data the decomposition is based on empirical yield values. The RYield reactor is programmed using a FORTRAN code written in the CALCULATOR block of the Flowsheeting options. This code is designed primarily to control the early decomposition yields. It determines the yields by considering the component qualities of the biomass feedstock, (pine). The

decomposed organic matter is formed of basic elements that are transported to the pyrolyzer, which is simulated by the RGibbs model components, the RGibbs model component is designed to simulate the pyrolysis reaction by determining the equilibrium composition of the final products. The RGibbs model components operates on the principle of Gibbs free energy, which states that a system will reach equilibrium at lowest possible Gibbs free energy state, the RGibbs model components calculates the products by the most thermodynamically stable distribution under the specified operating condition of the reactor, it considers all possible reactions and phase equilibria this includes the formation of liquid, gases and solids during pyrolysis

Pyrolysis takes place in the RGibbs reactor under high temperatures of 550°C in an inert environment. The absence of oxygen is crucial in order to prevent combustion and ensure efficient thermal decomposition. The high temperature facilitates the breaking down of organic compounds into three products bio-oil, synthetic gas and biochar which are the primary products of pyrolysis. The RGibbs reactor is employed for simulating the thermal degradation of biomass because to its ability to simulate reactions that reach equilibrium.

To model bio-oil components in the RGibbs reactor using Aspen Plus, it is important to select the model compounds that accurately represents bio-oil composition. The components include acids, phenols, furans, sugars and ketones. These groups define the behaviour of bio-oil in the simulation. Acid compounds found in bio-oil such as acetic acid are important due to their impact on the corrosiveness and stability of fuel. Phenols are important because they contribute to the aromatic content and thermal stability of bio-oil and ketones provide information about the oxygenated nature of bio-oil and the presence of alcohols in bio-oil indicates its potential as a renewable fuel

By incorporating these compounds into the RGibbs reactor model in Aspen Plus, we can simulate the thermodynamic behaviour of bio-oil under various conditions, predict the outcomes of different processing strategies, and optimize the production processes The RGibbs model determines the chemical and phase equilibrium by minimising the system's Gibbs free energy. This enables accurate predictions of the final composition of products. RGibbs reactor is different from RYield reactor because Ryield reactor is used to specify known yields and RGibbs leverage thermodynamic principles to determine the equilibrium state making it ideal for modelling combustion and pyrolysis where the reaction pathways leads to a stable equilibrium.

The pyrolyzed products (P-BIOMAS) is sent to the cyclone separator (CYC), this is modelled using the SSplit reactor model to separate the pyrolyzed products into two different phases solids and gaseous products. The solids (biochar) is collected as a valuable by-product while the gasses are directed to a separate stream for further processing

**Table 4:** Compounds used to model bio-oil in Aspen Plus

Compounds	Chemical Formula	CAS Number
2, 3 Epoxy-1-Propanol	C3H6O2	556-52-5
2-Butyne-1,4-Diol	C4H6O2	110-65-6
Acetic acid	C2H4O2	64-19-7
Furfural	C5H4O2	98-01-1
Furfural-Alcohol	C5H6O2	98-00-0
Ethyl-Benzoate	C9H10O2	93-89-0
Isoeugenol	C10H12O2	97-54-1
5-Hydroxymethylfurfural	C6H8O3	67-47-0
Vanillin	C8H8O3	121-33-3
Levogluconan	C6H6O2	498-07-7
Acetol	C3H6O2	116-09-6
Phenol	C6H6O	108-95-2

Bio-oil is a very complex liquid that has lot of complex mixtures of organic compounds in it some stable compounds some are not. The compounds of bio-oil can be categorised into these components.

- Phenolic compounds
- Acids
- Aldehydes
- Sugars
- Ketones
- Anhydrous sugars
- Other oxygen, nitrogen and sulphur-containing compounds

**Phenolic compounds:** These constitute a substantial fraction of bio-oil. Phenolic chemicals are mostly derived from the thermal degradation of lignin. During pyrolysis, the depolymerization process breaks down the lignin component of biomass into other phenolic chemicals. Phenolic molecules play a role in determining the colour, odour, and chemical reactivity of bio-oil.

**Acids:** Bio-oil comprises a diverse array of organic acids that mostly result from the breakdown of polysaccharides such as cellulose and hemicellulose. They enhance the acidic and corrosive properties of bio-oil. Unrefined bio-oil has high acidity levels, which can expedite the deterioration of metals and materials with prolonged exposure.

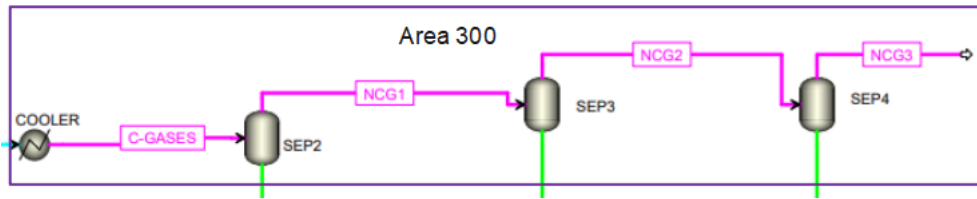
**Aldehydes:** These are carbonyl compounds characterised by a central carbon atom that is coupled to a hydrogen atom and a formyl group. Aldehydes are formed by a highly intricate breakdown process involving numerous pathways of carbohydrates and lignin found in biomass during pyrolysis. Aldehydes play a significant role in the reactivity and functioning of bio-oil, making them a crucial component in bio-oils.

**Sugars:** These compounds are generated by pyrolysis as a result of the incomplete degradation of biomass. They are consistently produced in very small quantities. Sugars are predominantly obtained from the cellulose and hemicellulose components of biomass. Sugar is produced through the cleavage of glycosidic linkages present in the polysaccharides found in biomass. While the majority of polysaccharides are converted into volatile substances during pyrolysis, a small portion remains due to incomplete decomposition.

**Ketones:** These compounds are characterised by the presence of a carbonyl group, which consists of a core carbon atom linked to two additional carbon atoms in a C=O arrangement. They are generated from the breakdown of sugars during pyrolysis. The bio-oil commonly contains ketones such as acetone and its associated derivatives.

**Other oxygen, nitrogen and sulphur-containing compounds:** Bio-oil comprises a diverse array of molecules that include oxygen, nitrogen, and sulphur atoms within their chemical structures. Illustrations of such chemicals include nitrogenous compounds such as pyridines, sulfur-containing compounds like thiophenes, and oxygenated compounds like ethers and esters.

### 7.3 Pyrolysis vapour cooling and recovery of products



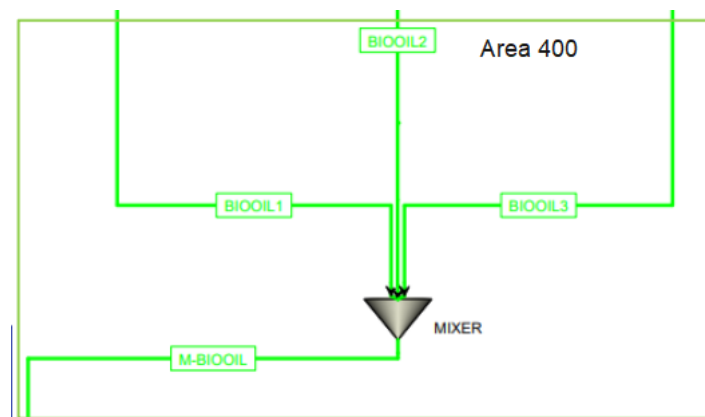
**Figure 15:** Condensation of Biooil

The pyrolyzed products after being efficiently separated into two different phases by the cyclone, the gas stream is containing synthetic gas and bio-oil is sent to Area 300 for further processing known as condensation. The aim of this stage is too collect and condense the bio-oil at the different temperature levels to maximise recovery of bio-oil. The gaseous stream is first sent to a cooler which serves as the first stage of temperature reduction, the cooler reduces the elevated of the pyrolyzed products from 550°C to 300°C. This pressure drop is very significant as it prepares the gas stream for the first phase of condensation. The cooling process does not only reduce the thermal energy of the gases abut aso initaties the condensation of heavier fractions of bio-oil.

After the gas stream passes through the cooler it is transferred to a series of condensers which is modelled as Flash 2 separators. The Flash 2 separator further reduces the temperature of the gas stream to 150°C. At this temperature, a substantial amount of bio-oil containing the heavy fractions and a mix of middle fractions condenses and is collected out of the gas phase. The gas stream now at 150°C moves on to the next condenser which lowers the temperature further down to 50°C the middle fractions of the bio-oils are collected and the gases are sent to the final condenser that reduces the temperature to 0°C the lowest temperature in the process, cooling the gas stream to this temperature ensure that the remaining bio-oil vapour is condenses out of the gas stream and the bio-oil collected at this point is the lightest fractions. This staged condensation process is critical for optimizing the recovery of bio-oil and separating it into fractions that may have different chemical compositions and uses.

Multi-stage cooling and condensation method ensures the process is efficient and effective the different fractions collected can be tailored to different applications such as fuel, chemical feedstock and other industrial uses.

### 7.4 Combination and collection of products recovered.



**Figure 16:** Collection of Bio-oil

After condensation in Area 300, the condensed bio-oil extracted at different temperatures 150°C, 50°C and 0°C which has various fractions (Light, Middle and Heavy) are collected and combined into a homogenous mixture with the aid of a MIXER component before sending it to the next processing stage. The condensed bio-oil streams are labelled as BIOOIL1, BIOOIL2 and BIOOIL3.

Area 400 illustrates the convergence of bio-oil streams into a single mixer. The purpose of the MIXER ensure that the different fractions are thoroughly blended resulting in a consistent and uniform product. The MIXER operates by continuously receiving the incoming bio-oil streams and agitating them to achieve homogeneity.

### 7.5 Hydrogen production

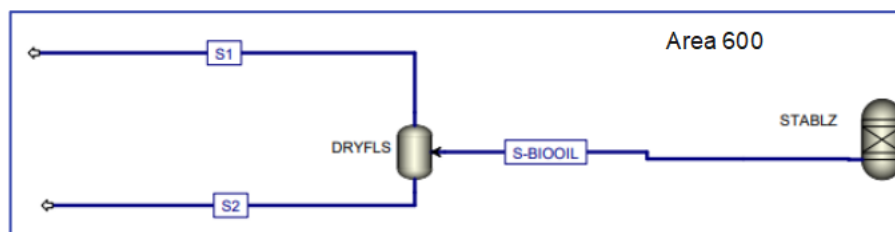


**Figure 17:** Hydrogen Preparation

The stage utilises externally provided hydrogen from a specialised plant that focuses on producing pure hydrogen. This guarantees that the hydrogen being introduced into the system is of extremely high purity. Pure hydrogen is crucial for the enhancement of bio-oil because impurities might result in catalyst contamination and unfavourable reactions during the stabilisation process of the bio-oil. Prior to being dispatched to the Stabilisation reactor, the hydrogen would undergo a sequence of preparatory processes.

The careful management and arrangement of hydrogen in Area 500 emphasise the significance of accuracy and excellence throughout the entire bio-oil manufacturing workflow. The system optimises the efficiency of hydrogenation reactions in Area 600 by maintaining the purity and appropriate pressure of hydrogen, resulting in the production of higher-quality bio-oil products. Furthermore, the acquisition of pure hydrogen from external plants underscores the significance of implementing a bio-oil production system. Partnering with specialised hydrogen manufacturers guarantees a dependable provision of top-notch hydrogen, which is crucial for the uninterrupted functioning of the facility.

### 7.6 Stabilization of bio-oil



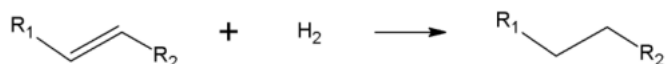
**Figure 18:** Stabilization Process of Bio-oil

The M-BIOOIL, a homogeneous bio-oil gotten from Area 400, is directed to the stabilisation reactor, which is simulated using the RGibbs reactor model. In addition, a pure compressed hydrogen stream in Area 500 is also introduced into the reactor. The reactor is operated at a high pressure of 80 bars and a moderate temperature of 180°C. These operating conditions create the necessary environment for the chemical reaction required to stabilise the bio-oil. These conditions serve to inhibit thermal degradation and the formation of tar and other

undesired by-products that would reduce the quality and quantity of the bio-oil, as well as result in less desirable products. The stabilisation process primarily targets hydrogenation reactions.

### 7.6.1 Primary reactions that occur during stabilization

- Hydrogenation:** This is the process of adding hydrogen to the bio-oil to saturate unsaturated compounds, reduce acidity, stabilize reactive compounds by reducing the oxygen content of those compounds. This process is very crucial for improving the thermal and chemical stability of bio-oil making it suitable for commercialization, storage, transportation and use as other chemical feedstock.



**Figure 19:** An example of an Hydrogenation reaction [57]

- Hydrodeoxygenation:** This is the process of removing oxygen from compounds via the addition of hydrogen to oxygen-containing compounds to form water and other new compounds. This process reduces the acidity and increases the density of the bio-oil



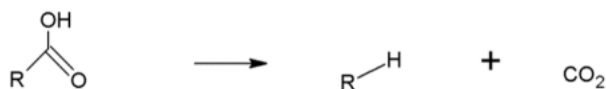
**Figure 20:** Hydrodeoxygenation reaction

- Decarbonylation:** This involves the removal of carbon monoxide (CO) from the bio-oil. This reaction helps reduce the oxygen content of the bio-oil.



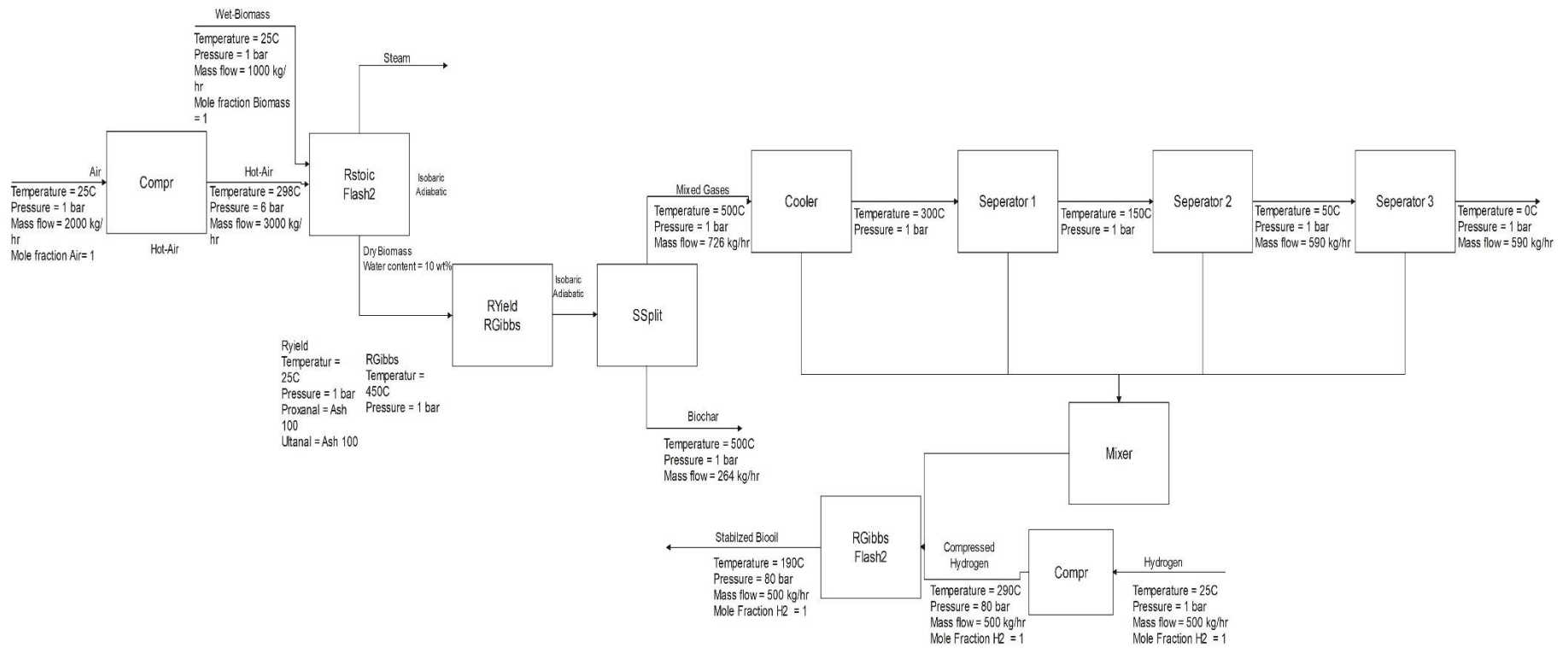
**Figure 21:** Decarbonylation reaction [57]

- Decarboxylation:** This involves the removal of carbon dioxide (CO<sub>2</sub>) in scarboxy compounds in bio-oil. This reaction helps in reducing the oxygen content.



**Figure 22:** Decarboxylation reaction [57]

After stabilization the mixture of hydrogen gases and stabilized bio-oil flows into the separator labelled as DRYFLS. These components effectively separate the gases from the bio-oil. The gases separated may include hydrogen and water vapour which are directed away and the hydrogen is recycled and sent back to the stabilization reactor.



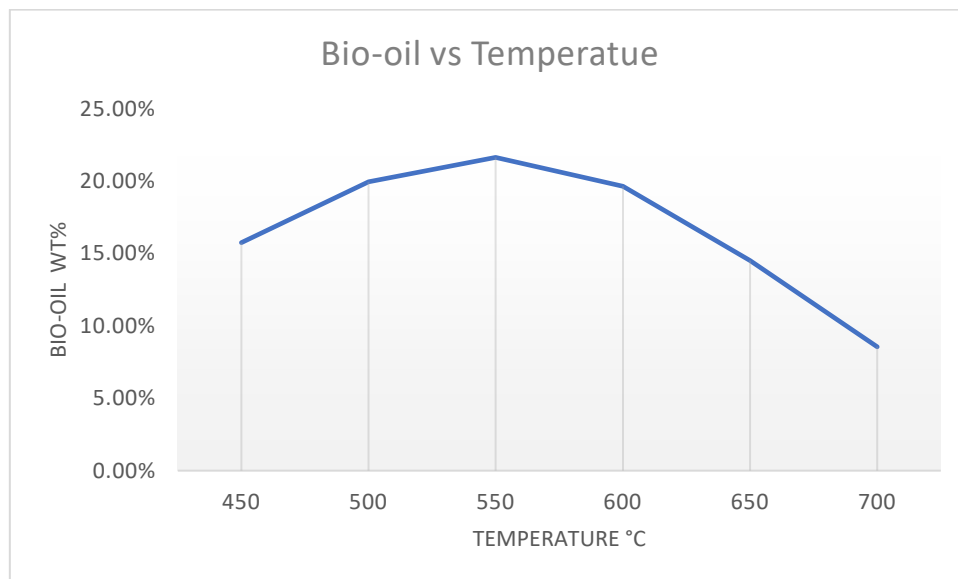
**Figure 23:** Block process diagram summary of the process description

## 8.0 Result and Discussion

### 8.1 Pyrolysis Process and Temperature Optimization for Maximum Bio-Oil Yield

Air from the environment was collected with the aid of a blower in the Aspen Plus software to ensure a steady and continuous flow of air at a consistent pressure into the drier (RStoic). A compressor was not used for this process due to its tendency to elevate the pressure and the temperature of the air being extracted from the environment which could lead to inconsistent drying conditions and potential thermal degradation of the biomass. Also, compressors consume more energy resulting in higher operational costs and increased environmental impact while the blower's ability to provide air at ambient temperature and pressure while minimizing energy consumption makes it a more suitable choice for air extraction for the environment. The extracted air is sent to a dryer (RStoic) with the biomass feedstock drying the biomass till it contains 10% according to Razier *et al* moisture content which is a suitable or required amount for effective pyrolysis of the biomass.

The dried biomass is then sent to a decomposer and pyrolyzer which is a single plant equipment that operates on adiabatic and isobaric conditions. The biomass is subjected to pyrolysis and decomposition at the same time, which results in the creation of biochar which is a solid, bio-oil which would then be condensed and collected, and syn-gas that are not condensable. For the purpose of determining the ideal temperature for maximum bio-oil yield for fast pyrolysis for pine biomass feedstock, experimental testing was conducted at temperatures ranging from 450°C to 700°C. The temperature was gradually raised by 50°C increments until it reached 700°C.



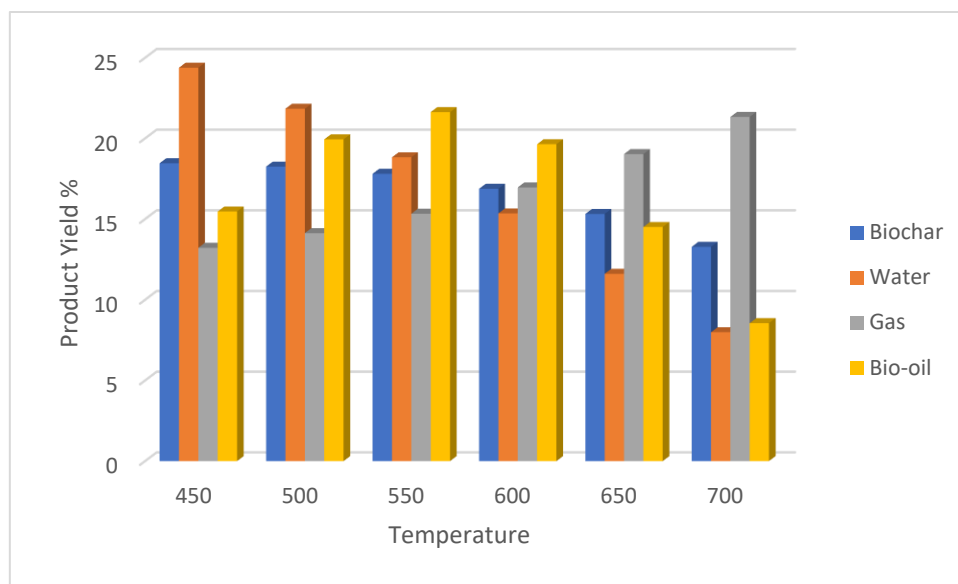
**Figure 24:** A graph of Bio-oil Yield against Temperature

Presented above is a visual representation of a graph that plots the yield of bio-oil (wt%) against temperature. The graph reveals that the quantity of bio-oil recovered after pyrolysis reaches its highest point at 550°C. This suggests that the best temperature for the pyrolysis of pine biomass feedstock to produce the highest yield is 550°C. This may be explained by the equilibrium that exists between the thermal degradation of biomass and the secondary phase reaction processes that take place at high temperatures. At low temperatures ranging from 450°C to 500°C the bio-oil yield is relatively low this is due to incomplete decomposition of the biomass, small little

residence time and insufficient energy to break down complex organic molecules into bio-oil. As the temperature gradually increases to 550°C the heat provided is sufficient to enhance the breakdown of the biomass feedstock into smaller molecules thereby increasing the yield of the bio-oil.

As can be observed in the figure that is shown above, the yield of bio-oil begins to decrease as the temperature increases over 600°C and continues to rise above 700°C. Moreover, this can be explained by secondary cracking events that take place within the reactor, which ultimately result in the creation of gases that are not capable of condensing. The bio-oil that is obtained during pyrolysis undergoes further degradation into simpler compounds (non-condensable gas) when subjected to extremely high temperatures, which results in a decrease in the amount of bio-oil that is produced.

## 8.2 Analysis of Pyrolysis Products at Various Temperatures



**Figure 25:** A graph of the primary product of pyrolysis against temperature

The graph above shows the result of the three main products of pyrolysis against different temperature ranges (450°C – 700°C) with the temperature difference between them being 50C.

### 8.2.1 Effect of Temperature (450°C – 500°C) on Pyrolysis products

As can be seen from the graph, the highest level of bio-oil production occurs at a temperature of 550 °C, which indicates that this is the ideal temperature for pyrolysis in order to achieve high levels of bio-oil production. With temperatures ranging from 450 C to 500° C, the yield of bio-oil is relatively low, while the yield of water is high, and the yield of synthetic gas is slightly higher.

Bio-oil yield is low at these temperatures due to incomplete decomposition of biomass components such as cellulose and hemicellulose, there are three primary components of any woody feedstock namely hemicellulose, cellulose and lignin. There is a low bio-oil yield in this temperature range (450 -500) because of insufficient thermal energy that is significant for cracking of the biomass lignin structure which is very crucial for producing bio-oil, lignin which is more thermally stable than hemicellulose and cellulose requires a higher temperature to decompose into more complex compounds. At this temperature range the major product was water this is due to the biomass feedstock undergoing a reaction known as dehydration reaction because the thermal energy is sufficient to trigger dehydration reaction but not enough to pyrolyze the biomass.

There was slight production of synthetic gas at this temperature range this indicate that biomass gasification is possible but the thermal energy is not enough to convert the biomass to synthetic gas, The gases produced at the temperature range are primarily due to pyrolysis of lighter volatile compounds which are easily converted into gas at such low temperatures.

Biochar is the second main primary product of at this temperature range, several factors contribute to the high production of biochar compared to other products like bio-oil and synthetic gas. At temperatures ranging from 450°C – 500°C the thermal energy is enough to provoke some certain reactions like dehydration, but it is also enough to provoke other reactions like depolymerization and fragmentation. At this temperature the energy is enough to break down hemicellulose and partially cellulose into simpler or volatile organic compounds but not enough to break down more thermally stable compounds like lignin. Lignin and cellulose partially decompose to form a carbon-rich solid residue known as biochar. From Table 4 the component analysis shows that the biomass feedstock contains 21.66% hemicellulose, 46.97% cellulose, 27.65% cellulose and 2.70% extractives this further explains why biochar was produced as the second primary product during pyrolysis at these temperatures.

### **8.2.2 Effect of Temperature (550°C) on Pyrolysis products**

According to the graph in Figure 24, the temperature of 550 °C is the ideal temperature for the pyrolysis of pine biomass feedstock in order to get a high yield of bio-oil that is produced. The thermal degradation of components of biomass, such as cellulose and hemicellulose, is nearly complete when the temperature is at this point. According to [58] cellulose decompose at 260C to 300C, hemicellulose decompose at slightly lower temperature 220°C – 260°C and lignin decomposes at high temperature ranging from 280°C to 500°C. This makes 550C the ideal temperature for the production of bio-oil, because volatile compounds can be broken down into simpler compounds reducing secondary cracking reactions and less synthetic gas production. At this temperature, there is a moderate level of water production which can be explained by simple dehydration of the biomass feedstock which is typically at a temperature below 400°C, before the temperature reaches 550°C, water is also formed during the breakdown of oxygenated compounds in the biomass. At this temperature, there is also a slight production of synthetic gas as volatile compounds are converted into gases at the beginning of the pyrolysis. Biochar production at this temperature is also very moderate due to the partial decomposition of lignin.

### **8.2.3 Effect of Temperature (600°C – 700°C) on Pyrolysis products**

From Figure 13 it can be seen that the pyrolysis yields significantly more synthestic gases. This is because of a secondary cracking reaction. The elevated temperature provides sufficient energy to break down complex organic molecules into volatile matter but the temperature is also high enough to break the volatile matter down further into simpler gaseous compounds. This leads to the production of more synthetic gases. Bio-oil contains complex compounds that are thermally unstable compounds so at such high temperatures the unstable compounds break down further reducing the yield of the bio-oil.

## **8.3 Practical Implications for Bio-oil Production**

From Figure 13 the observed trends have practical implications in optimizing bio-oil through pyrolysis:

- **Optimal Temperature:** It is recommended that the biomass be dried to a moisture content of 10% prior to pyrolysis in order to achieve a high output of bio-oil. Additionally, the pyrolysis process should be carried out at a moderate temperature of approximately 550° C. This temperature range balances the decomposition of biomass and minimizes secondary cracking reaction of bio-oil into gases.
- **Feedstock composition:** The composition of the biomass feedstock influences the optimal temperature range and also the bio-oil yield. Feedstock containing more cellulose and less lignin should be more favourable for the production of bio-oil, feedstock containing more lignin would require a higher temperature to decompose.

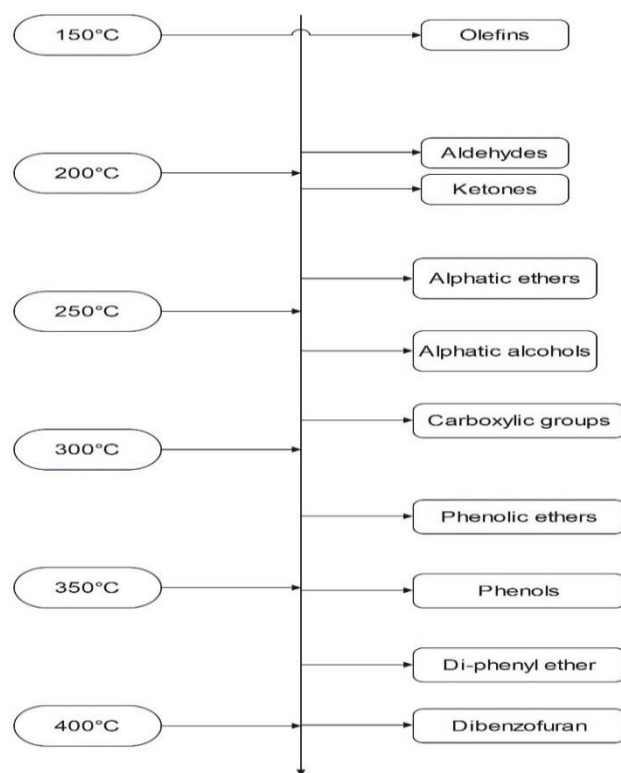
The bio-oils were condensed using three condensers, each operating at various temperatures to achieve the highest possible yield of condensed bio-oil. The utilisation of multiple condensers provides significant operational and economic benefits the gaseous pyrolysis products passing through the cooler and condenser with an elevated temperature of 550°C. Relying on a single condenser for the bio-oil condensation process would subject the equipment to significant and continuous thermal stress, resulting in rapid deterioration and frequent replacement of plant equipment. Such an interruption in the production process would result in financial losses and incur additional expenses for purchasing replacement equipment and hiring additional workers. In addition, the load and stress on the condensers will be evenly distributed in order to improve heat exchange and maintain consistent performance across all three condensers. Moreover, from an economic standpoint, the initial investment in extra condensers is balanced by the long-term savings resulting from reduced equipment replacement frequency and maintenance costs, as well as the promotion of sustainable plant operation. The condensed bio-oil was transferred to the reactor for stabilisation. The stabilisation process involves subjecting the bio-oil to hydrogenation and hydrodeoxygenation at elevated pressure and moderate temperatures in order to enhance its quality and storage stability. The table below presents the bio-oil yield obtained from the condensers after pyrolysis at the optimal temperature of 550°C, as well as the bio-oil yield after stabilising.

**Table 5:** Comparison of Bio-Oil Component Yields Before and After Stabilization

Bio-oil Components	Bio-oil Yield wt% after Pyrolysis	Bio-oil Yield wt% after Stabilisation
2, 3 Epoxy-1-Propanol	$2.33496 \times 10^{-16}$	0.07551739
2-Butyne-1,4-Diol	0	0.052856145
Acetic acid	99.99999999	1.088150233
Furfural	$1.69993 \times 10^{-14}$	0.009732835
Furfural-Alcohol	$9.26091 \times 10^{-17}$	$2.04409 \times 10^{-05}$
Ethyl-Benzoate	$0.36745 \times 10^{-17}$	$5.21442 \times 10^{-18}$
Isoeugenol	0	$5.62994 \times 10^{-28}$
5-Hydroxymethylfurfural	0	$2.11183 \times 10^{-08}$
Vanillin	0	$2.19679 \times 10^{-25}$
Levoglucosan	0	$5.18179 \times 10^{-20}$
Acetol	0	98.77284415
Phenol	$1.29104 \times 10^{-08}$	0.000139046
P-Hydroquinone	$8.26508 \times 10^{-14}$	0.000739734

The findings demonstrate that the stabilisation procedure effectively maintained the bio-oil's output while also improving its quality through the reduction of unstable and reactive constituents. This is demonstrated by the substantial alterations in the chemical composition of the bio-oil before and after stabilisation, as indicated in the corresponding data.

During the stabilisation process, two reactions are essential in improving the quality of bio-oils. The process of hydrogenation and hydrodeoxygenation occurs simultaneously when hydrogen is added to the bio-oil. This addition of hydrogen effectively saturates unsaturated compounds by lowering reactive species such as aldehydes, ketones, and olefins. Additionally, the hydrogen also reduces the oxygen content in the bio-oil. This also facilitates the extraction of water from bio-oil, which is a major problem in bio-oil. Bio-oil typically contains a large amount of water, which diminishes its effectiveness as a fuel and its ability to be stored for extended periods. These two reactions enhance the stability of the bio-oil, enhance its energy content, and mitigate its propensity to generate unwanted tars and other by-products when burned. The reactor is operated at a pressure of 80 bars and a temperature of 180°C in order to stabilise the process. The high pressure serves as a catalyst for the hydrogenation reactions, while the moderate temperature minimises the development of tar, which typically occurs at higher temperatures. Based on the research conducted by Jones *et al* [57] the level of reactivity exhibited by different oxygenated compounds in bio-oil is influenced by the temperature at which the processing takes place.



**Figure 26:** Reactivity scale of Oxygenated groups influenced by difference in temperature.

Figure 26 demonstrates that the oxygenated compounds of bio-oil are influenced by temperature. This suggests that different temperature ranges have diverse impacts on the components of bio-oil. Figure 26 demonstrates that lower temperatures promote the stabilisation of simpler molecules, such as olefins, aldehydes, and ketones. Conversely, elevated temperatures promote the formation of more intricate chemicals, such as phenols and

dibenzofurans, which may potentially lead to issues. The plant design for stabilising bio-oil was specifically configured to operate at a temperature of 180 degrees Celsius and a pressure of 80 bars. This was done to prevent the generation of undesirable by-products, such as tar, that can occur at extremely high temperatures. Typically, temperatures exceeding 200°C promote tar formation, complicating the stabilisation of bio-oil, reducing the yield of upgraded bio-oil, and diminishing its quality.

A study conducted by the National Renewable Energy Laboratory (NREL) shows that bio-oil can be effectively stabilised by using moderate temperatures and high pressure. This approach helps prevent the formation of tar by using moderate temperatures, while achieving effective hydrogenation by applying high pressure. The study examined several operating settings with the goal of optimising the hydrogenation efficiency while limiting tar generation.

### 9.0 Mass and Energy Balance

The table below shows the mass and energy balance of the bio-oil plant and also every individual equipment.

**Table 6:** Mass and energy balance for the bio-oil plant

<b>Mass &amp; Heat Energy Balance for Bio-oil Plant</b>										
<b>Plant Input</b>		<b>Feedstock Entering the Aspen Plus model Components</b>			<b>Equipment</b>	<b>Feedstock Leaving the Model Components</b>			<b>Plant Output</b>	
Feedstock	Kg/hr	Mass Kg/hr	Stream Inlet	Heat kW		Stream Outlet	Mass Kg/hr	Heat kW		Kg/hr
Air	2000	2000	Air	-0.158382	Blower	H-Air	2000	-0.158382		
		<b>2000</b>		<b>-0.158382</b>	<b>Total</b>			<b>-0.158382</b>		
Biomass	1000	1000	W-Biomass	-5502.02	Dryer	D-biomass	3000	-5192.02		
		2000	H-Air	-0.158382						
		<b>3000</b>		<b>-5502.18</b>	<b>Total</b>			<b>-5192.02</b>		
		3000	D-biomass	-5192.02	Separator 1	Steam	2000	-5191.73	Steam	2000
						D-Biomass2	1000			
		<b>3000</b>			<b>Total</b>			<b>-5191.73</b>		
		1000	D-biomass2	-5191.73	Decomposer	De-Biomass	1000	-430.423		
		<b>1000</b>		<b>-5191.73</b>	<b>Total</b>			<b>-430.423</b>		
		1000	De-Biomass	-430.423	Pyrolizer	P-Biomass	1000	-1580.08		
		<b>1000</b>		<b>-430.423</b>	<b>Total</b>			<b>-1580.08</b>		
		1000	P-Biomass	-1580.08	Cyclone	Gases1	735	-1580.08	Biochar	265
						Biochar	265			
		<b>735</b>		<b>-1580.08</b>	<b>Total</b>		<b>1000</b>			
		735	Gases 1	-1635.05	Cooler	C-Gases	735	-1740.21		
		<b>735</b>		<b>-1635.05</b>	<b>Total</b>			<b>-1740.21</b>		
		735	C-Gases	-1740.21	Separator 2	NCG1	728	-1798.74		
						Bio-oil1	7			
					<b>Total</b>		<b>735</b>	<b>-1798.74</b>		



The mass and energy balance of the bio-oil plant in Table 5 above shows that the mass input mass is equal to the output mass. This shows that all the materials streams are properly accounted for and the process model is balanced with no mass loss or unaccounted gains. The energy balance indicates that there is a negative energy balance this reveals that the total energy output is less than the energy input. This can be explained by critical attributed factors inherent to the biomass pyrolysis and stabilization process as shown in Figure 10.

It is important to understand that pyrolysis by nature is an endothermic process, this simply means it requires a substantial amount of energy to work. The energy needed to break the molecular bonds in the biomass is very significant and the absorption of this energy contributes to the negative energy balance. Furthermore, the various equipment used throughout the process consumes energy to perform their designated functions. The energy consumed from this equipment blower, dryer, decompose, pyrolyser and compressor consumes a substantial amount of energy significantly contributing to the overall energy deficit observed.

Also, energy losses are another crucial factor that have a significant impact on the energy balance. In any industrial process there are inherent inefficiencies leading to energy losses. This loss can occur due to inefficiencies in heat transfer, thermal radiation and other forms of energy dissipation. Like heat losses through the walls of the reactor and piping during transfer of product can result in a significant reduction in the net energy balance, despite the effort to insulate and minimise these losses they remain unavoidable during the plant working.

Additionally, the heat of vaporisation plays a role in negative energy balance. During the pyrolysis and stabilisation process. The liquid components are converted into vapour, which requires a considerable amount of energy. This energy is known as the heat of vaporisation is very significant and contributes to the overall energy deficit. Additionally in the process simulation cooling systems were used to lower the temperature of the produced mixture of bio-oil and non-condensable gases. The cooling process extracts energy from the system thus adding to the negative energy balance. Lastly, there is a dynamic interaction between different process streams and the phase changes they undergo require and release energy, the phase change from solid to gas and then gas to liquid requires and involves complex energy exchanges. These dynamic interactions can result in net energy consumption depending on the specifics of the reactions and separation occurring within each equipment unit,

The stabilization or upgrading of bio-oil typically includes chemical reactions such as hydrogenation, cracking, and deoxygenation. These reactions are predominantly exothermic, releasing heat as hydrogen is added to the bio-oil components to improve stability and reduce oxygen content. The heat released during these reactions adds to the overall energy output, thus contributing to the positive energy balance.

Hydrogen compression to 80 bars was an integral part of the process. Compressing gases increases their temperature due to the work done on the gas. This process is exothermic, with the resultant increase in temperature contributing additional thermal energy to the system. The energy required to compress hydrogen and the resultant heat generation must be considered in the energy balance, further explaining the surplus.

Efficient heat recovery mechanisms within the system can capture and utilize the heat generated during exothermic reactions, thereby reducing the need for external energy inputs. This efficiency can result in a net positive energy output, as the internal heat generated by the system contributes to maintaining process conditions without requiring additional energy.

## 10.0 Conclusion

The study that is reported in this thesis provides a significant addition to the field of renewable energy, namely in the production and upgrading of bio-oils that are obtained from biomass through the process of fast pyrolysis. This work has showed that careful management of temperature and pressure conditions can significantly improve the yield and quality of bio-oil. This was accomplished through the use of extensive process simulations and the optimisation of pyrolysis parameters. The findings shed light on the possibility of fast pyrolysis as a viable approach for the production of bio-oils, which have the potential to serve as a sustainable alternative to traditional fossil fuels.

The findings and recommendations of this research have significant repercussions for the various sectors that are involved in renewable energy. Given the enhanced understanding of the relationship between pyrolysis conditions and bio-oil qualities, it is possible that future efforts to optimise the production of bio-oil on an industrial scale will be guided by this understanding. In addition, the research highlights the significance of pre-treatment of biomass prior to pyrolysis, as this step has the potential to dramatically impact both the effectiveness of the process and the quality of the bio-oil that is produced. It has been demonstrated that the utilisation of techniques such as drying and size reduction of biomass feedstock prior to pyrolysis can enhance the production and stability of bio-oil, making these techniques essential topics for further investigation.

Despite the promising results, this study is not without its limitations. The simulations conducted were based on specific types of biomass and operating conditions, which may not fully capture the variability and complexity of real-world biomass feedstocks and industrial processes. Additionally, while the study focused on optimizing the pyrolysis process, other factors such as the cost and scalability of bio-oil upgrading techniques were not addressed in detail. These are important considerations that should be explored in future research.

Looking onwards, it is recommended that future research concentrate on the development of more sophisticated pre-treatment methods that have the potential to further enhance the effectiveness of bio-oil production strategies. Furthermore, there is a need for research into the integration of bio-oil production with other renewable energy systems. For example, the exploration of hybrid upgrading techniques that combine multiple processes, such as hydrotreating and catalytic cracking, could pave the way for the production of bio-oils of a higher quality with properties that are more comparable to those of conventional petroleum fuels.

In conclusion, this thesis offers significant contributions to the development of sustainable energy technologies by providing useful insights into the fast pyrolysis of biomass and the subsequent upgrading of bio-oils. The findings highlight the promise of bio-oils as a source of renewable energy and establish the framework for future research that will be focused at overcoming the problems that are connected with the production and utilisation of bio-oils.

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