

Interaction of biomass with NO_x during the re-burning process

Written by: Francis D'Souza



MURDOCH
UNIVERSITY

PERTH, WESTERN AUSTRALIA

Supervisor: [Mohammednoor Altarawneh](#)
SCHOOL OF ENGINEERING AND INFORMATION TECHNOLOGY

Abstract

The interaction between biomass and NO_x is very important to understand because it can revolutionise the way industrial furnaces are used. The technology that was discussed was re-burning. Re-burning is essentially changing the atmosphere in a furnace where the biomass is being combusted. This zone is known as the re-burning zone. The re-burning zone is a medium where NO_x and biomass can interact. The type of biomass that was experimented on was a wood-based biomass. In terms of the characterisation, an ultimate and proximate analysis was done in conjunction with a bomb calorimeter test. The results from the characterisation, when tested with four different sources of biomass, yielded that all the biomass samples have similar properties. The four samples that were tested were pine, eucalyptus, miscanthus and oak. Since they all had similar properties it was safe to perform a test on one of these biomass samples. The test that was being performed was the diffused reflectance infrared fourier transform spectroscopy analysis also known as the DRIFTS analysis and the sample of biomass that was chosen was the miscanthus as seen from the results of the characterisation, it made no difference which biomass sample was picked. The DRIFTS analysis was also done in four different atmospheres to assess the interaction between NO_x and biomass. The four different atmospheres included the following; inert atmosphere which would provide data for oxygen-fuel ratio when burning biomass, inert and NO_x . The conclusion that was drawn due to the DRIFTS analysis is that biomass can interact with NO_x in gas-gas and gas-solid reaction. This implies that NO_x can interact with wood-based biomass before combustion even occurs. This information is useful as it would help decrease the biomass emissions. The DRIFTS analysis did have its limitations and this was the fact that there no quantifiable data was extracted although this is easily fixed by running the same types of test in a thermogravimetric analyser (TGA) with the same atmosphere. This would yield the actual amount of NO_x that has interacted with the biomass.

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Chapter 1: Introduction

Nitrogen oxides can be shortened by referring to the acronym NO_x . NO_x can originate from many sources, but for the purpose of this thesis, the source of NO_x that will be discussed will be the NO_x that originates from the combustion of biomass. From literature, it is known that the average amount of NO_x in any biomass sample is 20 mg/kg. This can be considered to be a dangerous amount due to the impact NO_x can have on its surroundings. (Ehsan Houshfara, 2012)

Biomass is considered to be a very clean source of energy in comparison to fossil fuels. Forms of biomass include alcohol fuels, solid waste, landfill biogas and gas and biodiesel (Williams, 2012). Extracting energy from any of these sources is a cleaner alternative to fossil fuels. This is because of the efficiency of the combustion of the biomass since it produces a very low amount of off-gases. This is because there are very high amounts of volatiles within the biomass that produce the energy. There are four types of biomass which will be tested when it comes to the interaction between biomass and NO_x . These include pine, oak, miscanthus and eucalyptus. These four types of biomass are being tested because they are the most common types of biomass used in industry and are considered to be abundant.

In many cases, NO_x is the major source of acid rain which can be very harmful, both to wildlife and the environment. The acid rain can also spread and be dissolved in the oceans which can change the properties of seawater that would then, in turn, harm the eco-systems within the oceans. NO_x is also considered to be a greenhouse gas which can affect the climate due to the fact it can be caught in the ozone layer. (Heywood, 2006) When NO_x is caught in the atmosphere it can cause global warming which is already a major world issue. Due to the various issues caused by NO_x , a solution needs to be found. To decrease the amount of NO_x in a furnace when referring to biomass, the whereabouts of the origination of NO_x is needed. From literature, it can be perceived that NO_x originates from the combustion process in biomass. (Qian, 2011) Therefore, the proposed solution to reduce the concentration of NO_x in the reburning process.

To ensure accurate results, characterization tests of the biomass sample will need to be run. This is to make sure that the testing is accurate when the combustion of biomass is assessed in the Fourier atmosphere. There are three main types of characterization that will be done and

these will be done to assess various properties such as the chemical species in the biomass, components of the biomass such as the ash, volatiles, fixed carbon and moisture and the enthalpy of the biomass and how much energy it contains.

Characterization of the samples also helps in understanding whether there are any different trends within the biomass samples which are wood based. Different types of characterizations will need to be done because if in theory, the interaction between other forms of biomass was assessed then different forms of characterization would also need to take place since they would have different physical and chemical properties. This is because characterization is also dependent on the properties of the sample. For example, the characterization methodology of the wood-based biomass samples would differ from the biomass which originates from alcohol fuels. This is due to the different states of matter since the wood-based samples are solids whereas the alcohol fuels are in the liquid state. Overall the characterization of the biomass samples is important for the understanding of the reburning process. (Brown, 1989)

The reburning process is a process which has been used for coal. The intention of this thesis is to apply this same technology to the combustion of biomass. Re-burning is where the off-gases that are produced in the biomass are captured within the furnace. The captured off-gases in biomass mainly include carbon dioxide and NO_x gases. When a combustion reaction occurs with biomass in an atmosphere with the off-gases, according to the theory of reburning, 70-80% of the NO_x in the off-gas should decompose and form nitrogen and oxygen. (Yaman, 2003) This is because the oxygen that originates from the decomposed NO_x should be used for the combustion reaction in the furnace. The nitrogen from the decomposition can be considered to be inert and would not negatively impact the environment. To assess the effect of reburning, there are many types of atmospheres that are utilized as mentioned before in the reburning process. The first atmosphere would be normal conditions which would be the combustion of biomass in the air. The second atmosphere that is mentioned is the combination of air and NO_x which is the in the reburning zone. By assessing the combustion reactions in these two atmospheres a basic understanding of the reburning process is portrayed. To highlight these atmospheres and have a deeper understanding of the interaction of between NO_x and biomass with the atmosphere, two more atmospheres will have to be assessed. The two atmospheres in question are the inert atmosphere and the inert with the addition of NO_x . This is to further understand how NO_x affects the combustion process with the absence of air. This type of testing will be done in the dispersive fourier-transform infrared spectroscopy analyzer.

Chapter 2: Literature Review

NO_x is the shortened version of Nitrogen Oxides and they are the focal point of this thesis. It is of high importance in the industry to understand the emission of NO_x and how it can be harmful, both in the workplace and towards the environment. The main feature of NO_x emission will be assessed through the production of NO_x via Biomass and its surrogates and therefore reduction of NO_x will be the aim of the thesis. In this paper, literature will be reviewed in terms of the topics such as Biomass, Combustion Science and Nitrogen Oxides, Characterisation, NO_x mitigation techniques the Biomass Surrogates and the gaps in the Literature. Overall by exploring these topics a deeper understanding of the topic is shown.

2.1 Biomass

Biomass is defined as a source of fuel which originates from organic materials which were living or recently living and is overall considered to be categorised as a form of renewable energy. Biomass can come in solid and liquid state and overall the state of the biomass is dependent on the biomass's melting and boiling point. "Solid biomass covers a wide range of materials: woods, straws, agricultural residues, processing wastes, algae and seaweeds." (Williams, Jones, Pourkashanian 2012). Overall the four various types of biomass samples which will be monitored, which are solids and they consist of pinewood, oakwood, eucalyptus and miscanthus and in terms of liquid forms of biomass, two surrogates will be experimented instead of biomass which are benzaldehyde and furfural which are then compared to the solid form of biomass. It can be noted that Biomass is mainly used to produce various forms of energy which are utilised for both personal and industrial use.

"Essentially biomass used as a fuel can be divided into the following two major groups:

- (1) Biomass, grown directly for use as a primary fuel,
- (2) Traditional bioenergy (e.g. biomass for cooking)" (Williams, Jones, Ma, Pourkashanian 2012)

In terms of biomass as traditional bioenergy, it is mainly for personal use because it can be used in cooking, whereas biomass utilised as a primary fuel is important because it relates to the industry. It should be noted that biomass was considered before the rise in fossil fuels. "The early use of biomass was based on easy accessibility and availability, but the use decreased in many countries due to shortages in the 19th Century and by the emergence of fossil fuels." (Williams, Jones, Ma, Pourkashanian 2012). Although currently there are other forms of fuel, the world is heading towards an energy and environmental crisis mainly due to fossil fuels

which are running out and is causing harmful carbon emissions. This has caused the search for better alternatives and biomass, hence biomass being grown directly for primary fuel and this is highlighted in terms of the expansion of biomass in the market. “There is an expanding market in the use of biomass for supplying both transport fuels and electricity/heat.” (Williams, Jones, Ma, Pourkashanian 2012) Since there is an expanding market, this can only mean that research on the combustion of biomass and all the factors in it are very useful for industrial and research purposes.

2.1.1 Chemical Structure Biomass

The chemical structure of biomass varies depending on the type of biomass. Different types of biomass have different chemical structures and energy content. The different chemical structures can be assessed and characterised by methods such as the following.

Elemental/Ultimate Analysis which allows the detection of the core elements the biomass sample is made of. The ratio of each of the elements will be different for the type of biomass whereas other sources say that proximate analysis maybe use as proximate analysis finds the weight percentage of moisture, volatiles, fixed carbon and ash within the biomass. Although it can be agreed that the inductively coupled plasma-mass spectrometry (ICP-MS) analysis can be used to support the elemental and proximate as the ICM-MS Analysis can help by picking up trace elements in which the other two methods couldn't and this overall ensures the accuracy of the characterisation. In conjunction with the three methods, the different types of biomass need to be categorised as homogeneous or heterogeneous and this is because this is a direct factor of reaction rate which is important to note. As the elemental, proximate and ICP-MS analysis cannot determine whether the biomass will be homogeneous or heterogeneous then the fourth type of characterisation method is introduced which is XRD Analysis. The XRD analysis can identify the phase of the crystalline material which is useful when determining if a biomass is homogeneous or heterogeneous.

The knowledge of the chemical structure of biomass is important because “All biomass species contain the nutrients P, N and K and the other major essential elements Ca, Na, Mg and Si with the concentrations of these nutrients being heavily dependent on the type of biomass, the growing conditions and harvesting time” (Williams, Jones, Pourkashanian, 2012). Although when characterising the ultimate analysis cannot find P, K, Ca, Na, Mg and Si which further cements the need the ICP-MS analysis as it can pick up those elements.

2.1.2 Biomass vs Fossil Fuels

From earlier readings, it has been known that biomass was used before fossil fuels but due to the shortages in biomass, fossil fuels were introduced and were considered to be the superior option because of its abundance and low cost. Although nowadays in consequence to extensive uses, the storages of fossil fuels are depleting and it's a known fact that fossil fuels are dangerous to the environment. This means that alternative pathways need to be researched. Pathways such as the reconsideration of biomass. The advantages and disadvantages of both biomass and fossil fuels have been listed below.

Disadvantages of fossil fuels

- Produce large amounts of carbon dioxide which are dangerous for the environment
- Limited supply
- Time for a new supply takes millions of years

Advantages of fossil fuels

- Low cost
- Abundant
- Reliable

Disadvantages of biomass

- Produce more carbon than coal
- Has to be burned

Advantages of biomass

- Renewable source of energy
- Can absorb carbon emissions which have been produced making it carbon neutral
- Low cost for large amounts
- Comes from more than one source

Taking those general advantages and disadvantages into account. The cementation of why biomass is the superior form of energy can be seen by comparing the energy contents and emissions of NO_x, CO and smoke. In literature, graphs have been produced to compare biomass and biodiesel.

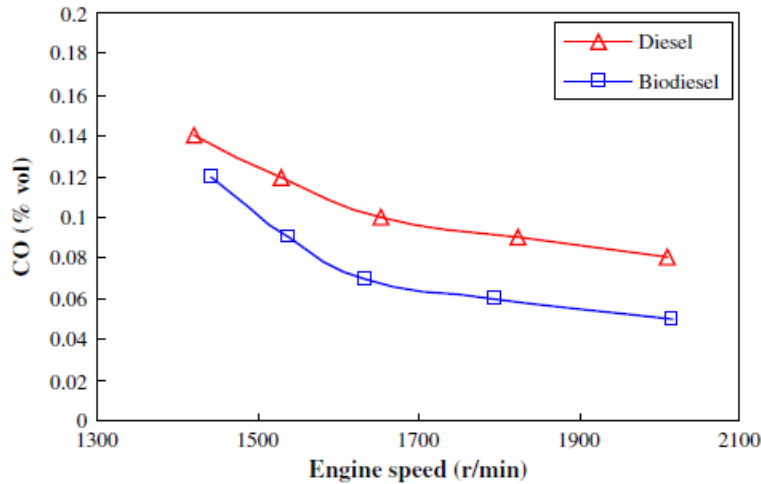


Figure 1: CO emissions in vol% of both Diesel and Biodiesel with changing Engine Speed

In Figure 1 it can be noted that CO is produced instead of CO₂ meaning there is a lack of oxygen as discussed later on. Diesel in comparison to biodiesel has a higher volume percentage of CO emission. Therefore from this graph found in literature, it can be assumed that biodiesel generally produces lower amounts of CO.

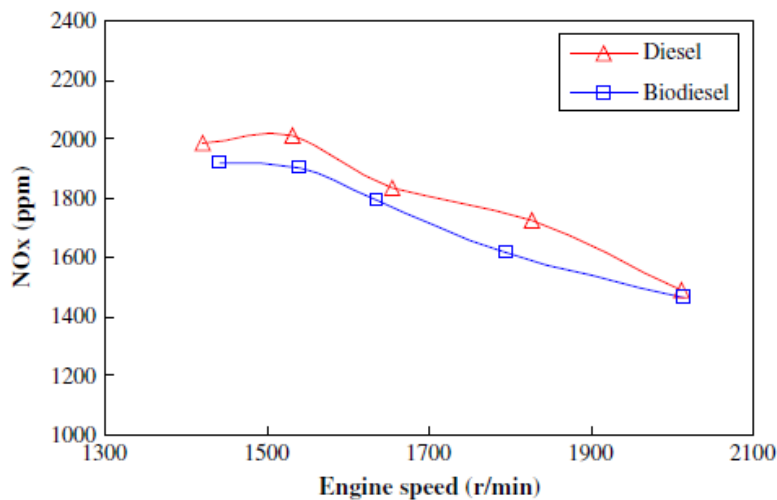


Figure 2: NO_x emissions in ppm of both Diesel and Biodiesel with changing Engine Speed

In Figure 2 it can be noted the ppm of NO_x produced from diesel is generally higher than the NO_x produced from biodiesel. Although in the graph it shows that at around the 2000 r/min mark there is approximately the same amount of NO_x in ppm produced. This may hint that at higher r/min biodiesel may produce more NO_x.

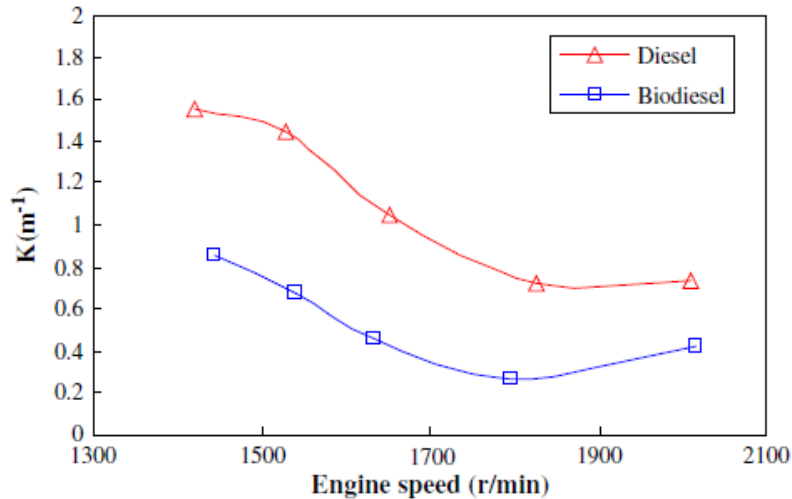


Figure 3: Smoke Emissions of both Diesel and Biodiesel with changing engine speed

In Figure 3 it can be seen that the amount of smoke produced from biodiesel in comparison to normal diesel is significantly lower at all r/mins. Hence from this graph found in literature, it can be seen that biodiesel produces less smoke than diesel.

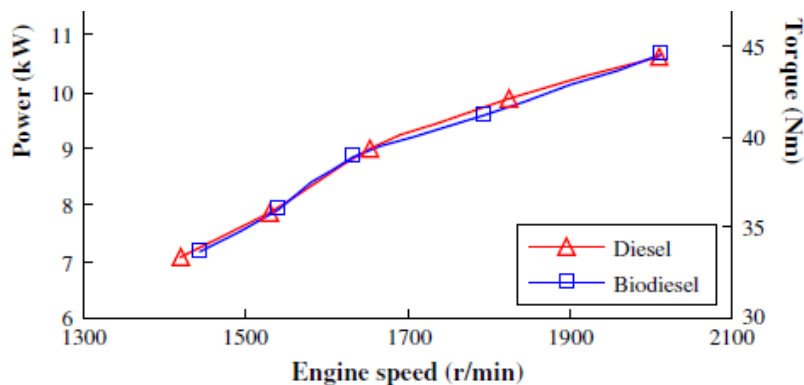


Figure 4: Comparison of Diesel and Biodiesel Power and Torque with changing Engine speed

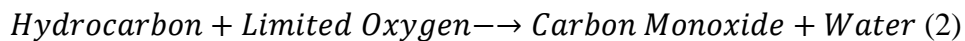
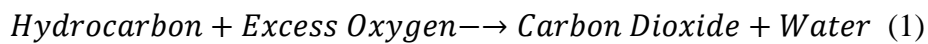
In can be seen from Figure 4 that the power output and the torque produced from the biodiesel and the diesel are of similar values meaning that in terms of energy output and the efficiency there is almost no difference.

Overall it can be noted the from figures 1, 2 and 3 that biodiesel is more or less, safer than regular diesel and in terms of their energy contents and production they are similar. With all the factors taken into account this overall means from the experimentation within the literature that biomass based fuels are superior to fossil fuels.

2.2 Combustion Science

2.2.1 Defining Combustion

Combustion can be simply defined as the process of reacting fuel with oxygen to discharge advantageous energy. There are mainly two types of combustion which can be classified as complete or incomplete. The completion and the incompleteness are dependent on the amount of oxygen. In general, the following reactions will occur for complete and incomplete reactions.



As seen from reaction (1) if there is excess oxygen then the formation of carbon dioxide and Water occurs in the products and the overall reaction is considered complete whereas in the case of reaction (2) there is carbon monoxide formed in the products due to the insufficient amount of oxygen. Overall this is because in the molecular compound CO_2 there are 2 oxygen molecules and is considered to be completely formed whereas CO only consists of one oxygen molecule and can be considered incomplete as CO_2 has not formed. Most of the oxidants in chemical reactions are air but there is another oxidant which will be investigated which is NO_x . Understanding the concept of combustion is important because this is one of the foundations of the process of NO_x reduction.

2.2.2 Relation between Combustion and Biomass

Combustion is very important for biomass as this is how the energy from biomass is obtained. Depending on the biomass various products can form but in general, most biomass produces NO_x gases. This is important to note because NO_x gases consist of oxygen and nitrogen so theoretically when separated, nitrogen can be safely released into the atmosphere and oxygen can be used for combustion reactions and this can mainly be done through the process of reburning. To understand this, a deeper investigation of NO_x and its reaction mechanisms are required.

2.3 Nitrogen Oxides (NO_x)

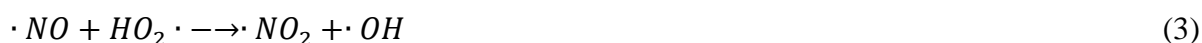
Nitrogen oxides are the group of gases which have nitrogen and oxygen within their molecular structure. NO_x gases primarily threaten the atmosphere as off-gases from a reaction containing Biomass but can also harm other aspects such as humans, animals, plant life and the soil. A few of the examples of nitrogen oxides include the following:

- NO = Nitric Oxide
- NO₂ = Nitrogen Dioxide

These gases are the main focus of the thesis as they are produced from the burning of the biomass sample. In many of the articles, NO_x gases are always presented as the problem when it comes to biomass.

Nitric oxide is a colourless gas and usually has a free radical. Nitric oxide has major effects on the environment and can make soil acidic and deplete the ozone layer.

In terms of making soil acidic the following reactions occur:



HNO₃ which is produced from reaction 4, is nitric acid and can acidify soil and have major effects in rain making it acid rain. This acid rain can then harm ecosystems and other wildlife.

Nitrogen dioxide is also a contributor to acid rain and in a combustion reaction is usually produced from the oxidation of nitric oxide. It is also considered to be highly reactive and can form other NO_x and is considered to exist in equilibrium with N₂O₄ and the reaction can be seen in equation 5.



2.3.1 Reaction Mechanism

In terms of NO_x, there are three main formational mechanisms. These three formational mechanisms consist of the thermal NO_x, Fuel NO_x and Prompt NO_x.

Thermal NO_x is the formational mechanism where NO_x that is produced from the result of high-temperature oxidation which is done through the combustion process with air. "At high temperatures, such as those occurring within the combustion chamber of a diesel engine, N₂ and O₂ can react through a series of chemical steps known as the Zeldovich mechanism. NO_x formation occurs at temperatures above 1500 °C, and the rate of formation increases rapidly with increasing temperature" (Hoekman and Robbins, 2012). In essence, it can be seen that the factors that affect this source of NO_x include the temperature and the residence time of the nitrogen. It is known as a fact that around 1875 K that nitrogen and oxygen gas disassociate into their molecular states which can allow the reaction to happen if there is a sufficient residence time. "Thermal NO_x is formed by a reaction mechanism involving oxygen and nitrogen radicals. The formation rate is mainly a function of temperature and contact (residence) time" (Mahmoudi, Baeyens, Seville, 2010). This is in relation to the Zeldovich mechanism. When this happens the following three principle reactions which are based on the Zeldovich mechanism occur.

"The most important reactions to include are:



Reactions (6) and (7) were first proposed by Zeldovich for the formation of NO from atmospheric N₂."(Heywood, 2012)

Another study on the Zeldovich mechanism states that "It is generally accepted that in the combustion of lean and near stoichiometric fuel-air mixtures the principal reactions governing the formation of NO from molecular nitrogen are those originally proposed by Zeldovich." (Bowman, 1975) This connotes that the Zeldovich mechanism is also dependent on the fuel/air ratio which an integral part of the reburning process. Overall the key point of the Zeldovich mechanism is that it is reversible means that with the utilisation of the reburning process NO_x can also be separated into its component molecules and could be overall safer. The other two methods fuel NO_x and prompt NO_x aren't as important and have mechanisms which are not

completely understood thus these two methods will be discussed in the gaps in the literature section.

Since the reaction is reversible Le Chatalier's principle can be noted. Reburning uses the concept of Le Chatalier's principle as partial pressures of the captured NO_x is directly exerting itself into the system and if affecting how much air can get into the system. Since there is NO_x in the system Le Chataliers principle takes effect and decreases the amount of air thus making the NO_x the primary source of oxygen in the system meaning the Zeldovich mechanism and the reversible reaction can be executed.

2.3.2 Reburning

Reburning is the process where the NO_x concentration in the input is captured and the initial NO_x produced from the biomass is trapped within the furnace. This is done because if there is air which is used for its oxygen in the combustion decreases, then the reaction will have to find alternative ways for the combustion reaction to continue and will turn to the NO_x in the system. The NO_x will then be reduced producing oxygen for the combustion reaction and nitrogen which is environmentally safe. In general, for the reburning process, there are three main zones and they include the primary, reburning and combustion.

- The primary zone is the first stage and is where the initial process occurs and the majority of the fuel is burnt. The conditions these fuels much can be considered to just under fuel-lean conditions.
- The reburning zone is considered to be the second stage because all the NO_x from the primary zone is turned into their consecutively molecular form N_2 and O_2 and the O_2 is used to fuel the combustion zone.
- The combustion zone is where combustion occurs and the oxygen from the combustion zone comes from the air and the NO_x in the reburning zone.

In essence, these three zones are pretty much the steps to the reburning process.

2.4 Biomass Surrogates

The two biomass surrogates which will be utilised are benzaldehyde and furfural. The purpose of these surrogates is for two main reasons. To test the efficiency of the experimentation and to test if the surrogates are viable if unknown dangerous problems with biomass were to occur. The surrogates are different to the biomass in terms of the state of matter. This is important to note as biomass are usually solids. The 2-D and 3-D chemical structure of the surrogates have been reproduced on the freeware program molView.

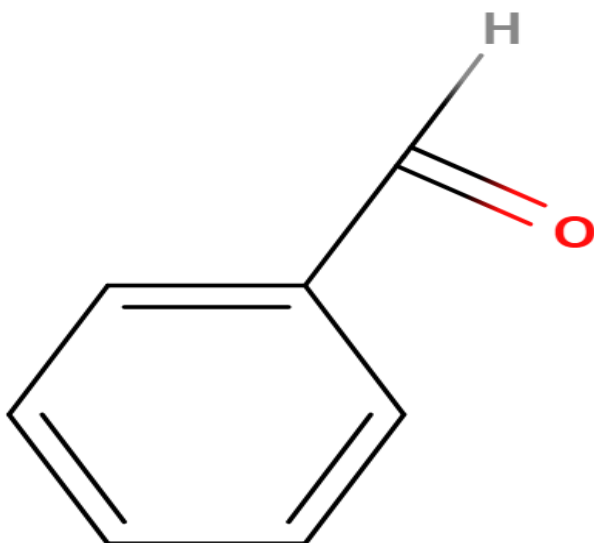


Figure 5: The 2-D Model of Benzaldehyde

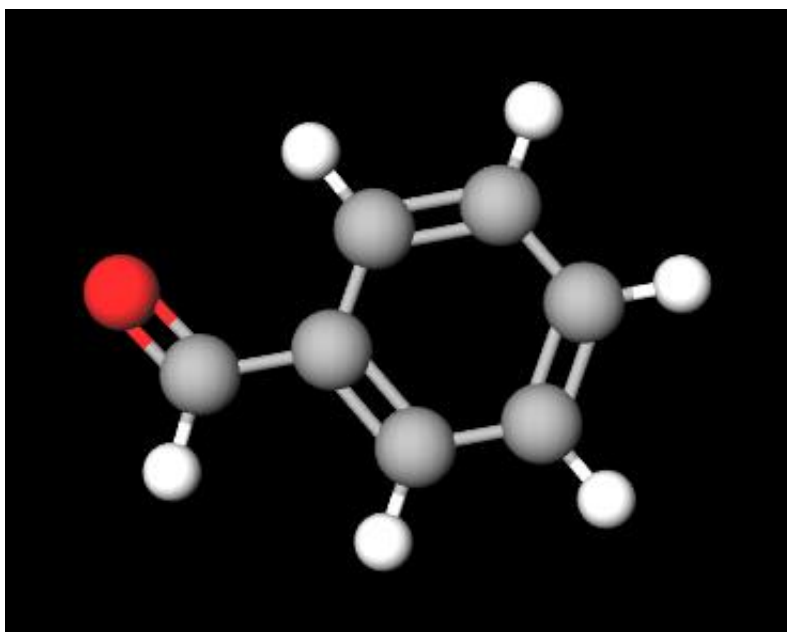


Figure 6: The 3-D Model of Benzaldehyde

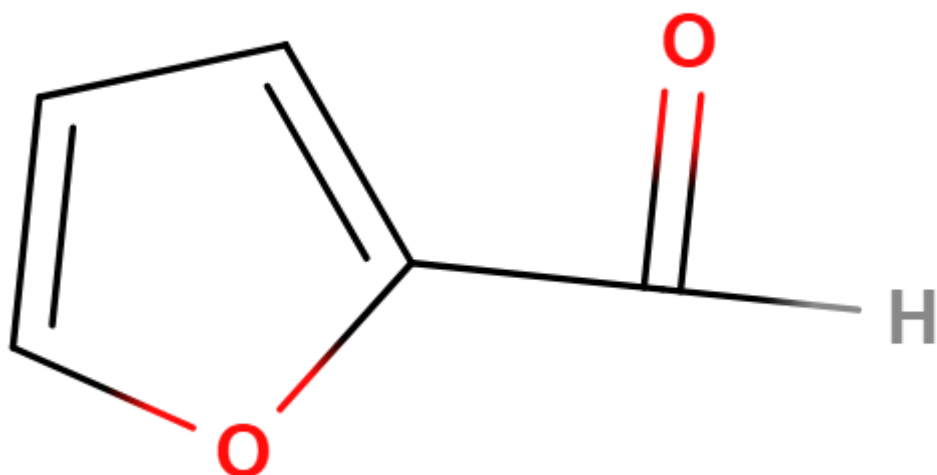


Figure 7: The 2-D Model of Furfural

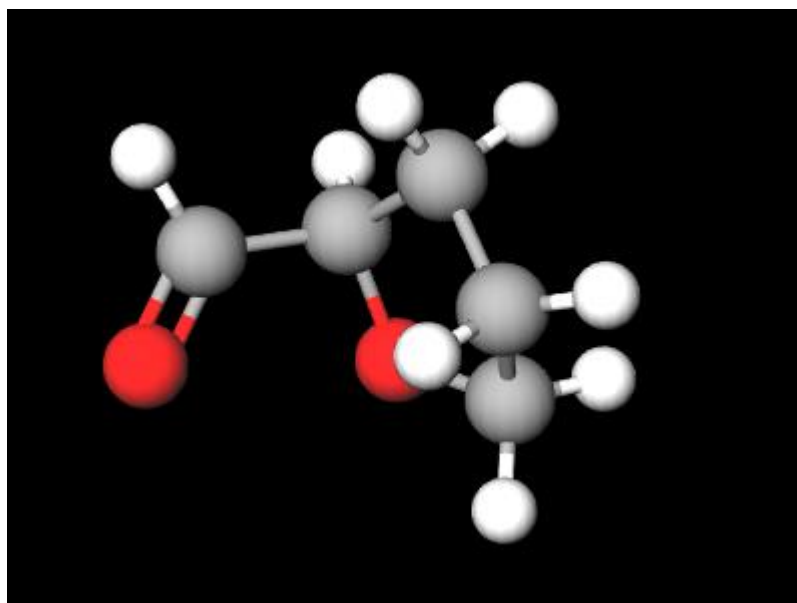


Figure 8: The 3-D Model of Furfural

In the cases for the 3-D Models Figure 2 and Figure 4, the white spheres represent the hydrogen molecules, the grey spheres represent the carbon molecules and the red spheres represent the oxygen molecules. The lines connecting the molecules are the bonds and a single line is a single bond whereas double bonds are signified through two connecting lines.

2.5 Gaps in Literature

Also in terms of Figure 2, since as the graph stops at a point where the NO_x emissions of both biodiesel and diesel meet meaning that there is an uncertainty of how NO_x emissions could progress at higher engine speeds.

Fuel NO_x, it can be applied to biomass fuels since during the combustion of biomass but it has been narrowed down to two potential pathways in terms of the production of NO_x but the pathway can only be confirmed with the full understanding of the mechanism at hand.

Prompt NO_x, it is only known that this type of NO_x is formed at the first stage of combustion and usually needs low-temperature combustion thus it needing to be at the very first stage of the combustion reaction. Although there is conflicting research stating

In terms of the gaps in the literature, there are gaps in understanding the mechanisms which take place when fuel and prompt NO_x are formed. Alternatively, within the production of fuel and prompt NO_x in a combustion reaction, the production of fuel and prompt NO_x can be captured and reversed into their molecular states using the Zeldovich mechanisms which are reversible reactions.

It can be seen from this review that the main ideas taken away were that biomass tends to be safer in terms of gas emissions but is just as efficient when it comes to the energy contents. Also that there are three types of NO_x which are thermal, fuel and prompt and that the mechanisms at hand in terms of thermal NO_x is the Zeldovich Mechanism which has three characteristic reactions. Whereas the mechanisms for fuel and prompt aren't fully understood. Overall reviewing the literature on these topics has been helpful in showcasing why biomass is important and also why the NO_x emissions in biomass need to be reduced and how they can be reduced via reburning.

Chapter 3: Methodology.

In general, there are four types of methodologies to be considered and these are the methodologies for the ultimate analysis, proximate analysis, bomb calorimeter which are for the characterisation of the sample and dispersive fourier-transform infrared spectroscopy (DRIFTS) which is for the experimentation of the sample itself.

3.1 Methodology for Characterisation

3.1.1 Ultimate Analysis

An ultimate analysis is pretty much an elemental analysis where elements such as hydrogen, nitrogen, sulphur and oxygen and a measurement of how prominent they are in the sample. The machine that is used is flash 2000 CHNS/O analyser which uses a 2 milligrams of the sample that should be accurately weighed to three decimal places. It should be weighed in a lightweight tin capsules. The machine then drops them periodically at a temperature of 1020 °C through an uninterrupted flow of helium. As the sample is, the helium stream is transiently enriched with pure oxygen. Once the tin container is primed via the oxidation due to the introduced oxygen stream, flash combustion then takes place. The flash 2000 CHNS/O analyser then achieves quantitative combustion by passing a mixture of gases over tungstic oxide. To then remove the excess oxygen from the mixture of gases, it is passed over copper which also reduces the NO_x to nitrogen. This gas then goes to a chromatographic column and then onto a thermal conductivity detector and the gases that are produced are CO₂, N₂, SO₂ and H₂O. The amount of oxygen is analysed via weighing the sample which is then passed through a silver capsule that is then heated to 1060 °C. Most of the other gases are removed through the fitted traps and the oxygen is converted to carbon monoxide via passing it over nickel-coated carbon. (Michael Nefedov, 2017)

Since the machine is automatic and will produce the data once the sample is fed. The main methodology that is required for the ultimate analysis is the sample preparation.

Sample Preparation for Ultimate Analysis

Since the biomass samples have volatile materials within them, the samples need to be prepared in a way that the volatile materials are not used up when the flash combustion takes place within the flash 2000 CHNS/O analyser. Therefore, liquid nitrogen should be added to the container and should be kept very dry. This ensures that all the moisture and volatiles within the sample is immediately frozen and is unable to escape. At this point, the sample should be very cold and the container should be shaken. After shaking the container, it should be exposed to the room temperature where when given time the sample should match the ambient temperature.

It should be noted that the container should not be opened so none of the ambient moisture is exposed to the sample. This then creates the homogenised sample which is ready for the flash 2000 CHNS/O analyser and this sample will have a consistent volatile and moisture content which should be the same as the initial sample.

3.1.2 Proximate Analysis

The aim of the proximate analysis is to determine the ash, moisture, volatile matter, fixed carbon and the calorific value. This type of analysis requires the use of a thermo-gravimetric analyser. The TGA heats up the biomass sample in an inert atmosphere to remove the moisture from the sample and this temperature should be above the boiling point of water. After the moisture is removed, the sample should further be heated up to remove the volatiles which provides the energy for fuels. The higher the amount of volatiles, the higher the energy in the biomass sample. The sample should then be cooled down and the atmosphere should be changed to an oxidative atmosphere which would then remove the fixed carbon from the biomass. As the components of the biomass are being removed, the change in mass of the biomass is being measured and therefore each of the weights of the biomass can be measured.

Step 1: Sample Preparation and run for proximate analysis

When preparing the sample, the crucible that should be made up of alumina. This is because temperatures of 950°C will be reached and any normal crucible could theoretically melt and affect the characterisation of the samples. Every time the experiment is performed, the crucible should be sterilised to remove any potential organic and inorganics that could be within the crucible. These organics and inorganics are due to previous experimentation of dust contamination in general. The removal of organics should be done before the removal of the inorganics. A blank sample should be run when running the TGA for the first time meaning that step 4 should be ignored when running through the process the first time.

Step 2: Removal of Organics from Alumina Crucible

To remove the organics from the crucible, the alumina crucible should be drowned in 50% concentrated nitric acid. The nitric acid dissolves away the organics. After the sample is washed, the nitric acid should be rinsed out with water. By rinsing the crucible with water, the organics are also washed away. The crucible at this point in time is still not considered clean since there are still in-organics within the crucible.

Step 3: Removal of In-organics from Alumina Crucible

To remove the in-organics from the crucible, the crucible should be completely dry. Since the removal of organics comprehended the alumina rinsed in water, the water should be removed as thoroughly as possible. When the dry alumina crucible is ready, it should be set on a fire source. This heats the crucible and burns up all the inorganics. The crucible should over the fire source until the crucible is heated to a point where it is a bright orange colour. After the crucible is cooled down, the inorganics are visible and can be removed via a tissue. After the removal of the inorganics, the crucible is ready to be loaded with the sample.

Step 4: TGA machine calibration

Once the crucible is clean and ready it should be put into the thermo-gravimetric analyser. The crucible should be put into the machine without anything within the crucible. This allows the mass of the crucible to be cancelled out leaving only the mass of the sample. After measuring the weight of the blank alumina crucible, the sample can then be loaded into the crucible. Time should be given to the machine since it measures the exact weight of the crucible and there can be fluctuations when measuring the weight. After the exact weight of the crucible is calculated, the sample is ready to be loaded

Step 5: Loading the sample into the alumina crucible

The weight of the sample should be approximately 10 milligrams and it should be in a powdered form where the particle size is below 300 microns in regards to the diameter. When loading the sample into the crucible, the surface of the sample should be flat and should be filled to the brim. To flatten the sample when put into the crucible, an object with a flat circular head which has a smaller circumference than the crucible can be used. The sample should not be crushed too hard when being flattened. Once the sample is flat and filled to the brim of the crucible, the sample is considered to be ready.

Step 6: TGA Operation

The gas flow rate should be set at 60 mL/min at standard temperature and pressure conditions. The temperature program then needs to be set and should fulfil the following parameters shown in Table 1.

Table 1: Temperature Program for the TGA

Step #	Initial Temperature (°C)	Final Temperature (°C)	Heating Rate (°C/min)	Isothermal Regime (min)	Gas Atmosphere	Implication
1	30 (Room Temperature)	115	20	-	Nitrogen	Removes Moisture
2	115	115	-	10	Nitrogen	Removes residual moisture
3	115	900	20	-	Nitrogen	Removes volatiles
4	900	900	-	15	Nitrogen	Removes residual volatiles
5	900	700	20	-	Air	-
6	700	800	20	-	Air	Removes fixed carbon
7	800	800	-	30	Air	Removes residual fixed carbon
8	800	30 (Room Temperature)	-	-	Air	Sample cools down

After the temperature program is set, the sample can then be tested and the data can be obtained.

Step 7: Running the samples

The blank sample should ignore step 4, but the overall procedure after should include steps one through to five and then repeated with miscanthus, eucalyptus, oak and pine. This characterises the four samples and determines the ash, moisture, volatile matter, fixed carbon and the calorific value.

3.1.3 Bomb Calorimeter

To characterise the biomass and assess the heat of combustion for each of the types of biomass, the bomb calorimeter is the perfect type of apparatus that should be used. The combustion reaction is done within the bomb calorimeter and the enthalpy is unknown. When the reaction takes place, the change in temperature is recorded. The reaction that takes place is within the bomb calorimeter should be conducted within a fixed volume.

Steps 1-7 Assembling the bomb calorimeter

Step 1: 2000 mL of water should be added to the measuring cylinder and the temperature of this water should be higher than the lowest measurable value on the calorimeter thermometer which is 24 °C.

Step 2: 0.5 g of the biomass sample should be placed into a compact tablet and should be weighed. The tablet should be accurately weighed once it has been released from the press and this weight should be recorded.

Step 3: The cap of the bomb should be put on and the swing ring should be unscrewed. The ring should be swung to support one side and the nickel-chromium crucible should be inserted.

Step 4: The firing wire should be attached and firmly clamped between the two electrodes. Once the wire is attached, a 10 cm of firing cotton should be placed around it in a way that it hangs off the crucible and the latter should be swung back into place.

Step 5: When the crucible is swung back into place, the table of the sample should be placed firmly on the firing cotton. There should be a good amount of contact between the tablet and the cotton.

Step 6: One millilitre of distilled water should be pipetted into the bomb. The cap should be placed on the bomb and screwed down the sealing sleeve. The bomb should be tightened by hand and tools should not be used.

Step 7: After the bomb has been assembled, it should be stood on top of the apparatus and the firing circuit test plug should be inserted and the bomb switch should be depressed simultaneously.

Steps 8-15 Readyng the bomb calorimeter

Step 8: When the bomb is being filled, the firing circuit test plug should be removed. The fill tube should be connected to the bomb and the union should be tightened by hand directly after the oxygen cylinder is connected. The oxygen should be let into the bomb at a very slow rate and should not displace the original air content. The maximum pressure should be 20 bar. (Note: The bomb should never be overfilled)

Step 9: The oxygen cylinder should be shut off and the filling tube should be removed from the bomb. A pressure relief valve can be used to reduce the pressure.

Step 10: There should be a small flow of water which is flowing through the jacket cooling coils. The bomb should then be placed into the calorimeter pail. The water that is placed in the pail should be the same or higher temperature than the bomb so the jacket heating circuit can operate to equilibrium internal and external water temperatures which have to be done before the firing of the specimen. If the temperature of the jacket is too high, it should be cooled by increasing the flow of water through the cooling coils. Another possibility is to heat the water within the pail through the use of a hot plate. The amount of water should cover the bomb just slightly. The bomb should also be placed in three supports which are within the pail and it should be ensured that there is no sign of a gas leakage. If there is a leakage that has occurred, the o-ring seating in the cap should be checked and the process should be restarted.

Step 11: The calorimeter pail should be placed on the water jacket and it should be made sure the short locating peg should be on the side of the pail and engages the slot in the vertical position which is on the front left-hand foot of the spider support within the water jacket. The bomb should be turned so the electrode socket and the inlet tube line up in parallel which is to the front of the apparatus with the electrode socket is to the right. The changes facilitate the bomb firing pin.

Step 12: The cover of the water jacket should be rotated 90° and should be lowered over the bomb which includes the thermometers and thermistors.

Step 13: The bomb contact pin should be covered and it should engage the socket on the bomb. It should be noted that the “Ready to fire” lamp lights should be flashing if done correctly.

Step 14: The heater switch should then be turned on and the initial temperature of the pail should be adjusted correctly and should be equivalent to the above of the outer jacket, temperature stabilisation and equilibration which is in between the pail. The jacket will eventually be indicated by the light of the heater flashing on and off. (Note: The temperature of the calorimeter vessel and jacket should stabilise before moving on.)

If the pail temperature is higher than the pail of the jacket, then it will be possible for the heating rate to increase via increasing the balance of the thermistor bridge. This sort of equilibrium takes approximately 15 minutes to occur.

If the pail temperature is less than the jacket, then it is possible to lower the latter by increasing the cooling flow of water through to the cooling coils. If this fails, then the water from the pail should be removed and the experiment should be restarted.

Step 15: The temperature stabilisation should be achieved and can be checked on the calorimeter and thermometer. If the lower temperature rises 4°C , then the results will be off the scale and the calorimeter thermometer will need to be replaced with one containing a higher scale.

Steps 16-19 Firing and the resetting the bomb calorimeter

Step 16: Once the temperature is stable and the correct thermometer temperature is reached, note the initial the from the reader and the initial temperature of the calorimeter to 0.001°C . The fire switch should then be depressed and the sample should ignite. Successful firing can be detected when the pail thermometer moves. This should be within 30 seconds of firing.

Step 17: The apparatus should be left for 10 minutes before obtaining the final equilibrium temperature. After the 10 minutes take the results, wait another 5 minutes and then make sure that the two readings are 0.002°C of each other.

Step 18: After completion, the water jacket cover should be raised and the heater should be switched off. The graphite release tool can be used to discharge the bomb.

Step 19: The flow of cool water should run through the jacket cooling coils and the jacket should be lowered.

Step 20: Perform steps 1-19 with the three remaining biomass samples.

3.2 Methodology for Experimentation

3.2.1 Dispersive Fourier-Transform infrared spectroscopy (DRIFT)

The DRIFTS test is used because it analyses the chemical properties of the biomass sample. This is done by using an infrared beam which is shone through the sample. When the infrared beam passes through the sample the beams of the infrared laser are altered. This alteration is absorbed and measured. By measuring the altered infrared beam, the chemical properties of the biomass sample can be seen.

Before the sample can be prepared a blank sample for the crucible should be taken to get a baseline. This sample can be done in any atmosphere but for the purpose of this experiment, it was done within the inert atmosphere. The cover of the sample is a mercury cadmium telluride (MCT) detector because it tunes the infrared light that passes through sample so there are no saturated peaks so that results from the DRIFTS analyser are consistent. MCT detectors heat up very quickly so liquid nitrogen should be put into the analyser so the detector is at a relatively low temperature. This should be done before every test. This is also because the sample is heated up so combustion can occur.

In terms of sample preparation, the biomass sample should be mixed with Potassium Bromide (KBr). The sample should be 10 grams and the ratio should be 98% KBr and 2% biomass. This dilution of the biomass is done to get a clearer reading of the absorption spectra. This is because KBr doesn't absorb any infrared light from DRIFTS machine meaning all the infrared absorbed by the sample will be purely based on the biomass.

In addition, if the temperature is constantly increased then the biomass sample should combust creating a change in properties of the biomass sample. This will be done within four different atmospheres.

3.2.1.1 Atmosphere 1: Inert

The inert atmosphere contains pure nitrogen. This is because nitrogen is un-reactive and is important to understand the oxygen-fuel ratio when combusting biomass. It is also a controlled atmosphere and will be used to compare and contrast the other atmospheres.

3.2.1.2 Atmosphere 2: Inert with the addition of NO_x

This atmosphere is considered to be a reactive atmosphere and is used to see how the interaction between NO_x and biomass will occur without the interference of oxygen. This atmosphere will mainly be compared to the inert atmosphere and in consequence, will highlight the effect of NO_x on biomass.

3.2.1.3 Atmosphere 3: Air

This atmosphere is a baseline atmosphere for a furnace will illustrate how biomass decomposes and produces NO_x. It is also considered to be a reactive atmosphere.

3.2.1.4 Atmosphere 4: Reburning

This atmosphere is the crux of the experiment and will show how the interaction of NO_x and biomass will occur via reburning. This is because the reburning atmosphere consists NO_x and air.

The concentration of the NO_x in industrial furnaces range from 600 to 800 mg/kg and therefore to emulate this atmosphere, the concentration of NO_x that has been used in the DRIFTS analyser is 600 mg/kg.

Chapter 4: Results and Discussion

All of the working out for the calculations in this chapter regardless of whether they are for the characterisation of the actual experimentation is done in detail in the appendix.

4.1 Ultimate Analysis (Characterisation)

Table 2 Results for the Flash 2000 CHNS/O Analyser (Ultimate Analysis)

Flash 2000 CHNS/O Analyser, approximately 2 mg sample, as received							
	C (%)	N (%)	H (%)	S (%)	O (%)	Total	Ash Content
Eucalyptus	45.55	0.35	6.27	0.00	42.65	96.91	3.09
Miscanthus	44.40	0.70	6.14	0.00	37.76	90.85	9.15
Pine Wood	46.53	0.50	6.40	0.00	39.50	94.71	5.29
Oak Wood	47.85	0.10	5.89	0.00	40.18	95.97	4.03

The results in Table 2 for the ultimate analysis show the mass percentage of each of the different types of chemicals within each of the biomass samples. When all the percentages for the CHNS/O species had been added up they gave a number far less than 100 and this was due to ash contributing to the weight of the biomass. Also on the table, it can be seen that the rank of the species was consistent for all of the biomass samples. The ranks in descending order were carbon, oxygen, hydrogen, nitrogen and lastly sulphur. It should be noted that there is zero sulphur in all of the biomass samples hence why biomass is such a clean energy source.

Table 3 Mass Fraction for the biomass samples via Ultimate Analysis

Mass	C (g)	N (g)	H (g)	S (g)	O (g)	Total	Ash+Water
Eucalyptus	0.000911	0.000007	0.000125	0.000000	0.000853	0.001938	0.000062
Miscanthus	0.000888	0.000014	0.000123	0.000000	0.000755	0.001817	0.000183
Pine Wood	0.000931	0.000010	0.000128	0.000000	0.000790	0.001894	0.000106
Oak Wood	0.000957	0.000002	0.000118	0.000000	0.000804	0.001919	0.000081

The actual mass of each of the type of species can be calculated including the ash and this is due to the known sample size that was used which was 2 milligrams. By multiplying the percentage by the initial mass, the mass of each of the species is known. The results are then shown in Table 3.

In regards to all the calculations done refer to Chapter 7.1 in Chapter 7

4.2 Proximate Analysis (Characterisation)

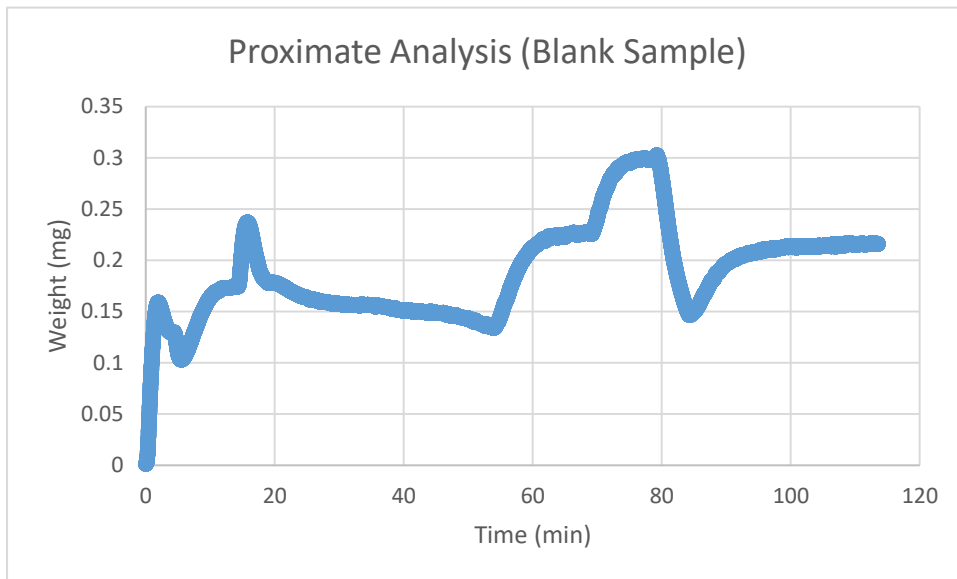


Figure 9: Blank Sample for Proximate Analysis

A blank sample is weighed because the weight of the crucible has to be calibrated into the system which can be seen in Figure 9. This is because whenever the samples were tested in the TGA, they included the mass of the alumina crucible. By taking a blank, the mass can be subtracted from each of the samples to ensure accurate results. Figure 9 also shows how the mass of the crucible changes as the temperature changes and also creates a baseline which can be subtracted from the raw data. Since the computer can subtract the blank sample, the rest of the graphs which have the data already have this blank subtracted. Taking a blank for the proximate analysis is important because if it wasn't taken, then the weight of the crucible would be included within the weight of the biomass and the trends for all of the samples would be very different. This would also make it harder when finding the mass of the ash in the sample since it is the remaining element in a proximate analysis. In regards to Figure 9, it can be seen that the mass changes over time. This may be due to the constantly increasing temperature. It can be also noted in the 80-minute mark, the mass seems to drop and this is due to the fact the inert gas is leaving the atmosphere. Also, when it increases at the 90-minute mark, this is due to the fact the oxygen is entering the atmosphere.

Figure 10 through to Figure 17 contain an orange line at 80 minutes to represent the change in atmosphere. On the left side of the orange line is an inert atmosphere and on the right side of the orange line is the oxygen enriched atmosphere. The regions are denoted by their chemical formula on either side of the orange line.

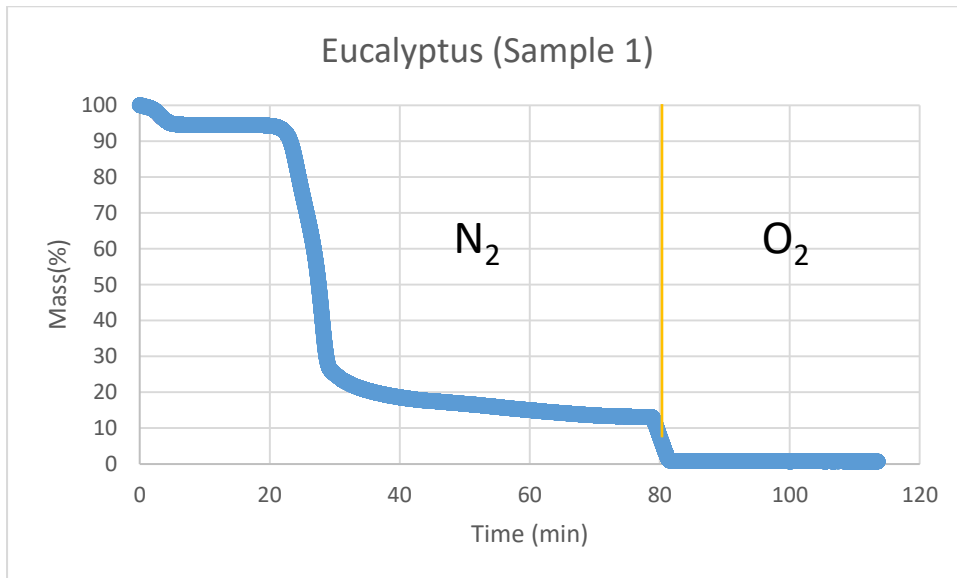


Figure 10 Proximate Analysis for Eucalyptus (Sample 1)

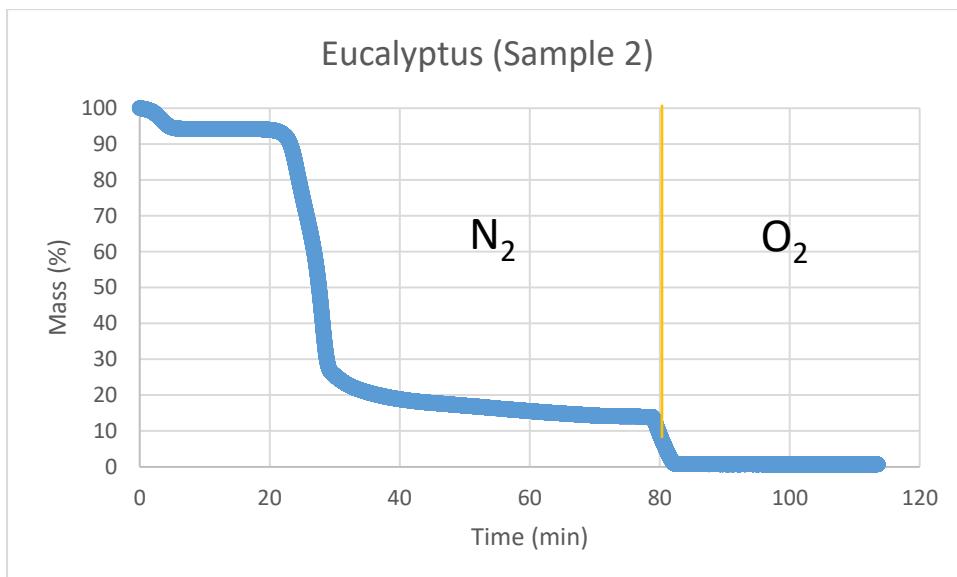


Figure 11: Proximate Analysis of Eucalyptus (Sample 2)

Figures 10 and 11 have the proximate analysis of the eucalyptus sample. Figure 10 is the first run and Figure 11 is the second run. From these figures, there is no outliers meaning that this is the standard trend for the proximate analysis of eucalyptus.

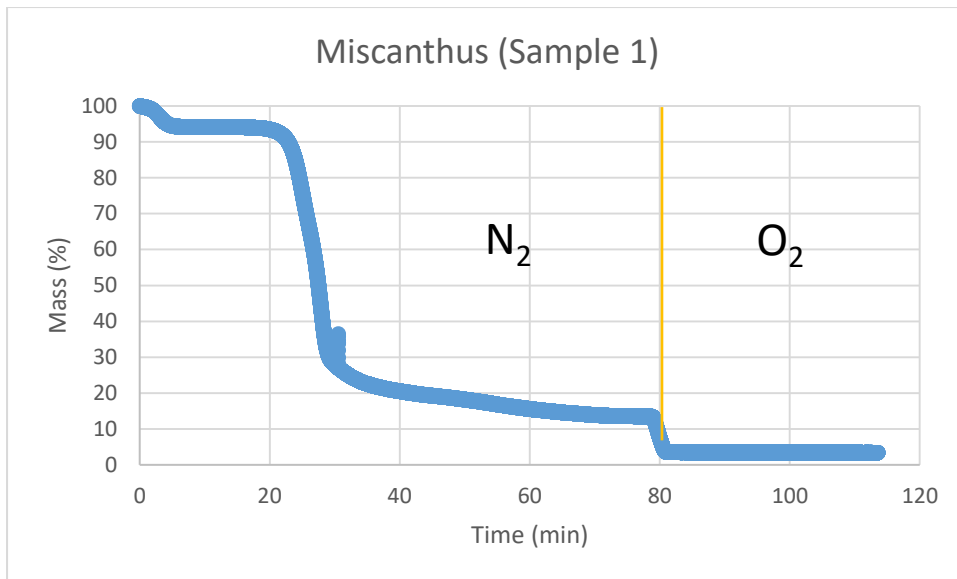


Figure 12: Proximate Analysis of Miscanthus (Sample 1)

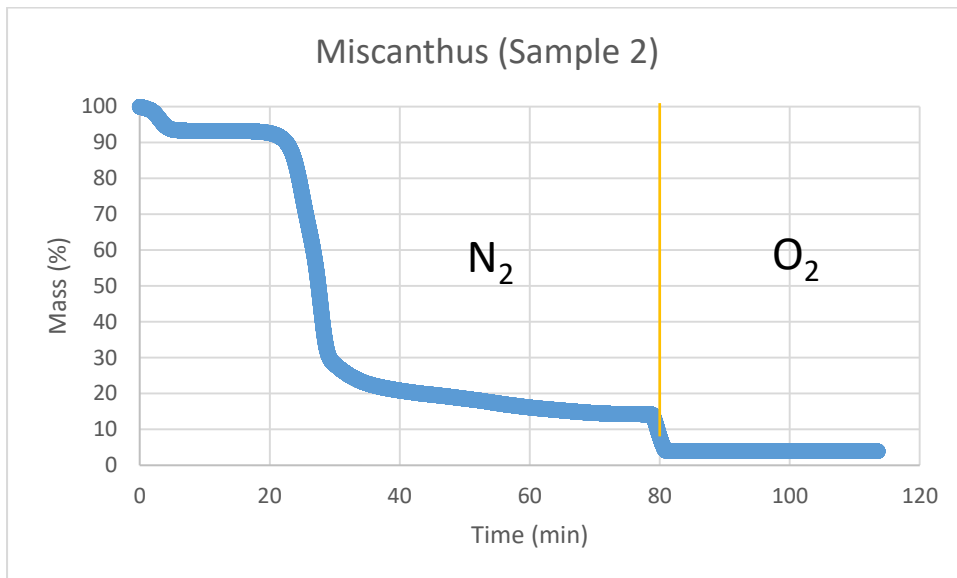


Figure 13: Proximate Analysis of Miscanthus (Sample 2)

In Figure 12 it can be seen that there is a spike at the time between 20 and 40 minutes. This is showing that some of the biomass samples was lingering during that time and took a while to separate from the biomass sample. This meant that there was an extra amount of ash within the sample would result in a lower enthalpy. The miscanthus sample was run again as shown in Figure 13 has similar traits to Figure 10 and Figure 11. This would then mean that the spike in Figure 12 is an abnormality and should not really be expected from miscanthus samples. It is also interesting to note that for both Figure 12 and Figure 13, the mass percentage does not end at 0 meaning that there is a notable amount of ash in the sample which coincides with the data from the ultimate analysis.

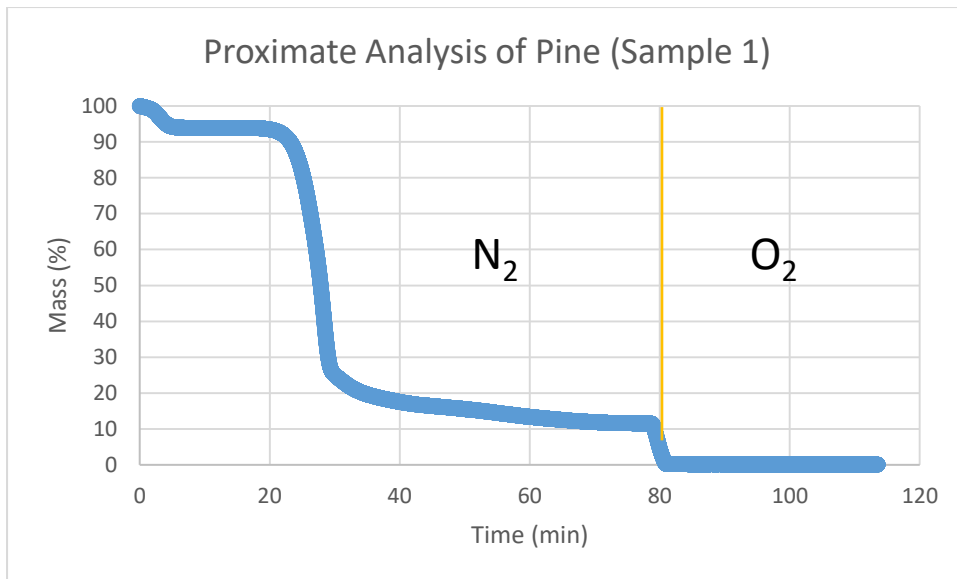


Figure 14: Proximate Analysis of Pine (Sample 1)

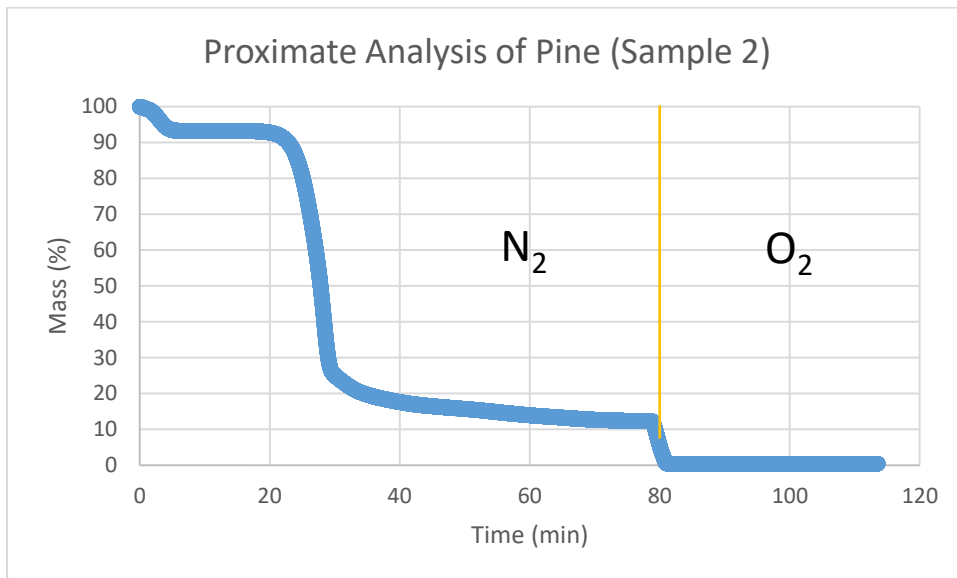


Figure 15: Proximate Analysis of Pine (Sample 2)

The trends from Figure 14 and Figure 15 are very similar to the trends in Figures 12-15. This may be due to the fact that these biomass samples are wood based. Since the trends from Figure 14 and Figure 15 are relatively the same, then it can be concluded that this would be the standard trend for the proximate analysis of pine.

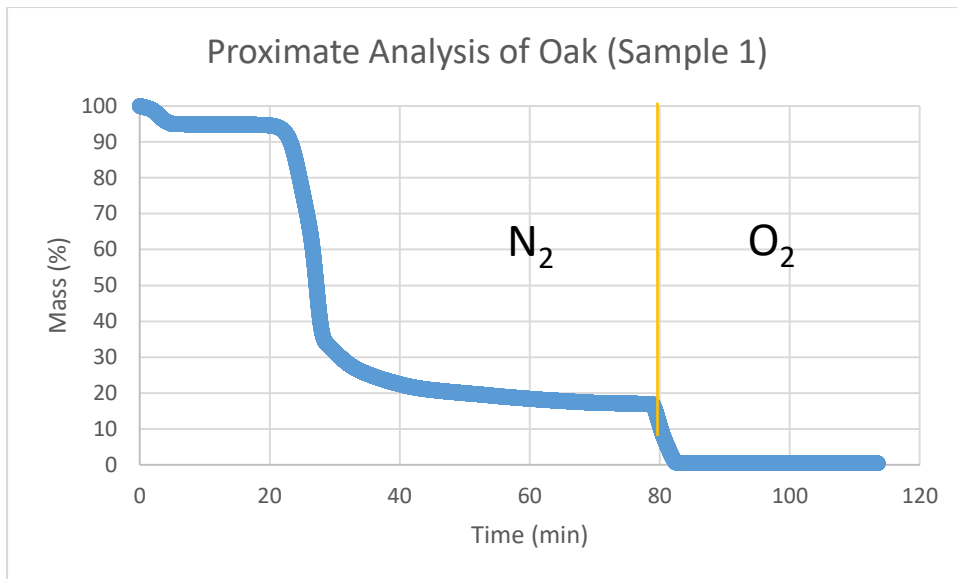


Figure 16: Proximate Analysis of Oak (Sample 1)

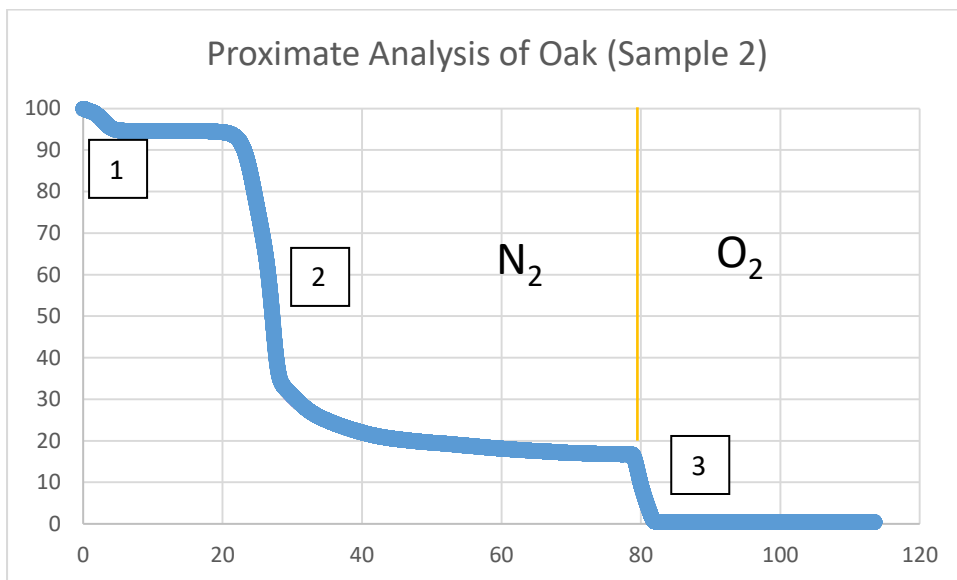


Figure 17: Proximate Analysis of Oak (Sample 2)

The consensus for Figure 10 through to Figure 17 is that they all have the same drops with very slight variation. Using Figure 17 as an example, region 1 is where the first drop occurs and this represents the amount of moisture in the sample. Region 2 is the second drop and this represents the volatiles within the sample. Region 3 is indicative of the fixed carbon mass. Overall the ash is the mass remaining. This analysis can be applied to all the figures mentioned earlier. Overall the results of the proximate analysis are consistent and that all the samples are the same in terms of its nature.

Table 4: Step Change for Sample 1 for Proximate Analysis

Step Change for Sample 1								
	Initial Mass	Moisture	Residual Moisture	Volatiles	Residual Volatiles	Fixed Carbon	Residual Fixed Carbon	Ash
Eucalyptus	100.0	95.5	89.7	23.4	7.1	1.3	0.8	0.00
Miscanthus	100.0	95.0	89.8	34.6	10.6	3.5	3.5	0.00
Pine	100.0	94.9	89.70	23.2	10.0	0.2	0.1	0.00
Oak	100.0	95.6	91.0	32.7	14.3	0.5	0.5	0.00

Table 4 illustrates the changes in mass for all of the figures within the proximate analysis. All of the figures listed above show various drops in terms of mass and these have been tabulated. It is a general consensus that the lower the mass percentage, the more of that type of component there is although this is a rough estimation. The first drop is the moisture and it seems that from the tabulated data that oak has the highest amount of moisture and eucalyptus drops the lowest in terms of residual moisture. The next drop is the fixed carbon and in terms of this, it would seem that the drop from the residual moisture column to the volatiles is very steep and this is illustrated in the figures above. It would seem that the amount of volatiles that drops to the lowest mass percentage would be the pine. In terms of the residual volatiles, the biomass that drops to the lowest percentage is the eucalyptus. With regards to the fixed carbon, the lowest drop would be for the pine whereas the mass percentage for miscanthus is relatively higher. For the step drop from the fixed carbon to the residual fixed carbon it is important to note that the amount of mass for the miscanthus is relatively high in comparison to the other three biomass samples and this is due to the very high ash content.

Table 5: Mass Percentages of Sample 1 for Proximate Analysis on air-dried basis

Sample 1				
	Moisture	Volatiles	Fixed Carbon	Ash
Eucalyptus	10.3	82.5	6.4	0.8
Miscanthus	10.2	79.1	7.2	3.5
Pine	10.3	79.7	9.9	0.1
Oak	9.0	76.7	13.8	0.5

Once the amount of moisture, volatiles, fixed carbon, their residual components and ash are calculated from the step changes then the mass percent can be calculated. In Table 5 the mass percentages of the component and its residual have been added together and have been shown on the table. From the table it can be seen that oak has the least amount of moisture and pine has the highest amount of moisture. This would mean that if combustion were to occur for the samples, oak would release the least amount of steam and pine would release the most. In terms of the volatiles, eucalyptus has the most amount of volatiles and oak have the least amount of volatiles. It would mean that in an inert atmosphere, eucalyptus would release the highest amount of energy and oak would release the lowest amount of energy. In terms of the fixed carbon, oak has the highest amount of fixed carbon and eucalyptus have the least amount of fixed carbon. Therefore, in an oxidative atmosphere, eucalyptus would release the lowest amount of energy and oak would release the highest amount of energy. The ash content for all of the biomass samples seems low with the exception of the miscanthus. It can be seen from the table above that miscanthus has a very large amount of ash and this is also seen in the ultimate analysis where the column for ash content in Table 2.

Table 6: Step Change for Sample 2 for Proximate Analysis

Step Change for Sample 2								
	Initial Mass	Moisture	Residual Moisture	Volatiles	Residual Volatiles	Fixed Carbon	Residual Fixed Carbon	Ash
Eucalyptus	100.0	94.2	90.9	23.7	12.1	0.8	0.7	0.0
Miscanthus	100.0	93.4	89.1	26.3	12.1	4.1	4.0	0.0
Pine	100.0	93.3	89.7	23.3	10.0	0.5	0.4	0.0
Oak	100.0	93.2	90.7	32.3	14.5	0.6	0.5	0.0

This is the second test run for the proximate analysis the and this was done to confirm the findings in the first test run. It can be seen that the lowest step change from the initial mass to the moisture stage would be the oak. In terms of the residual moisture, the biomass sample with the lowest mass would be the miscanthus. In terms of the volatiles, the lowest mass percentage would be the pine. It is also important to note that oak has a relatively high mass percentage at this point in time. In terms of the residual volatiles, the lowest mass percentage would be the pine again and this is the same for the fixed carbon and residual fixed carbon. This would overall mean that pine has the least amount of ash and would be relatively efficient as an energy source.

Table 7: Mass Percentages for Sample 2 for Proximate Analysis on air-dried basis

Sample 2				
	Moisture	Volatiles	Fixed Carbon	Ash
Eucalyptus	9.1	78.7	11.5	0.7
Miscanthus	10.9	77.0	8.1	4.0
Pine	10.3	79.7	9.6	0.4
Oak	9.3	76.2	14.0	0.5

When the residual mass percentages were combined with the larger component, Table 7 is created. It can be seen that the highest amount of moisture is within the Miscanthus and the lowest amount of moisture is with the eucalyptus. In terms of the volatiles, the highest amount is with the pine meaning it would provide the highest energy in an inert atmosphere and the lowest amount of volatiles would be the oak which would provide the lowest energy in an inert atmosphere. With respect to the fixed carbon, oak has the highest amount of fixed carbon meaning it would provide the highest amount of energy in an oxidative atmosphere and miscanthus has the lowest amount of energy meaning that

In regards to all the calculations done refer to Chapter 7.2 in Chapter 7

4.3 Bomb Calorimeter (Characterisation)

Table 8: Raw Data for Bomb Calorimeter Calibration

Benzoic Acid	
Mass (g)	0.49
Initial Temp (°C)	21.37
Final Temp (°C)	22.66
Enthalpy (J/g)	26452.50
Change in Temperature	1.29
Heat Capacity (J/K)	41930.70

In Table 8, the mass, initial temperature, final temperature are the given variables. The enthalpy is extracted from the literature. The change in temperature is calculated by subtracting the initial temperature from the final temperature. The heat capacity was calculated by getting the enthalpy value and dividing that by the change in temperature and multiplying that by the mass. This, in turn, gives the heat capacity of the apparatus which can be used for further calculations.

Table 9: Raw Data for the standard solution

Sample (N-Standard)	
Mass (g)	0.51
Initial Temp (°C)	22.75
Final Temp (°C)	24.73
Change in Temperature	1.98
Enthalpy (J/g)	42101.82

To check the accuracy of the calculated heat capacity from Table 8, a bomb calorimeter for the standard was done and the results can be seen in Table 9. The mass was 0.51 grams which were weighed and the initial and final temperature were given from the experimentation of the bomb calorimeter. By subtracting the final and initial temperature, the change in temperature can be calculated and with this, the enthalpy can be solved. The enthalpy is calculated by multiplying the change in temperature by the mass which is then multiplied by the heat capacity. This gave a good value for the enthalpy of the standard solution as it was similar to the literature value.

Table 10: Energy calculations for the Bomb Calorimeter

Data				
	Pinewood	Oak	Eucalyptus	Miscanthus
Mass (g)	0.46	0.52	0.52	0.52
Initial Temp (C)	24.56	25.22	25.96	26.59
Final Temp (C)	25.39	26.16	26.88	27.48
Change in Temperature	0.83	0.94	0.92	0.89
Enthalpy (J/g)	15943.02	20377.39	20116.12	19248.79

From Table 10, it can be seen that the enthalpy of all the biomass samples was calculated. The given variables were the masses, initial and final temperatures of all the samples. The change in temperatures was calculated by subtracting the initial temperature of the sample by the final temperature of the sample. The enthalpy of the biomass samples could then be calculated by getting the mass and multiplying it by the change in temperature and the heat capacity of the apparatus calculated in Table 8.

Table 10 also illustrates that the enthalpies for each of biomass samples vary. The enthalpy of the eucalyptus is the lowest with 15943.02 J/g and this is most likely due to it having a lower mass than the other samples. The oak and the eucalyptus samples have similar enthalpies where the miscanthus is marginally below them. This because as found from the results from the proximate analysis, there are high amounts of ash within miscanthus itself resulting in a lower enthalpy. This energy that has been calculated combined with the ultimate analysis and by knowing the mass of each of the species, the energy for the components of the biomass can be calculated as seen in Table 11.

Table 11: Energy calculations for each of the component species

Energy	C (J)	N (J)	H (J)	S (J)	O (J)	Total	Ash+Water
Eucalyptus	18.32578	0.140813	2.522561	0	17.15905	38.98906	1.243176
Miscanthus	17.09293	0.269483	2.363751	0	14.53669	34.97505	3.522528
Pine Wood	15.25747	0.031886	1.878087	0	12.81181	30.60102	1.285007
Oak Wood	19.50116	0.040755	2.400456	0	16.37527	39.11236	1.642417

Table 11 is a rough approximate of the energy held by each of the species. This is logical because since there is no sulphur within the biomass samples, no energy is produced. From all the biomass samples it can be seen that carbon and oxygen produce the most amount of energy whereas the energy from the nitrogen and hydrogen are somewhat negligible. This concludes that if the reburning technology is effective, then the energy that is lost through oxygen via the NO_x can be reused improving the overall efficiency of the furnace.

In regards to all the calculations done refer to Chapter 7.3 in Chapter 7

4.4 DRIFTS Analysis (Experimentation)

Due to the overall consensus of the characterisation that all the biomass samples are similar in their chemical properties, it is relatively safe to test only one of the samples and sample that was tested for this purpose was the Miscanthus. The data for DRIFTS analysis is mainly qualitative and has to be analysed from graphs. The data was recorded at many temperatures but for the purpose of this thesis, has been done at 3 different temperatures. The temperatures were done at the temperatures of 30 °C, 300 °C and 600 °C. The trendlines shown in each of the graphs are in ascending order of temperature meaning that lowest line is the ambient temperature, the line above it is at 300 °C and the line above that is 600 °C. It should also be noted that the x-axis of all the figures in this section are the wavelength and the y-axis of all the figures are of a unit of intensity which is known as kubelka-munk.

The raw data from the DRIFTS analysis have been shown below in Figure 18-Figure 21.

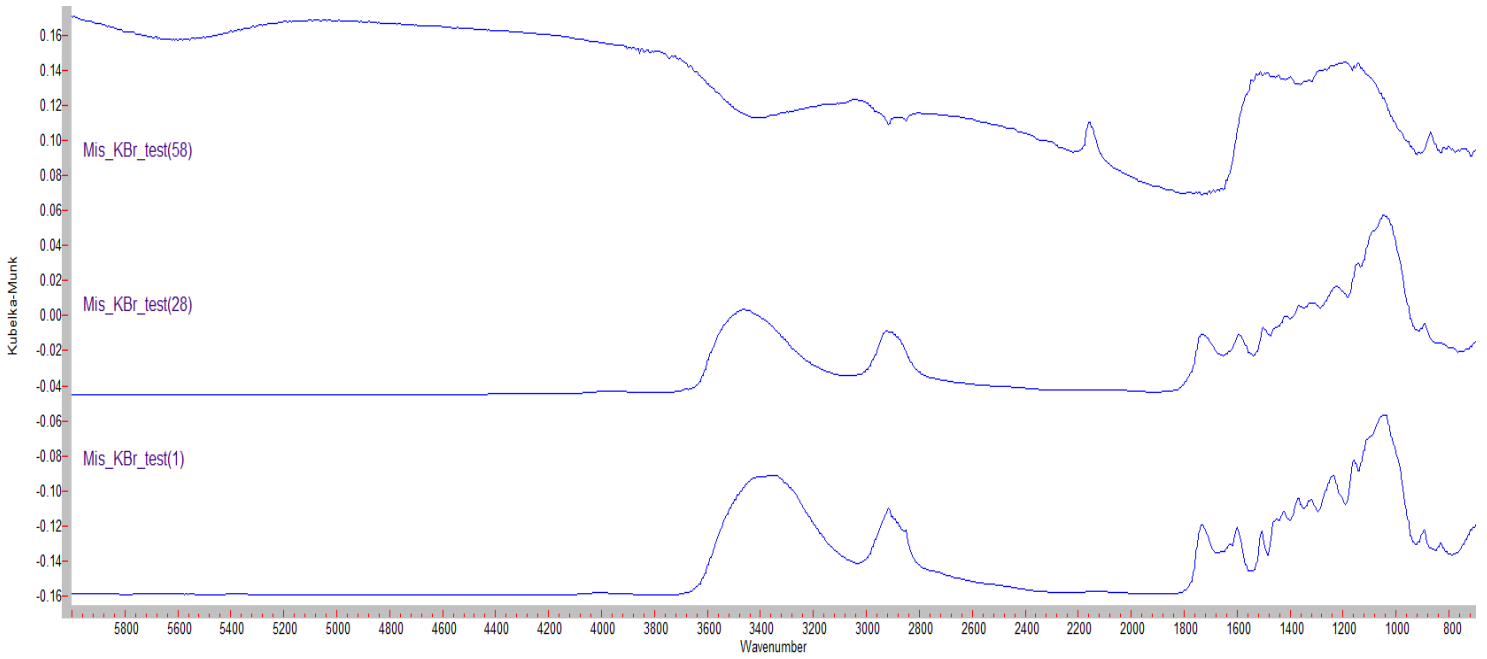


Figure 18: DRIFTS test of biomass in an inert atmosphere

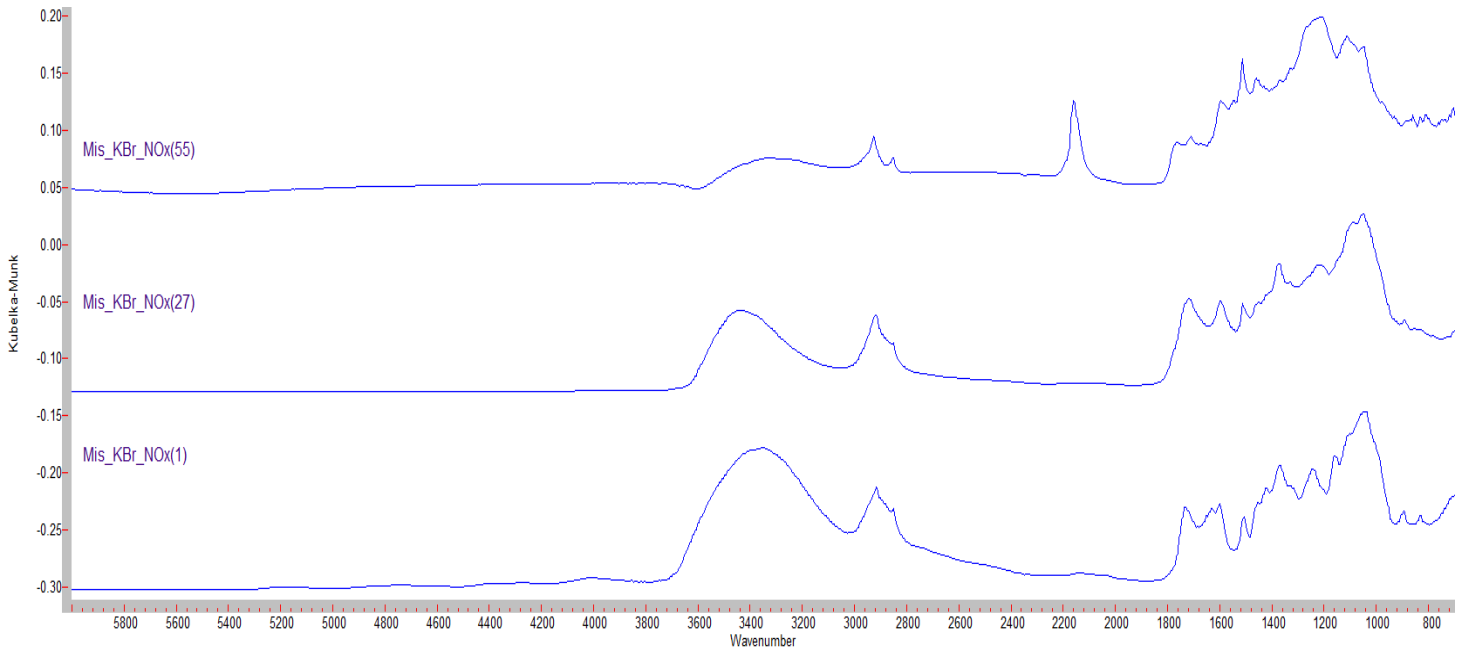


Figure 19: DRIFTS analysis of biomass in an atmosphere which contains Inert + NOx with labelled regions

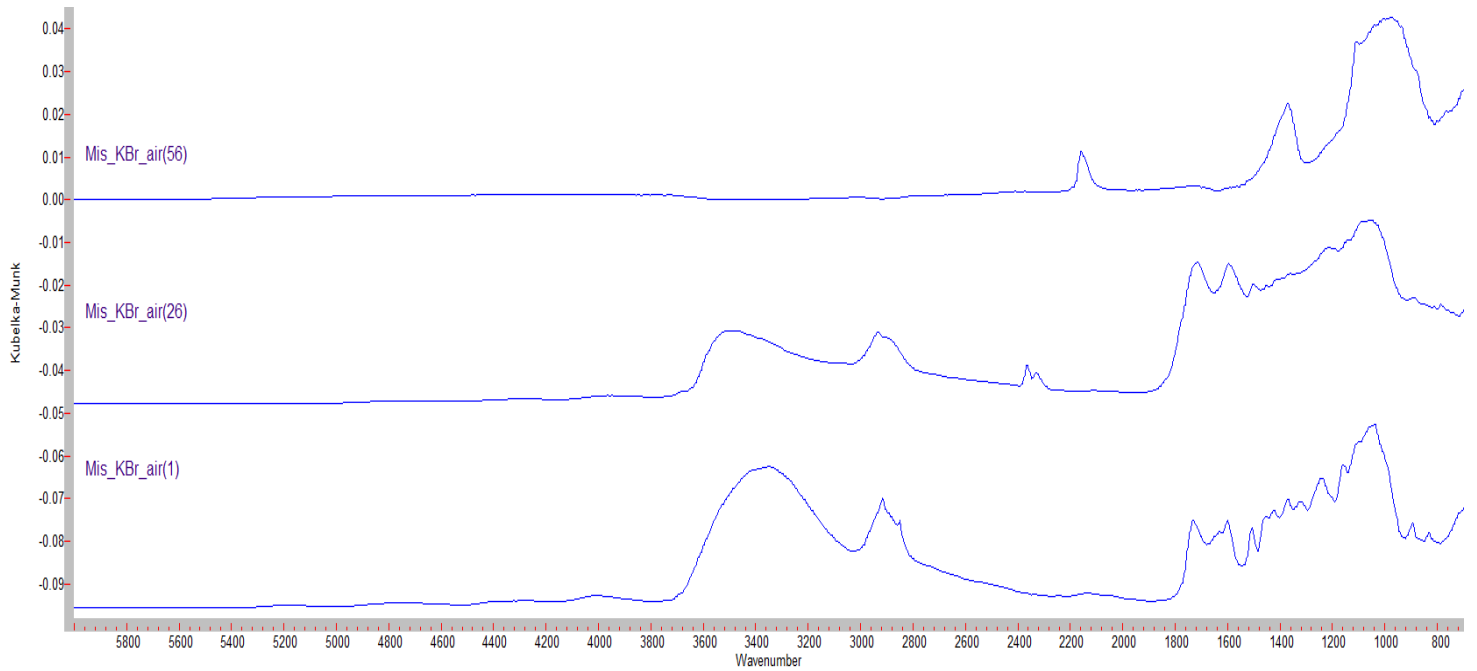


Figure 20: DRIFTS analysis of biomass in the combustion atmosphere

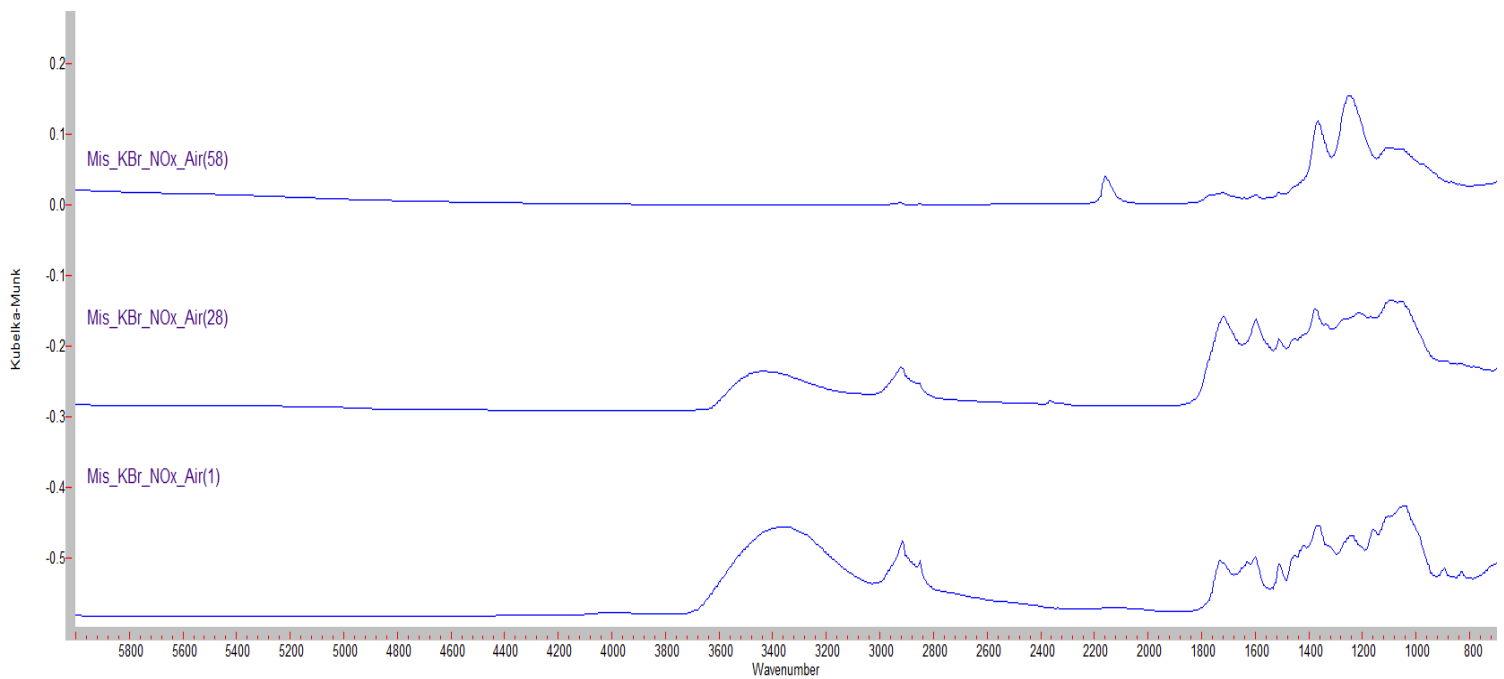


Figure 21: DRIFTS analysis of biomass via reburning with labelled regions

The Figure 18-Figure 21 have various peaks and to interpret and convey the raw data, the regions have been tabulated in terms of their chemical bonds. This is also done because some of the chemical bonds have more than one peak and is therefore more convenient in terms of illustrating the data.

Within the spectra, the first spike in all the cases represents the O-H bonds and are represented by the peak nearest the number 1 in Figure 22. This would mainly be the moisture within the biomass. The second spike in the spectra represents C-H bonds and is represented by the peak closest to the number 2. The region that is filled with peaks represent the C-C bonds and can be seen near the number 3. The peak that is on the left of 4 and is very large, it represents the nitrile bonds. The nitrile bonds are C-N bonds and are important. By observing these four regions, the data will be analysed on a quantifiable basis. Figure 22 and Figure 23 both represent what takes place within the primary zone of a furnace. In terms of reactions for Figure 22 and Figure 23, the reactions that take place are similar to the reactions that take place within the combustion and reburning zone. Due to the purpose of the primary zone is determining the fuel lean conditions, the reactions that take place are covered within the combustion and reburning zone.

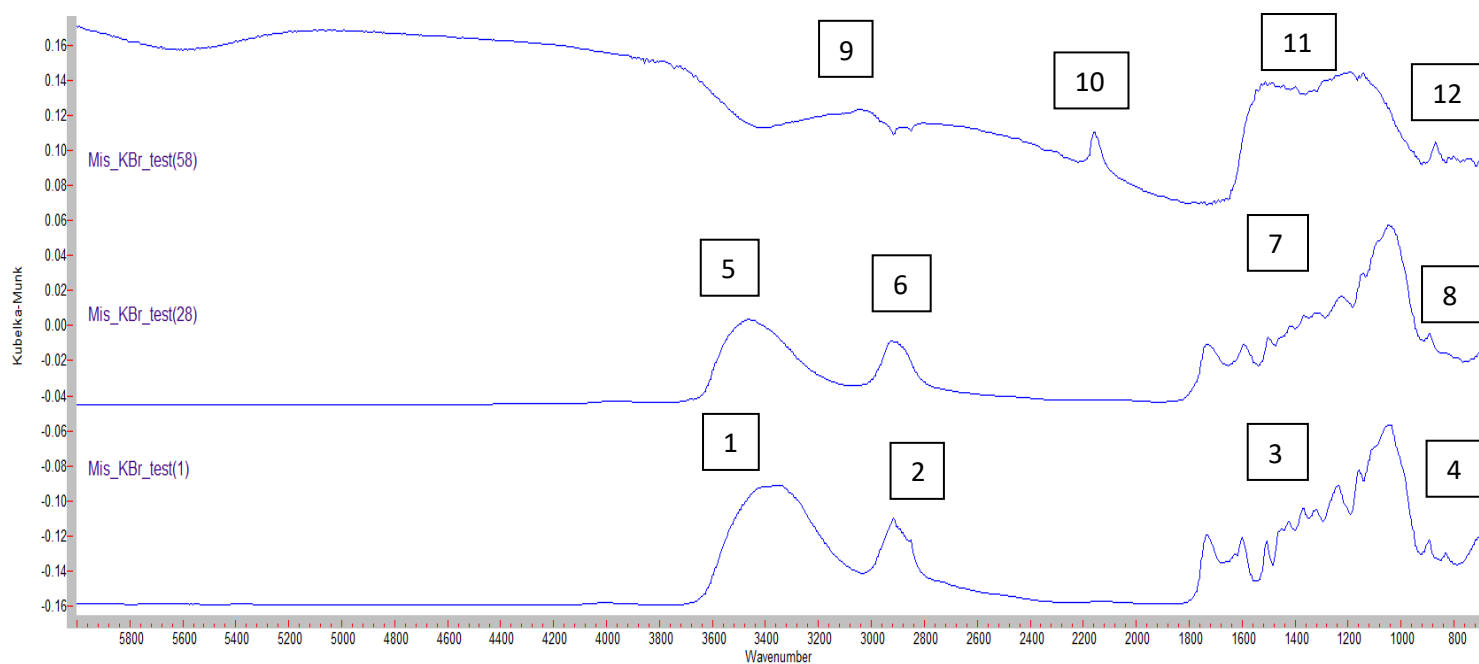


Figure 22: DRIFTS test of biomass in an inert atmosphere with listed regions

Figure 22 highlights the interactions between biomass and combustion in an inert atmosphere. It can be seen as the temperature rises the peaks in region 3 seem to disappear and this is most likely due to the combustion of the biomass being released into the atmosphere. Since the peaks seem to flatten out but still increase, this would mean that the peaks in region 3 would represent the volatiles and the spikes that are shown in region 10 would represent the fixed carbon within the miscanthus. Overall this a controlled atmosphere and provided insight into the fact that some of the peaks are convoluted.

The reactions that take place are combustion reaction of biomass and the decomposition of NO_x . This is because the biomass combusts with the high temperature and the minimal O_2 from the atmosphere and this produces NO_x which then decomposes to fuel the biomass combustion.

Table 12: Reference for inert atmosphere regions at 30 °C

	Region 1 (O-H Bonds)		Region 2 (C-H Bonds)		Region 3 (C-C Bonds)		Region 4 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	0.16	0.13	0.14	0.11	0.16	0.06	0.13	0.11
Wave Number	3200	3600	2800	3000	1000	1800	800	970

Table 13: Reference for inert atmosphere regions at 300 °C

	Region 5 (O-H Bonds)		Region 6 (C-H Bonds)		Region 7 (C-C Bonds)		Region 8 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	0.04	0.01	0.03	0.00	-0.03	0.06	0.00	0.01
Wave Number	3200	3700	2800	3000	1000	1800	900	1000

Table 14: Reference for inert atmosphere regions at 600 °C

	Region 9 (O-H Bonds)		Region 10 (C-H Bonds)		Region 11 (C-C Bonds)		Region 12 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	0.11	0.13	0.10	0.12	0.08	0.15	0.10	0.11
Wave Number	3000	3100	2100	2200	1000	1600	800	900

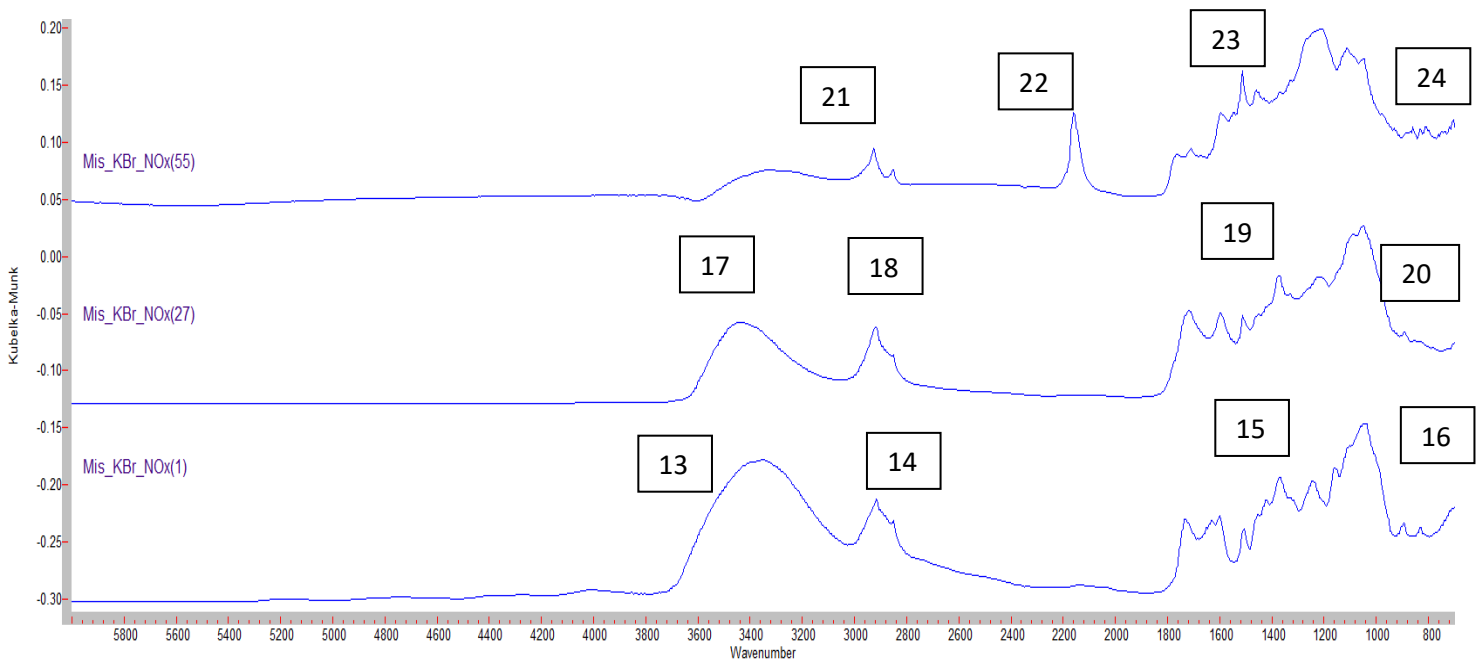


Figure 23: DRIFTS analysis of biomass in an atmosphere which contains Inert + NO_x with labelled regions

In this atmosphere, it can be assumed that all the interactions between biomass and NO_x are due to the NO_x in the atmosphere. This is because the other component of the atmosphere is inert meaning that it will not react and is relatively stable. This is also From Figure 23 it can be seen that there are more peaks within the region near 15 when compared to region 3. It can also be seen that region 16 is lower in comparison to region 4. From these two observations it can be theorised that since it is at room temperature, there is a gas-solid interaction between the biomass and the NO_x in the atmosphere. This means that the NO_x in the inert atmosphere is reacting with the biomass cause these peaks. The amount of nitrile peak seems to be lower when comparing region 4 in Figure 22 to region 16 in Figure 23 but this is due to the fact that the peaks in region 6 have increased due to the NO_x-Biomass interaction. When the biomass sample reaches 600 °C, it can be seen that there are peaks coming out of region 23. This is due to the NO_x in the atmosphere that is reacting to the biomass and interacting with it. Both the peaks at 30 °C and 600 °C show that NO_x can react with biomass both in a gas-gas or solid-gas reaction. Overall combusting the NO_x in an atmosphere which contains inert and NO_x made it clear that NO_x can interact with biomass at different phases of the biomass. By combusting in the solid phases, NO_x can interact with biomass in the pre-combustion phase.

The reactions that take place are inclusive of the combustion reaction of biomass and the decomposition of NO_x . In this case the NO_x decomposes due to the increasing temperature and then the oxygen produced from the decomposition will fuel the combustion reaction.

Table 15: Reference for inert + NO_x atmosphere regions at 30 °C

	Region 13 (O-H Bonds)		Region 14 (C-H Bonds)		Region 15 (C-C Bonds)		Region 16 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	-0.30	-0.17	-0.27	-0.20	-0.30	-0.15	-0.25	-0.23
Wave Number	3000	3700	2800	3000	1000	1800	800	1000

Table 16: Reference for inert + NO_x atmosphere regions at 300 °C

	Region 17 (O-H Bonds)		Region 18 (C-H Bonds)		Region 19 (C-C Bonds)		Region 20 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	-0.13	-0.07	-0.11	-0.05	-0.13	0.03	-0.09	-0.06
Wave Number	3200	3700	2800	3000	1000	1800	1000	800

Table 17: Reference for inert + NO_x atmosphere at 600 °C

	Region 21 (O-H Bonds)		Region 22 (C-H Bonds)		Region 23 (C-C Bonds)		Region 24 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	0.05	0.10	0.05	0.12	0.05	0.20	0.10	0.12
Wave Number	2800	3000	2100	2200	1000	1900	800	1000

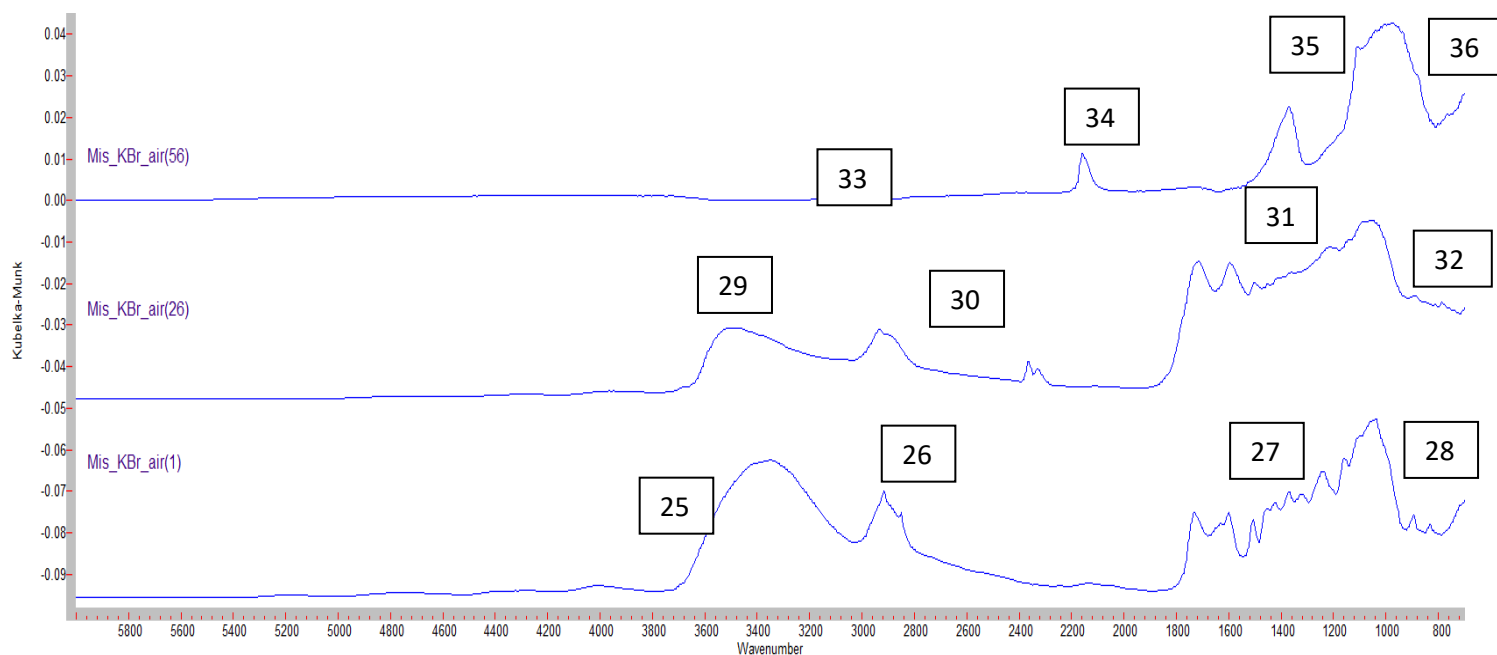
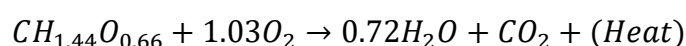


Figure 24: DRIFTS analysis of biomass in the combustion atmosphere with labelled regions

Figure 24 is a baseline for this thesis as this is the standard combustion atmosphere. This means that the peaks that will be seen in this graph reflect what the peaks would be in an actual furnace. When comparing regions 25, 26, 27 and 33, it can be seen that the O-H bonds disappear. It can be assumed since the difference in temperature, most of the moisture evaporates between the temperature of 30 °C and 300 °C. At the temperature of 600 °C, it can be seen that there are no O-H bonds. Region 12 is different to region 3 in Figure 22 since the peaks in region 3 are more noticeable. This is mainly due to that fact that in an oxidative atmosphere, fixed carbon can be removed resulting in the smoother graph. When comparing region 15 and region 21 of Figure 23, it can be seen that there are still peaks present in region 8 whereas region 15 has only one major peak. This is most likely due to the fact that there is an interaction between the NO_x and the biomass which causes these peaks. The absence of NO_x is therefore highlighted in region 15. Understanding the combustion conditions of biomass through the DRIFTS analyser helps in the gaining of more insight in regards to the re-burning process. It can be assumed the reaction that take place in Figure 24 are basic combustions reactions of biomass which are the following:



The above reaction illustrates the nature of combustion of biomass but due to the lack of knowledge of the kinetics and thermodynamics is needed via other forms of testing. This is the reaction that takes place in the combustion zone in a furnace.

Table 18: Reference for the combustion zone at 30 °C

	Region 25 (O-H Bonds)		Region 26 (C-H Bonds)		Region 27 (C-C Bonds)		Region 28 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	-0.09	-0.06	-0.09	-0.07	-0.09	-0.05	-0.08	-0.07
Wave Number	3100	3700	2800	3000	1800	1000	800	900

Table 19: Reference for the combustion zone at 300 °C

	Region 29 (O-H Bonds)		Region 30 (C-H Bonds)		Region 31 (C-C Bonds)		Region 32 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	-0.05	-0.03	-0.04	-0.03	-0.05	-0.01	-0.03	-0.02
Wave Number	3200	3700	2100	3100	1000	1900	800	900

Table 20: Reference for the combustion zone at 600 °C

	Region 33 (O-H Bonds)		Region 34 (C-H Bonds)		Region 35 (C-C Bonds)		Region 36 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	N/A	N/A	0.00	0.01	0.00	0.02	0.01	0.04
Wave Number	N/A	N/A	2000	1100	1500	1500	800	900

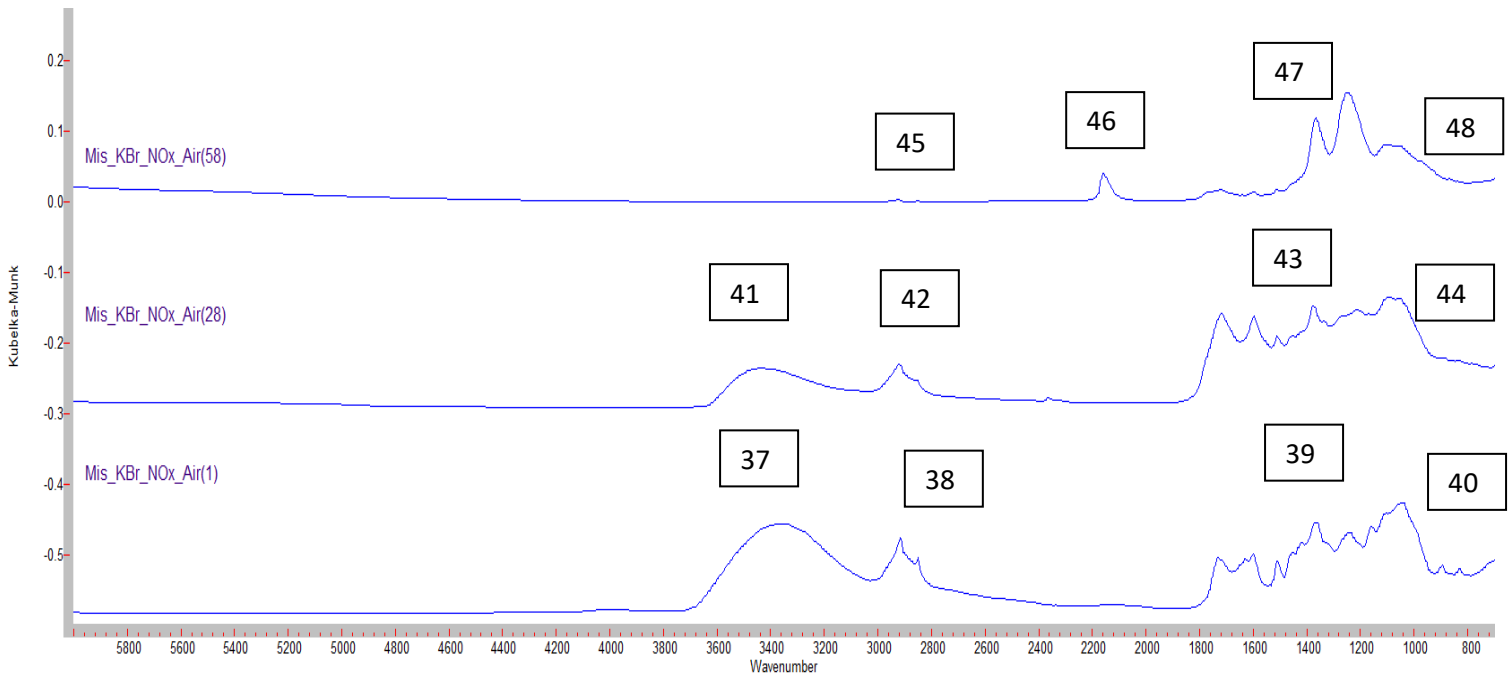
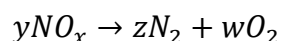


Figure 25: DRIFTS analysis of biomass via reburning with labelled regions

Figure 25 highlights the nature of the reburning technology. From region 14 it can be seen that there is already the gas-solid interaction between the biomass. This is because there are very visible nitrile peaks. In region 15, it can be seen that the graph is getting smoother and this may be due to the fact that the NO_x in the atmosphere is decomposing and forming nitrogen and oxygen. In region 16, it can be seen that most of NO_x gas has decomposed resulting in the relatively smooth wave with two peaks. These two peaks are the nitrile peaks which contain the C-N bonds. This shows that the biomass is also decomposing and the reburning is somewhat successful. Overall by comparing Figure 24 with Figure 25, it can be seen that there are more peaks in region 14 than in region 10 of Figure 24. This is due to the NO_x in the atmosphere being absorbed by the biomass reinforcing that there is a gas-solid reaction. It can also be seen that region 9 of Figure 24 is higher than region 17. This may be due to the fact there is purely just air in the combustion atmosphere whereas the atmosphere for the reburning also is inclusive of NO_x hence a lower peak. This is most likely because the NO_x interferes with the O-H bonds and overall decreases the amount of O-H bonds that can be detected by the DRIFTS analyser. To sum up, the reburning process is relatively effective as it showed that there are interactions between NO_x and biomass and it was seen that the various interactions impact both the pre-combustion phase which is when the biomass is a solid and the combustion phase which is when the biomass combusts.

The reaction that takes place in this condition is as follows:



Where z is half of y and the coefficient w is dependent on the coefficient y and subscript x.

This information is useful in learning for what is going on within the reburning zone of a furnace.

Table 21: Reference for the reburning zone at 30 °C

	Region 37 (O-H Bonds)		Region 38 (C-H Bonds)		Region 39 (C-C Bonds)		Region 40 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	-0.580	-0.450	-0.550	-0.480	-0.580	-0.400	-0.500	-0.480
Wave Number	3000	3700	2800	3000	950	1800	800	950

Table 22: Reference for the reburning zone at 300 °C

	Region 41 (O-H Bonds)		Region 42 (C-H Bonds)		Region 43 (C-C Bonds)		Region 44 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	-0.280	-0.230	-0.270	-0.220	-0.280	-0.100	N/A	N/A
Wave Number	3200	3700	2800	3000	1000	1900	N/A	N/A

Table 23: Reference for the reburning zone at 600 °C

	Region 45 (O-H Bonds)		Region 46 (C-H Bonds)		Region 47 (C-C Bonds)		Region 48 (C-N Bonds)	
	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max	Region Min	Region Max
Kubelka- Munk	N/A	N/A	0.030	0.050	0.030	0.150	N/A	N/A
Wave Number	N/A	N/A	2100	2200	1000	1600	N/A	N/A

Overall it should also be taken into account that the biomass hasn't reacted at 300 °C but is undergoing thermodynamic changes. This is due to peaks within the regions at temperature 30 °C and 300 °C are very similar. Hence to portray the similar peaks a table has been made which states which peak at 30 °C is similar to the peak at 300 °C.

Table 24: Similarities of regions at different temperatures

	Temperature (C)	
	30	300
Regions of Figure 22	1	5
	2	6
	3	7
	4	8
Regions of Figure 23	11	15
	12	16
	13	17
	14	18
Regions of Figure 24	22	26
	23	27
	N/A	28
	24	29
	25	30
Regions of Figure 25	35	37
	36	38

In Figure 22, Figure 23 and Figure 25, it should be taken into consideration that these are the figures that have four similar regions and don't really have any outliers. Figure 24 also have four similar regions, but in addition to these regions, there is a new peak spiking at 300 °C within region 30. It can be theorised that is due to the changing atmosphere since this is the only atmosphere that includes oxygen. It can therefore be assumed that this is a residual O-H bond appearing on the spectra. Taking a closer look at Figure 24, the peak in region 30 is very similar to the peak at region 34, meaning that the biomass is reacting at a lower temperature. This data also conveys the effects of oxygen and how it increases the reaction kinetics of biomass since the biomass is already reacting.

Chapter 5: Conclusion

There were many findings from conducting the methodology of this thesis. These included findings from the three types of characterisation. From the ultimate analysis, the main takeaway is that there is no sulphur within any of the wood-based biomass samples, carbon and oxygen are the most abundant elements within all of them. This information was important because it gave a deeper understanding of the components of the biomass samples. Although the limitations of the ultimate analysis were that the amount of moisture within the biomass sample was unknown. This was due to the idea that when the biomass is heated to 1100 °C by the ultimate analyser, it was found that the moisture from the biomass evaporated before it could be detected by the ultimate analyser and would therefore be difficult to differentiate between the mass of the ash and the mass of the moisture.

The results of the proximate analysis conclude that miscanthus has the highest amount of ash of all the biomass samples but overall all the samples are similar in nature. The proximate analysis also gave quantifiable numbers in regards to the amount of moisture, volatiles, fixed carbon and ash within the sample. The proximate analysis was useful because it helps differentiate the amount of ash and moisture which is what the ultimate analyser could not do. The main limitation of the TGA which was used for proximate analysis was that it only gave the masses but the enthalpy of the biomass samples could not be obtained. This then leads to further characterisation which utilised the bomb calorimeter.

The bomb calorimeter found the enthalpies of the biomass samples and the main take away from the results was that all the biomass samples have very similar enthalpies which reflected what was found via the proximate analysis. This was the idea that the amount of volatiles within each of the samples was all the same. Due to the characterisation matching up and all pointing to the fact that all the biomass samples are similar, the DRIFTS experimentation was only done with one of the biomass samples due to the time constraint.

In the DRIFTS analysis, each atmosphere yielded different qualitative data. In terms of the inert atmosphere, it was found that convolution of the peaks may be occurring meaning that there are peaks below the shown peaks. This information is useful because it helps understand the nature of biomass in a DRIFTS analyser. The atmosphere which contained the NO_x and inert gases provided insight into the fact that NO_x and biomass can interact in gas-solid reaction. This information can be utilised in furnaces to decrease the amount of NO_x produced. The combustion atmosphere provided data on how biomass would react if it were burnt in the same atmosphere as a furnace. This information is useful because it helped contrast the reburning atmosphere. In the reburning atmosphere, it was seen that the biomass is able to react with the NO_x and decompose. It can also be seen that in the interaction between NO_x and biomass, it occurs at a gas-solid and gas-gas phases. Therefore the information found via the DRIFTS analysis can be utilised by industry. Applying the reburning technology should decrease the amount of NO_x produced from industrial furnaces and would, therefore, provide a cleaner and safer work environment and world.

Chapter 6: Limitations and Recommendations

6.1 Limitations

Limitations of this thesis don't negatively impact the findings found from the experimentation but highlight the missed opportunities which are seen in hindsight after the experimentation phase of this thesis has occurred. There were many limitations when assessing the interactions between NO_x and biomass and these are time, equipment, methodology and sample size.

Limit 1: Time

The limitations of this thesis include the fact that when performing experimentation, time was a major limitation. This was because if there was more time, then more experiments and test runs could have been done and this would have further cemented the findings as they would have added an element of consistency.

Limit 2: Equipment

Another limitation was the equipment. This was because during experimentation, the initial experiment that was going to be done was with the TGA but it had broken down. Therefore an alternative was used to assess the interaction between biomass and NO_x. This was the DRIFTS machine which assessed the interaction via the infrared spectra and gave mostly qualitative data. The limitations of the equipment also include the fact they the machines did not emulate the temperatures that could be reached in a furnace. By not emulating the temperatures reached in an industrial furnace, the results are limited and can only be extrapolated when applying it to industry standards.

Limit 3: Methodology

The results that were obtained from the DRIFTS tests were limited to the fact that they only measured the wavelength and not mass so it is difficult to differentiate how much NO_x actually interacted with the biomass. Further characterisation of biomass samples could have been done. This is to better understand the mechanics of the biomass samples in combustion because some of the variations of the results may have been because there were other trace elements within the biomass sample

Limit 4: Sample size

The sample size is another limitation when performing this experiment. Other types of biomass and its surrogates could have been tested when comparing the interaction between NO_x and biomass. Since only wood-based biomass samples were characterised and only one of these wood sample were analysed via DRIFTS. If there was more variation in terms of the type of biomass then the results for the DRIFTS analysis could have been different.

6.2 Future Recommendations

Recommendations are useful for further research on the topic of assessing the interaction between biomass and NO_x . The list of future recommendations is varying experimentation method, assessing the kinetics and thermodynamics, further characterisation and having a larger sample size.

Recommendation 1: Varying Experimentation

Performing the experiment in the TGA would give an even deeper understanding of the interaction between the NO_x and biomass. This is because if the change in mass of the biomass was measured with varying temperature and atmosphere, then an understanding of the mass. Through having values for mass as time changes with increasing heat, quantitative data can be collected for the interaction between NO_x and biomass.

Recommendation 2: Assessing Kinetics and Thermodynamics

If the kinetics of the biomass samples were to be researched, the optimum time for NO_x to be produced from the biomass can be calculated. This is useful in extrapolating data for industrial standards and gain a deeper understanding of the rate of the interaction between the biomass and NO_x . Another recommendation is understanding the thermodynamic parameters for the interaction between NO_x and biomass. By understanding the thermodynamic values such as the entropy and the Gibbs free energy value, a deeper understanding would be acquired. Through understanding the entropy of the system, the amount of disorder can be measured and the interaction between NO_x and biomass would be further highlighted. The understanding of the Gibbs free energy value is useful in understanding the optimum reversibility of the NO_x and biomass interaction.

Recommendation 3: Further Characterisation

Further characterisation via the ICP-MS is another recommendation. This was mainly because in the proximate analysis there is an inconsistency with the first Miscanthus sample. This may be due to human error but further testing via the ICP-MS could confirm this. This is because of the ICP-MS.

Recommendation 4: Larger Sample Size

Having a larger sample size which contains other types of biomass other than wood would help highlight the interaction between NO_x and biomass. This would also illustrate that there are different forms of interaction between biomass and NO_x . This is because the experimentation that took place and the interactions that were measured were purely based on the fact that the types of biomass being tested were wood based.

Chapter 7: Appendices

7.1 Appendix 1: Ultimate Analysis

Since the sample size is 2 mg and the percentages are given Table 1 and Table 2, sample calculations have been done below.

Calculating Percentage of Ash + Moisture:

$$\textit{Total Mass Percent} = \%C + \%N + \%H + \%S + \%O + \%(\textit{Ash} + \textit{Moisture})$$

$$100 = 45.55 + 0.35 + 6.27 + 0 + 42.65 + (\textit{Ash} + \textit{Moisture})$$

Therefore:

$$100 - 45.55 - 0.35 - 6.27 - 0 - 42.65 = (\textit{Ash} + \textit{Moisture}) = 3.09$$

To get the specific mass for a specific component:

$$\textit{Mass} = \textit{Mass\%} * \textit{Initial Mass}$$

$$\textit{Mass} (g) = 45.55\% * 0.002g = 0.000911g$$

The above calculations are sample calculations and the rest of the data have been calculated via excel spreadsheets.

7.2 Appendix 2: Proximate Analysis

The step changes in Table 4 and Table 6 were extracted from the figures in Chapter 4.2. The calculations for the components, residual and ash have been explained below for sample 1 of the eucalyptus.

Calculation for sample 1 of eucalyptus for a component:

$$\text{Mass of Moisture}\% = \text{Initial Mass drop}\% - \text{Moisture drop}\%$$

$$\text{Mass of Moisture}(\%) = 100 - 95.51 = 4.49\%$$

To calculate the residual and the other components just subtract the mass from the column before it.

Calculations for total mass percent for the component of moisture for eucalyptus for sample 1:

$$\text{Total Moisture}\% = \text{Moisture}\% + \text{Residual Moisture}\%$$

$$\text{Total Moisture}\% = 4.49\% + 5.77\% = 10.26\%$$

Calculations for mass percent of ash:

$$\text{Ash} = 100\% - \text{Total Moisture}\% - \text{Total Volatiles}\% - \text{Total Fixed Carbon}\%$$

$$\text{Ash} = 100 - 10.26 - 82.61 - 6.35 = 0.78\%$$

The above calculations are sample calculations and the rest of the data have been calculated via excel spreadsheets.

7.3 Appendix 3: Bomb Calorimeter

Calculations for Benzoic Acid:

$$Q = 26452.50 \text{ J/C}$$

$$m = 0.49 \text{ g}$$

Change in temperature = Final Temperature – Initial Temperature

$$\text{Change in Temperature (T)} = 22.66 - 21.37 = 1.29$$

$$\text{Heat Capacity (J/C)} = \frac{Q}{m * T}$$

$$\text{Heat Capacity (J/C)} = \frac{26452.50}{0.49 * 1.29} = 41930.70 \text{ J/C}$$

Calculations for Sample:

$$m = 0.51$$

$$\text{Change in Temperature (T)} = 24.73 - 22.77 = 1.98$$

$$\text{Enthalpy (J/g)} = m * C * T$$

$$\text{Enthalpy} = 0.51 * 41930.70 * 1.98 = 42101.82 \text{ J/g}$$

Calculations for the biomass samples of Pinewood:

$$m = 0.46 \text{ g}$$

$$\text{Initial Temperature} = 24.56 \text{ C}$$

$$\text{Final Temperature} = 25.39 \text{ C}$$

$$\text{Change in Temperature (T)} = 25.39 - 24.56 = 0.83$$

$$\text{Enthalpy (J/g)} = m * C * T$$

$$\text{Enthalpy (J/g)} = 0.46 * 41930.70 * 0.83 = 15.943$$

The above calculations are sample calculations and the rest of the data have been calculated via excel spreadsheets.

Chapter 8: References

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