

PLASMA GASIFICATION OF ORGANIC WASTE

by

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DECLARATION

I, the undersigned, declare that the dissertation, which I hereby submit for the degree Master of Science in Applied Science: Chemical Technology at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at any other university.

.....

Signature

.....

Date

DEDICATION

This work is dedicated to my first born son Xihlovo Makaringe. When I found out I was pregnant with you I had just started my MSc degree, but I told myself I was going to finish it no matter how long it took. I want you to follow in your mother's footsteps. In our language there is a saying that says: "Dyondzo i xitlhangu xa vutomi", translating "Education is a weapon of life". For as long as you can, I want you to study and equip yourself with education. You were my inspiration to complete this degree. I wanted to be a good example to you, Son. I want you to learn to always complete what you have started. And stay positive at all times. I love you always.

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PLASMA GASIFICATION OF ORGANIC WASTE

Four biomass materials, namely peach pips, pine wood, bamboo and Napier grass, and one example of chemical waste, lithium hexafluorophosphate (LiPF_6), were studied. The biomass types were selected because they were easily accessible locally. The LiPF_6 waste is solidified in poly(methyl methacrylate) (PMMA). Gasification of this solid is of interest to industry.

Prior to the gasification studies, TGA-FTRI analyses were conducted on the biomass samples. This was done to study their thermal behaviour under nitrogen as well as under oxygen. The results indicated that, in general, pyrolysis of biomass takes place in three stages, namely hydration, active pyrolysis, and passive pyrolysis. These stages occur at different temperatures depending on the type of biomass as well as the heating rate used. The conversion efficiency of these materials is increased under oxygen, due to the fact that combustion takes place in the presence of oxygen, either partially or fully, depending on the amount made available. TGA results obtained under nitrogen were used to compute the kinetic parameters of each biomass material.

Because their fluffy nature led to feed problems, bamboo and Napier grass were excluded from the plasma gasification experiments. Results obtained during the gasification of peach pips and pine wood indicated that conversion efficiency slightly increases with an increase in temperature. Feed rate seemed to have minimal effect on both conversion efficiency and gas concentration; the energy conversion efficiency did, however, improve.

The conversion efficiencies obtained by TGA and by the plasma system, were roughly similar. Due to the higher temperatures, $\sim 1000^\circ\text{C}$, of the plasma reactor, the gaseous products obtained were predominantly carbon monoxide and hydrogen. On the other hand, carbon dioxide predominated in the TGA-FTIR experiments. Only a slight trace of monoxide was observed. Plasma treatment of PMMA encapsulated waste LiPF_6 also yielded carbon monoxide and hydrogen as main products.

The energy conversion efficiency observed for the plasma process was 30 – 40 %. This value is ratio of the combustion enthalpy of syngas yield and the electrical energy input into the plasma torch. The main heat loss was via the torch anode. This may be corrected by an improved thermo-mechanical design.

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LIST OF ABBREVIATION

α	Extent of conversion
β	Heating rate
AC	Alternating current
CFD	Computation fluid dynamics
DC	Direct current
DTA	Differential thermal analysis
DTG	Differential thermogravimetric
DSC	Differential scanning calorimetric
ER	Equivalence ratio
FTIR	Fourier transform infrared
GC	Gas chromatograph
HHV	Higher heating value
LHV	Low heating value
MHV	Medium heating value
PAL	Pelindaba Analytical Laboratories
PMMA	Poly(methyl methacrylate)
RF	Radio frequency
SSD	Sum of square of the difference
Syngas	Synthesis gas
TGA	Thermogravimetric analysis

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1 INTRODUCTION

Waste generation has been increasing significantly due to an increase in population and urban and industrial development worldwide. By 1998 waste generated in South Africa only had risen to 533 million tonnes per annum (Nahman et al., 2012). The generation of waste in South Africa is expected to increase as a result of population and economic growth at a predicted rate of 2-3% per annum (Nahman et al., 2012). Due to this increase in waste, there is an increased demand of waste services in terms of collection, transportation, storage, handling and treatment.

On the other hand, due to the increase in population, the energy demand is also increasing. The fossil fuels such as coal are primarily used for the production of energy worldwide. Though coal is available in abundance in countries like United State of America and Russia, resources are declining at an alarming rate due to high energy demand. Eventually the worldwide supplies of these fossil fuels will be exhausted.

Climate change is a major environmental problem. Carbon dioxide (CO₂) emission is the main concern when using fossil fuel as a source of energy. Concentration of CO₂ in the atmosphere will continue to rise unless major changes are made in the way fossil fuels are used to provide energy services (Berndes et al., 2003). As a solution to CO₂ emission problem, there is a call for greenhouse gas concentrations to remain at a level that would prevent dangerous anthropogenic interference with climate system (Berndes et al., 2003). As a response to this call, other cleaner sources of energy are being explored. Nuclear energy is a popular choice, but there are major safety concerns with nuclear.

Biofuel and energy from organic waste is a recent development. It serves as a waste treatment technology and clean energy solution while in turn closing the energy demand gap. Organic waste is gasified to produce synthesis gas which can either be converted to electricity or converted to biofuel through the Fischer-Tropsch process. Incineration is amongst other methods conventionally used for waste treatment (Tendler et al., 2005). However it results in the formation of tar and char which need further treatment (Gassner and Maréchal, 2009). Thermal plasma gasification is an innovative process for the waste treatment which seems to have distinct advantages.



This is due to the high temperatures found in plasma systems. In a plasma gasification process, the organic compounds are thermally decomposed into their constituent elements and converted into synthetic gas (syngas), which consists mainly of hydrogen (H_2) and carbon monoxide (CO) (Galeno et al., 2011). The inorganic materials are melted and converted into a dense, inert, non-leachable vitrified slag.

Necsa is in the process of developing such process for organic waste plasma gasification for the production of syngas, which will be further used for electricity generation. The effectiveness of this process depends on the quality of syngas, which in turn depends on the gasification process.

A laboratory scale organic waste plasma gasification system is currently used as a research facility by Necsa. The data collected during the series of experimental tests will be used as input into the design of the syngas production facilities. There are number of problems encountered during the operation of this laboratory system. One main problems is the carbon residues remaining after every experimental run which lead to the system having downtime for maintenance (mainly for the removal of carbon residues from the reactor, pipes and traps). The second main problem is the fluctuation in the gas yields. The ideal gas composition for the gasification process is to achieve high CO and H_2 yield with minimum CO_2 , tar, carbon residues and CH_4 . This has not been optimised.

The objective of this study was to investigate deferent parameters such as feed rate, operating temperatures, equivalence ratios, etc., which have direct influence in the quality of syngas produced and tar formation during biomass plasma gasification processes. The optimum parameters which will give high quality syngas product and no tar will be used when up scaling the system.

Different types of biomass behave differently when gasified. Therefore it was thought to be important to characterise each material used as a feed during gasification process. Hence this study was divided into two sections. The first part comprises the characterisation of four different biomass materials. Here the reaction rates of the materials were studied using thermogravimetric analysis (TGA).

The second part of the study was to study the operating parameters of a laboratory scale organic waste plasma gasification reactor. This included gasification experiments on four types of



biomass (viz. peach pips, pine wood, bamboo and Napier grass) as well as performing a preliminary gasification study on chemical waste. The chemical waste was scrap lithium hexafluorophosphate (LiPF_6), embedded in poly(methyl methacrylate (PMMA)). The aim here was to see whether PMMA would yield a significant amount of syngas.

2 LITERATURE SURVEY

2.1 PYROLYSIS

Pyrolysis is thermal decomposition which occurs in the absence of oxygen (Bridgwater, 2012). Biomass pyrolysis can result in the production of three products, viz. liquid, solid and gas. Their proportions can be varied by adjusting the process parameters. The product distributions from different modes of pyrolysis are shown in Table 1.

Table 1. Typical product weight yield (dry wood basis) obtained by different modes of pyrolysis of wood (Bridgwater, 2012)

Mode	Condition	Liquid	Solid	Gas
Fast	~500°C, short hot vapour residence time ~1 s	75%	12% char	10%
Intermediate	~500°C, hot vapour residence time ~10-30 s	50% in 2 phase	25% char	25%
Carbonisation (Slow)	~400°C, long vapour residence hours — days	30%	35% char	35%
Gasification	~750-900°C short hot vapour residence time- seconds	5%	10% char	85%
Torrefaction (Slow)	~290°C, solids residence time ~10— 60 min	0%	80% char	20%

2.2 GASIFICATION

Operation of the pyrolysis process in a lean oxygen environment is called gasification. Gasification is a process in which combustible materials are partially oxidized or partially combusted (Phillips, 2006). As it can be seen from Table 1, gasification generates 85% gas, 10% solids and 5% liquids when operated at temperatures between 700 and 900 °C. The gases produced during gasification are combustible synthesis gases, also known as syngas, which can be further processed to produce chemicals, fertilizers, liquid fuels, hydrogen and electricity

(Rozelle and Der, 2015). Operation of the gasification process in the presence of oxygen (partial oxidization rather than complete oxidization) increases the yield of these gases and eliminates/reduces the tar production (Hlina et al., 2011). To achieve near complete conversion of biomass to syngas, gasification processes are typically operated above their stoichiometric oxygen-fuel ratio.

2.2.1 ADVANTAGES OF GASIFICATION PROCESSES

Gasification is among the cleanest and most efficient technologies. Less CO₂ is emitted during gasification because there are not enough oxygen atoms available to fully react with the feed material (Phillips, 2006). In turn instead of producing CO₂ (which is an environmental pollutant), the carbon feed is converted primarily to carbon monoxide (CO), and the hydrogen in the feed is converted to H₂ rather than H₂O (Phillips, 2006).

The other advantage of gasification is that a fraction of the heating value (known as a cold gas efficiency) available in the feed stock remains in the product gas. Due to this, most gasifiers are operated with no water cooling to minimize heat losses.

As indicate in Table 1, another advantage of gasification is minimum tar yield. It is very important to have less tar or no tar in the product gas because tar would condense at low temperatures and lead to clogged or blockage in fuel lines, filters and engines (Han and Kim, 2008).

Different types of gasifiers have been studied and designed with the attempt of exploring these advantages. Some of these gasifiers are discussed in Section 2.2.2. Plasma gasifiers are of particular of interest for this study.

2.2.2 TYPES OF GASIFIERS

There are three main types of gasifiers conventionally applied in coal gasification processes. These are moving bed, fluidized bed and entrained flow gasifiers. A brief background of these gasifiers is given here. There is, however, a constant development of new technologies in order to achieve, among others things, a simplified, efficient and tar free syngas production system. These systems can handle a variety of feed stock such as biomass, municipal waste, medical waste, and so on. Plasma gasification is an example of a recently developed technology and is

discussed here as of primary interest.

2.2.2.1 MOVING BED

A moving bed gasifier is a countercurrent flow reactor where the feed stock (in the form of large particles and fluxes) is loaded from the top of the gasifier and moves slowly downwards through the bed while reacting with oxygen containing gas which is introduced at the bottom (Figure 1). The remaining ash after gasification drops out at the bottom of the reactor. In a moving bed gasifier, the reaction happens in 4 stages, namely the drying zone at the top of the reactor, the carbonization zone, the gasification zone, and lastly the combustion zone at the bottom of the reactor.

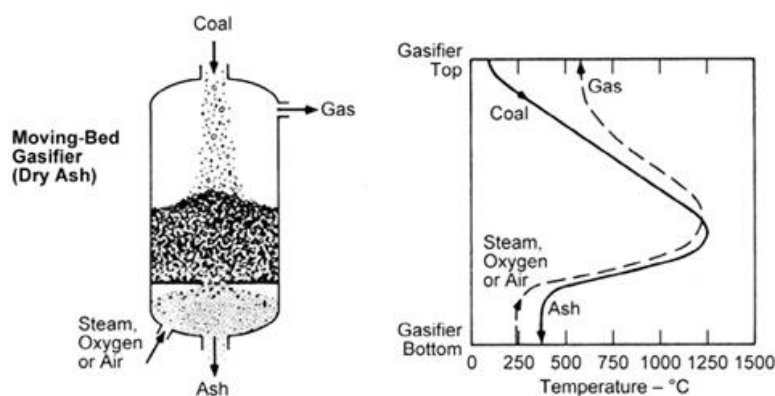


Figure 1. Moving bed (Phillips, 2006)

2.2.2.2 FLUIDIZED BED

A fluidized bed gasifier is one of the most frequently used gasification reactors (Meng et al., 2011). They have excellent heat and mass transfer between the gas and the solid phases with the best temperature distribution throughout the bed created by their back mixing. The flow of the oxidant into the reactor is sufficient to float the particles, but not too high to flush the particles out of the bed. The particles size required to sustain the bed is small (< 6 mm). In a fluidized bed, the feed enters at the side of the reactor while the oxidant enters at the bottom (near the bottom) with sufficient velocity to fully suspend or fluidize the reactor bed (Figure 2).

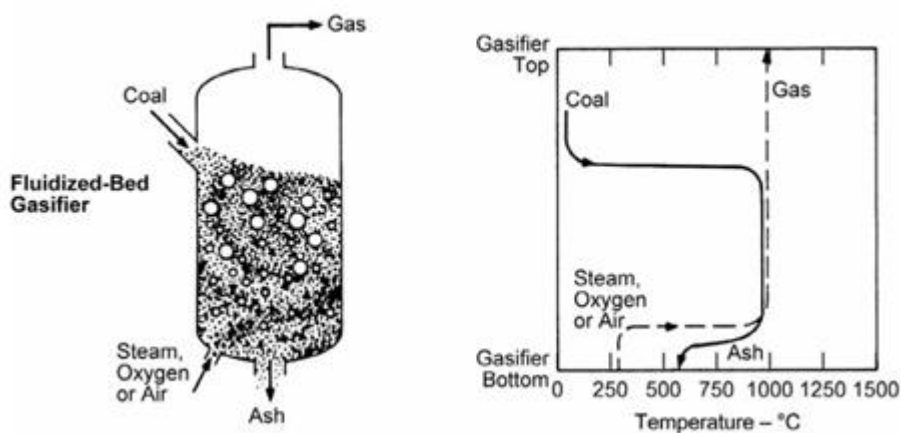


Figure 2. Fluidized bed gasifier (Phillips, 2006)

2.2.2.3 ENTRAINED FLOW

This is a co-current flow reactor where the finely ground feed stock is fed co-currently with the oxidant from the top of the reactor. Entrained gasifiers operate at high temperatures due to their short residence time, resulting in a high carbon conversion efficiency. Because of these high operating temperatures, the syngas produced is tar free and the ashes are melted into vitreous slag (Figure 3). However, these high temperatures tend to shorten the life of the system components.

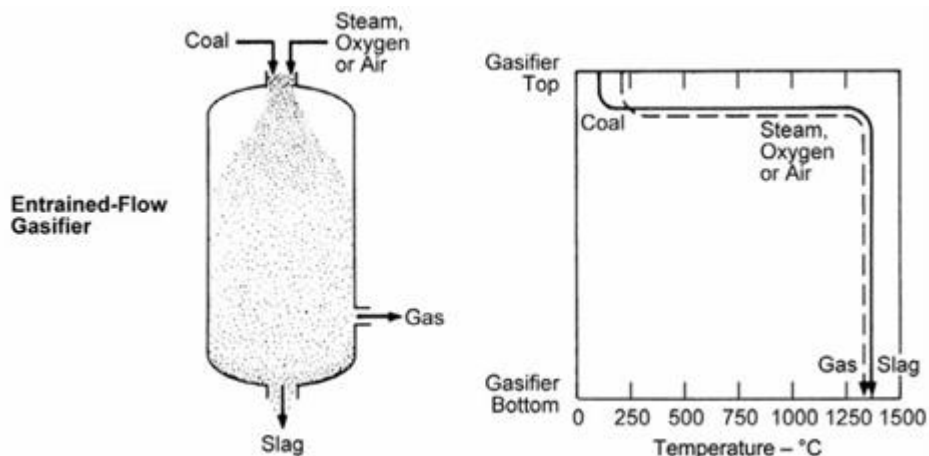


Figure 3. Entrained flow gasifier (Phillips, 2006)

2.2.2.4 PLASMA GASIFIERS

Plasma reactors are known and used for treatment of a wide range of material including scrap

metal, hazardous waste, municipal and industrial waste and landfill material to derive useful material or to vitrify undesirable waste for easier deposition (Dighe et al., 2010).

In a plasma gasification process electric arc generators (plasmatrons or plasma torches) are used (Rutberg et al., 2011; Lemmens et al., 2007; Tendler et al., 2005) (Figure 4). Here the arc (or arcs, in case of multiple torches) is sustained inside a discharge chamber. The plasma flow is injected into the plasma chemical reactor/gasifier by means of nozzle of various types.

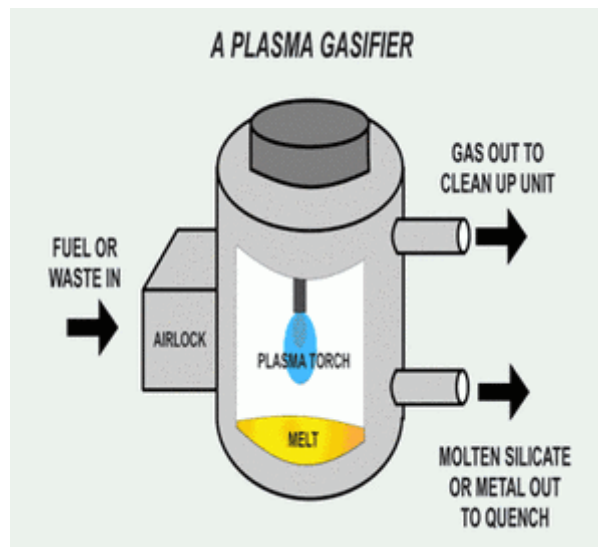


Figure 4. Plasma gasifier

Several plasma gasification configurations, as illustrated in Figure 5, are possible (Popov et al., 2011).

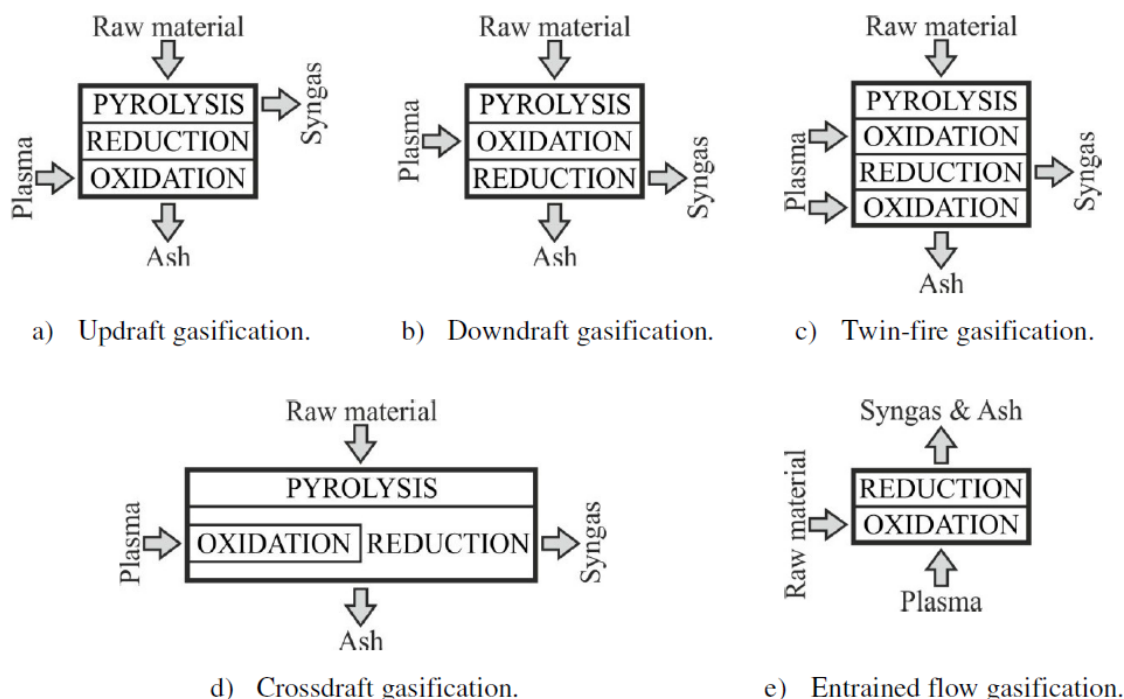


Figure 5. Various ways of organization plasma gasification (Popov et al., 2011)

Conventionally organic materials are processed using pyrolysis reactors which mostly results in a formation of tars and production of poor quality syngas. The required tar content for most syngas application is of the order 0.05 g/m^3 or less (Han and Kim, 2008). To improve the pyrolysis results, plasma reactors have been coupled with pyrolysis reactors (Luche et al., 2012). The plasma acts as a purification stage by reducing the production of tars and aerosols, and produces a hydrogen rich syngas. However the pyrolysis reactors could be eliminated and plasma reactors could be used alone as gasification medium.

In 2006, Europlasma announced a new gasification process which maximizes mass yield from biomass by using an external source to feed the endothermic reaction.

2.2.3 PLASMA TECHNOLOGY

Plasma technology was used in the sixties primarily for space related activities (Pfender, 1999; Fauchais and Vardelle, 1997). It gradually transitioned to a well-established interdisciplinary science with a wide range of important application in material processing in the eighties (Boulos, 1991). The understanding of interaction between thermal plasmas and particulates has been researched and has successfully been applied in the areas such as arc

welding, arc cutting, plasma synthesis of fine powders, plasma waste destruction, etc (Pfender, 1999). Adapted from their waste destruction application (Camacho, 1996) the technology has recently being utilised for their application in biomass gasification due to their high temperatures and high energy densities along with their corresponding fast reaction times (Gomez et al., 2009).

2.2.3.1 WHAT IS A PLASMA?

Plasma can be defined as the fourth state of matter (Boulos et al., 2013). The general principle of physics is that matter changes its state as energy is supplied to it. Solids become liquid, and liquid become gas. When even more energy is applied to gases, they ionise and become the energy rich plasma state (Figure 6). Hence it is called the fourth state of matter. A high amount of energy is needed to produce a plasma. Plasma consists of a mixture of electrons, ions and neutral species in local electrical neutrality (Boulos, 1991).

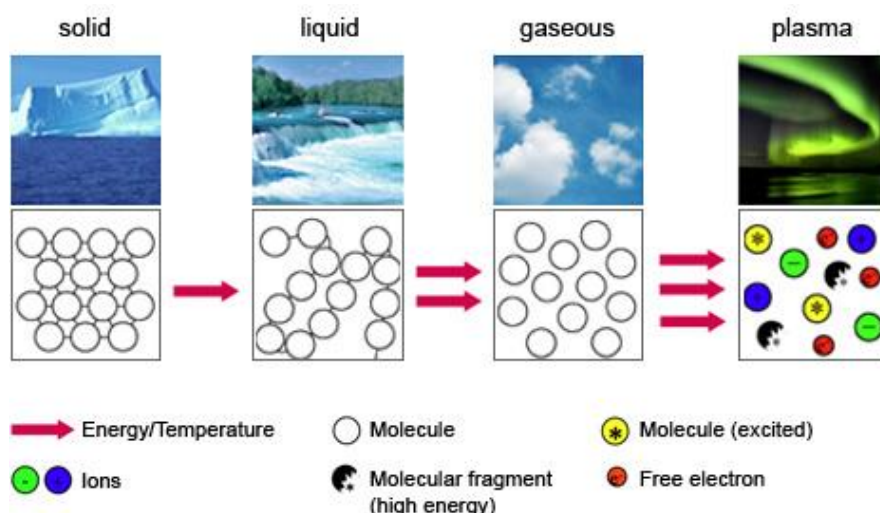


Figure 6. Four states of matter

Plasmas can be divided into two categories: thermal plasmas and non-thermal plasmas. Thermal plasmas are atmospheric plasmas characterised by high enthalpy content and temperatures around 2000 – 20000 °C (Venkatramani, 2002). Non-thermal plasmas are low pressure plasmas characterised by high electron temperatures and low ion and neutral particle temperatures. Thermal plasmas are widely used for plasma processing and metallurgical applications. They have recently also found application in biomass gasification processes, as

mentioned above.

2.2.3.2 THERMAL PLASMAS

Thermal plasmas are normally generated by passing an electric current through a gas (Boulos et al., 2013). This is done in a plasma torch by direct current (DC), alternating current (AC), radio frequency (RF) and other discharges. The direct current (DC) plasma torches are widely used and they consist of a water cooled cathode and anode. The two electrodes are separated by an insulator which has an inlet for a plasma gas. When a plasma gas is introduced in the electrode gap and a DC arc is established between the electrodes, the arc is pushed through the anode nozzle resulting in a high temperature high velocity flame. The arc is a self-sustaining discharge with a voltage drop of a few volts near the electrodes. It is also highly turbulent. Any disturbance from equilibrium is undesirable since it tends to extinguish the arc (Venkatramani, 2002).

The features that make thermal plasma attractive is the high energy density ($\sim 10^6$ - 10^7 J/m³) which comes with high heat flux density ($\sim 10^7$ - 10^9 W/m²), high quenching rate ($\sim 10^6$ - 10^8 K/s) and high processing rate (Trelles et al., 2009).

2.2.3.3 PLASMA TORCHES

A plasma torch is a device used to produce thermal plasmas as mentioned earlier. There are different types and geometries of plasma torches. The two main types of plasma torches are transferred (Figure 7) and the non-transferred arcs (Figure 8). In a transferred geometry, the electric arc used to generate the plasma is maintained between one electrode of the torch (the cathode) and a conductive work piece that needs to be cut or melted (act as anode), located outside the torch (Favalli and Szente, 1998).

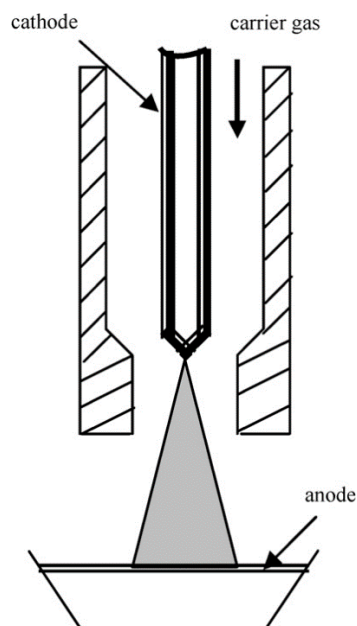


Figure 7. DC transferred arc plasma torch (Gomez et al., 2009)

A non-transferred torch uses two water cooled electrodes (cathode and anode) in order to maintain the electric arc (Favalli and Szente, 1998). The electric arc strikes between the two electrodes of the torch and it is kept inside the anode channel.

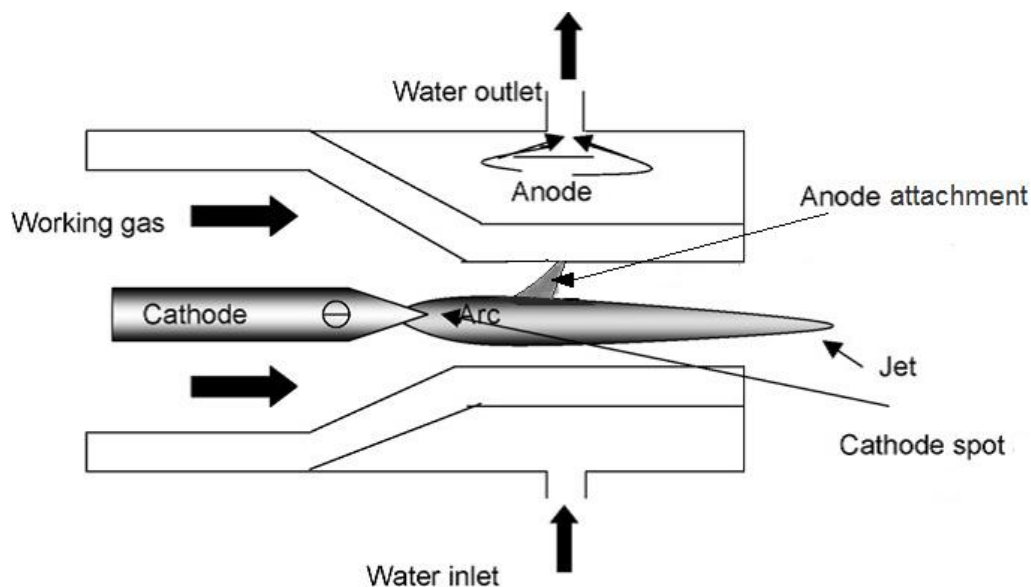


Figure 8. DC non-transferred arc plasma torch (Gomez et al., 2009)

Today plasma torches are used as unique heating tools in industrial processes. The industrial application of plasma torches includes waste destruction, experimental gas heating for solving the issues of aerodynamic heating of re-entry hypersonic vehicles, synthesis of nanostructure material, plasma chemistry and material deposition (plasma spaying) or removal (plasma etching) (Venkatramani, 2002; Murphy, 2001).

2.2.3.4 PLASMA ARC

There are three different arc modes of operating the torch that have been identified according to the voltage fluctuations (Figure 9). They are:

- Steady mode
- Take-over (quasi-periodic) mode and
- Restrike mode

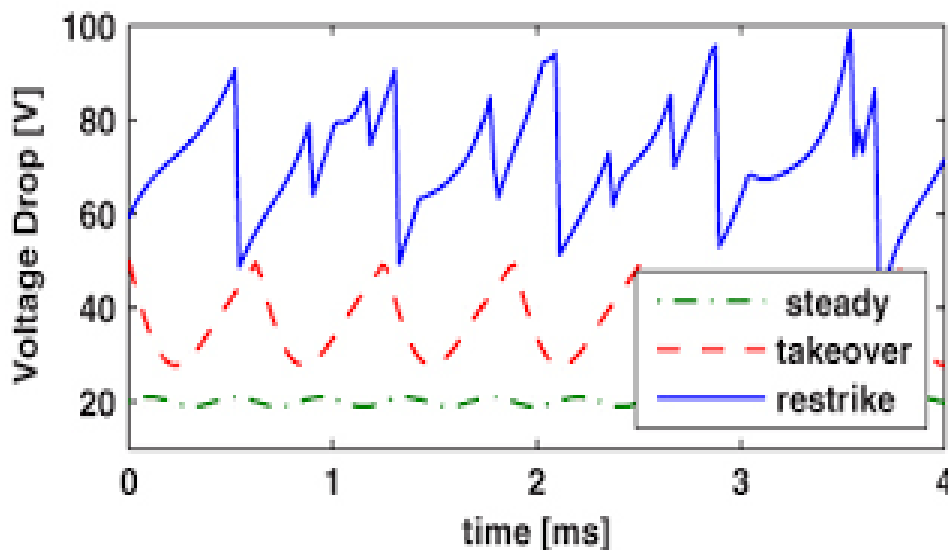


Figure 9. Basic arc operating modes (Duan and Heberlein, 2002)

These modes are described in the order of decreasing current or increasing flow rate. The steady mode is characterised by a fixed position of the anode attachment and negligible voltage fluctuation. The take-over mode is characterised by a periodic or quasi-periodic movement of the arc and fluctuating voltage while the restrike mode is characterised by the highly unstable, unpredictable movement of the arc and quasi-chaotic fluctuation of the voltage (Duan and

Heberlein, 2002).

The ideal movement of the arc is the quasi-periodic movement with high frequency and small amplitude as in a take-over mode. This allows uniform distribution of the thermal load over the anode while forcing the jet homogeneously (Trelles et al., 2006)

In a non-transferred arc plasma torch, the fluctuation behaviour of the arc may negatively affect the process. In plasma torches which are used for thermal spraying it may lead to a non-uniform heating of the injected powder particles (Dorier et al, 1999). This may negatively affect the quality and yield of the spray deposits. Plasma torches used for material processing and waste destructions are similar to the one used for thermal spraying (Favalli & Szente, 1998), the difference being the exclusion of the powder inlet, hence the fluctuation behaviour of the arc will have the same effects.

For transfer arc plasma torches, the process is characterised by a transferred electric arc that is established between the cathode and the anode (molten metallic work piece). In order to achieve a high quality and high productivity process, a plasma jet must be as collimated as possible and must have a higher achievable power density (Colombo et al, 2009). The fluctuation behaviour of the arc will therefore have an effect on the plasma jet.

In order to obtain design strategies to achieve the quasi-periodic movement of the arc (which result is a less fluctuating arc), a better understanding of the processes driving the dynamics of the arc inside the torch is required. The dynamics of the arc inside the plasma torch is a result of the balance between the drag force caused by the interaction of the incoming gas flow over the arc and the electromagnetic Lorentz forces caused by the local curvature of the arc (Trelles et al, 2006). Computational fluid dynamics (CFD) is used as a tool in many studies for a better understanding of the dynamics of plasma arcs (Klinger et al., 2003; Meng and Dong, 2011; Reynolds et al., 2010; Trelles et al., 2009).

2.3 GASIFICATION PRODUCER GAS

Synthesis gas (syngas) is the main product of the gasification process. It consists mainly of hydrogen (H_2) and carbon monoxide (CO). Traces of hydrocarbons such as methane are also found in a gasification product gas (Bridgwater, 2003). The H_2 and CO are produced during gasification according to the following reactions:



$C + H_2O = CO + H_2$	1
$CO + H_2O = CO_2 + H_2$	2
$C + 2H_2 = CH_4$	3
$C_xH_y + xH_2O = xCO + \left(x + \frac{1}{2}y\right)H_2$	4
$C + CO_2 = 2CO$	5

The most important reaction is Equation 5 known as Boudouard reaction. In this reaction carbon converts CO_2 to CO (one of the primary products of gasification) (Lemmens et al., 2007). It is of high interest to achieve low CO_2 emission since it is of no value in syngas and it is a pollution hazard. A high CO/CO_2 ratio is achieved at high temperatures and it is considered an important parameter for control of the gasification process (Lemmens et al., 2007)).

As mentioned in Section 2.2, gasification occurs in an oxygen starved environment. This also prevents the formation CO_2 since there are not enough oxygen atoms to react with the feed. Therefore the precise amount of oxygen as a reagent also plays an important role in the composition of the syngas.

Pure O_2 , air, steam, CO_2 , H_2 or a mixture of these could be used as reagents (Puig-Arnavat et al., 2010). When oxygen is used as a reagent a high quality syngas with a medium heating value (MHV) of $\sim 10\text{--}12 \text{ MJ/m}^3$ (Bridgwater, 2003; McKendry, 2002b) is produced. However the use of air introduces the presence of nitrogen in the final product which reduces the quality of the gas which in turn results in a low heating value (LHV) of $\sim 5 \text{ MJ/m}^3$ (Bridgwater, 2003; McKendry, 2002b; Rutberg et al., 2011). Higher heating value (HHV) of up to 40 MJ/m^3 is usually achieved when hydrogen is used as a reagent (McKendry, 2002b). This is presented in Figure 10.

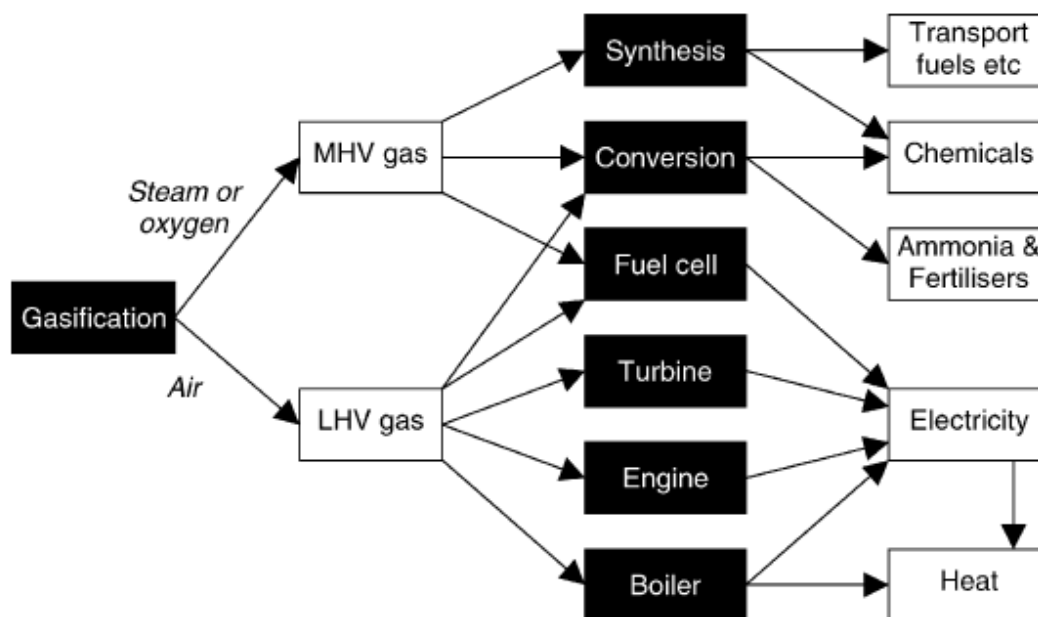


Figure 10. Syngas application (Bridgwater, 2003)

The storage or transportation of gas is very costly, therefore it has to be used immediately after production. Low heating value gas is used directly in combustion or as an engine fuel to produce electricity while medium heating value gas is used as a feedstock for conversion into other products such as liquid hydrocarbons.

2.3.1 TAR IN A GASIFICATION PRODUCT

Tar formation during the gasification process is one of the main problems to be dealt with. Higher molecular weight compounds in the product gas begin to condense at temperatures below 450 °C and form tar (McKendry, 2002b). The presence of tar in a syngas can be problematic because it can result in blocking and fouling of process equipment (Chen et al., 2003). It also hinders the process of removing the particulates from the gas.

Hot gas cleaning after the gasifier is the less preferred tar removal process (Figure 11). Two methods for tar removal are catalytic cracking using dolomite or nickel, and thermal cracking by partial oxidation or direct contact (Bridgwater, 2003; Chen et al., 2003). The use of CO₂ with a catalyst like Ni/Al as a gasifying agent could also be beneficial for tar reduction as it can transform char, tar and CH₄ into H₂ and CO

(Puig-Arnavat et al., 2010).

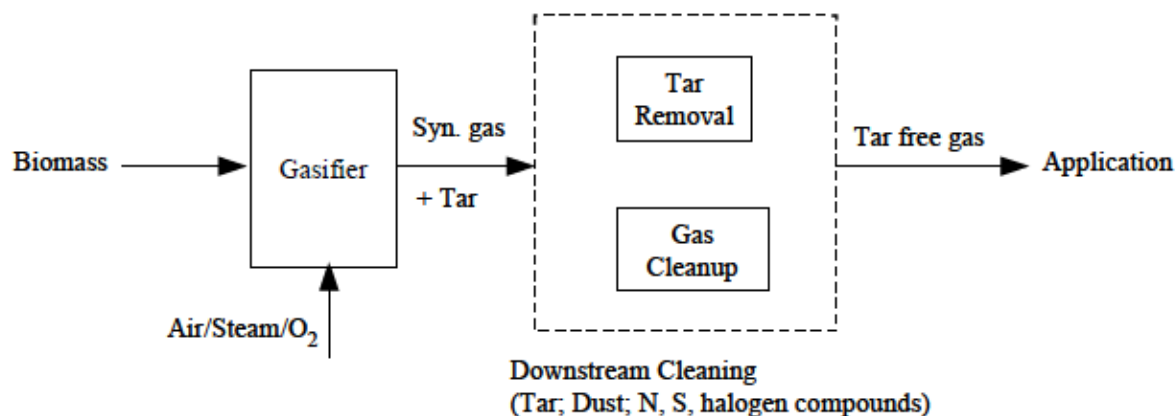


Figure 11. Tar reduction concept by secondary method (Devi et al., 2003)

Tar treatment inside the gasifier is the primary and most preferred method (Figure 12). It eliminates the secondary tar treatment methods during gasification processes. The operating parameters such as temperatures, feeding rate, gasifying reagent, equivalence ratio, residence time, etc., play an important role in the formation and decomposition of tar inside a gasifier (Dufour et al., 2009; Guo et al., 2014; Berrueco et al., 2015a).

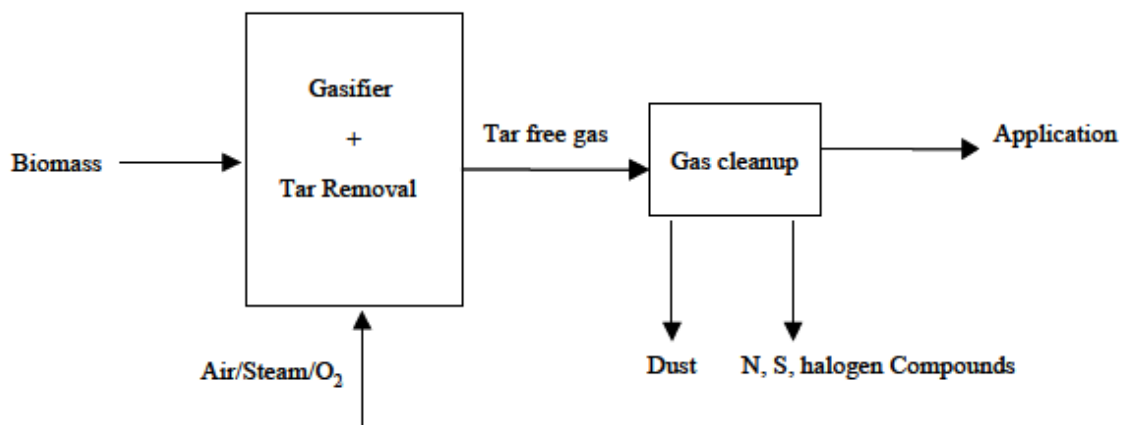


Figure 12. Tar reduction concept by primary method (Devi et al., 2003)

In order to get the best quality, tar free syngas, the design and the operation of the gasifier has to be optimised.

2.4 ORGANIC MATERIALS

Carbon containing compounds are generally defined as organic materials in modern chemistry. Organic compounds are predominantly combinations of hydrogen, carbon, nitrogen, and oxygen. Organic materials include the wood, feathers, leather, synthetic materials such as plastics and many more.

2.4.1 BIOMASS

Apart from being defined as organic material, biomass can also be defined as a renewable, storable and transportable energy source. It is available in different forms, such as wood, agricultural and forest residues, and garbage. Biomass consists of organic components such as hemicellulose, cellulose, lignin, lipids, proteins, starches and sugars. It also contains water, alkaline and alkaline earth metals, chlorine, nitrogen, phosphorous, sulphur, silicon and heavy metals.

2.4.2 THE MAJOR COMPONENTS OF BIOMASS

Hemicelluloses, cellulose and lignin are the three major components of biomass and they generally cover 20-40, 40-60, and 10-25 wt % of lignocellulosic biomass respectively (Yang et al., 2007).

Cellulose is a polysaccharide with a general formula of $(C_6H_{10}O_5)_n$ and average molecular weight of 300 000 – 500 000 g/mol (Yaman, 2004). The structural formula is shown in Figure 13. Cellulose is insoluble in water and forms the skeletal structure of most biomass. It is the most abundant natural polymer on earth, consisting of glucose-glucose linkages arranged in linear chains where every other glucose residue is rotated in the opposite direction (Kim et al., 2006). The yearly biomass production of cellulose is estimated to be 1.5 trillion tons (Kim et al., 2006). Starch and cotton are examples of cellulose.

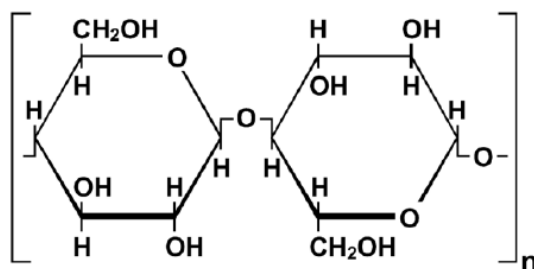


Figure 13. Structure of cellulose (Kögel-Knabner, 2002)

Hemicellulose, Figure 14, is the second most common polysaccharides in nature (Saha, 2003). Unlike cellulose, hemicellulose is complex and soluble in dilute alkali and consist of branched structures which varies depending on the type of wood material (Yaman, 2004). The main hemicellulose in hard wood is glucuronoxylan

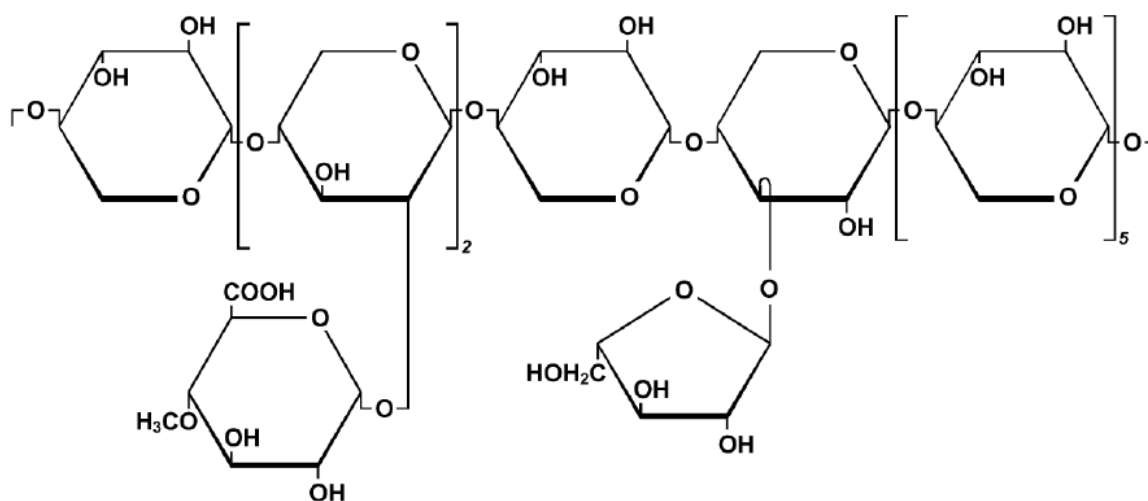


Figure 14. Structure of hemicellulose (Kögel-Knabner, 2002)

Lignin (Figure 15) is a highly branched, substituted, mononuclear aromatic polymer in the cell walls of certain biomass and is often bound to cellulose fibers to form a lignocellulosic complex (Yaman, 2004). Lignin protects the cell wall polysaccharides from microbial degradation, imparting decay resistance (Vanholme et al., 2010).

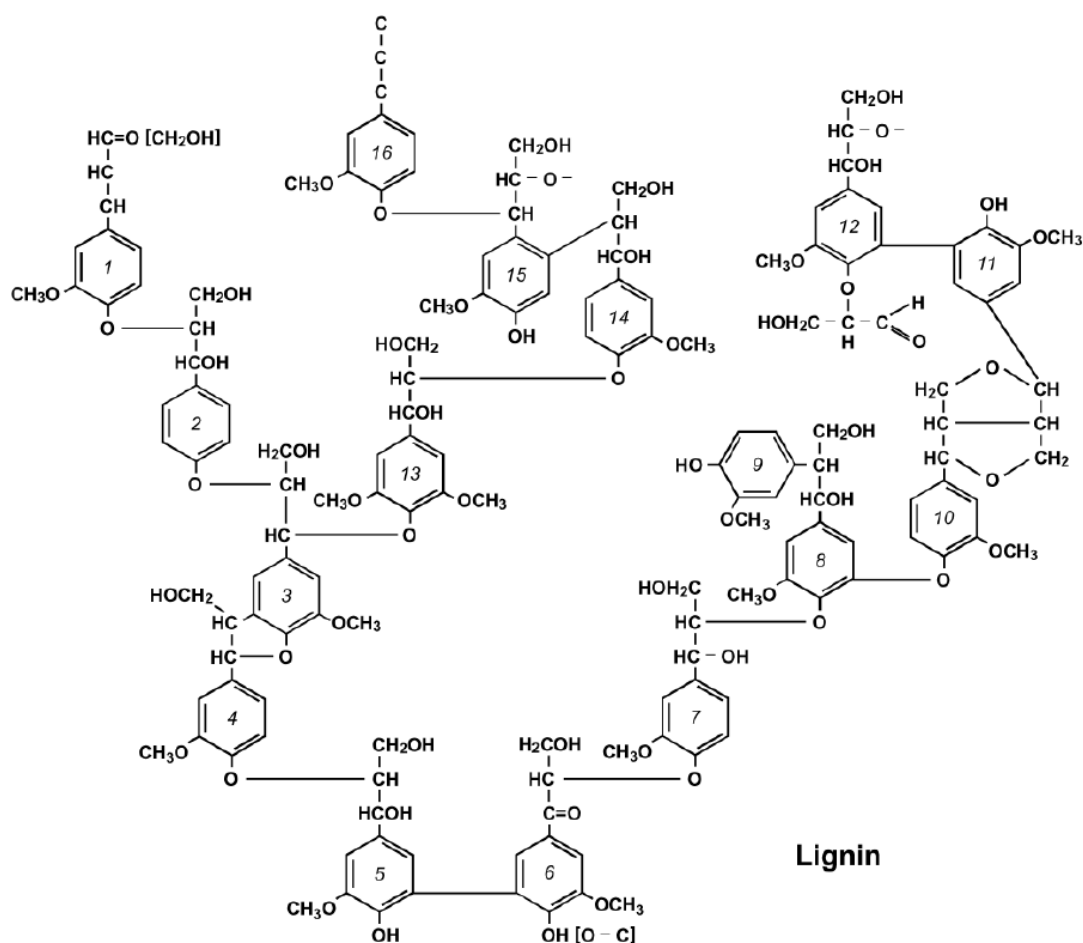


Figure 15. Structure of lignin (Kögel-Knabner, 2002)

2.4.3 BIOMASS CHARACTERISATION

Biomass characteristics such as heating value, moisture and ash contents as well as elemental composition has a significant effect on the design and operation of gasifying systems (Yin, 2011). Table 2 below shows the ASTM methods used to analyse these biomass properties.

Table 2. Methods of biomass fuel analyses (Demirbas, 2004)

Properties	Analytical method
Heating value	ASTM D 2015, E 711
Particle size distribution	ASTM E828
<i>Proximate composition</i>	
Moisture	ASTM E871
Ash	ASTM D1102 (873K), ASTM E830 (848K)
Volatile matter	ASTM E 872, ASTM E 897
Fixed carbon	By difference
<i>Ultimate elemental</i>	
Carbon, Hydrogen	ASTM E 777
Nitrogen	ASTM E 778
Sulphur	ASTM E 775
Chlorine	ASTM E 776
Oxygen	By difference
Ash elemental	ASTM D3682, ASTM D2795, ASTM D4278, AOAC 14.7

In order to determine the properties and composition of biomass, the analyses in Table 2 are performed on a specific biomass type (Reed et al., 1988). This is due to the fact that biomass shows a wide diversity and its composition is highly variable (Vassilev et al., 2010). There are various factors that influence the composition of biomass. The origin of the material (Ghetti et al., 1996), the type of the material, and the part of the plant (i.e. leaves, stems, seeds, roots, etc.) are some of the factors influencing the composition of biomass (Vassilev et al., 2010). However, the properties of biomass could still be generalised depending on their classification, namely woody, herbaceous, aquatic, manure, as well as contaminated and industrial biomass (i.e. municipal waste) (Vassilev et al., 2010; McKendry, 2002a). Of all these biomass groups the focus is more on the woody and herbaceous biomass due to their

lower moisture content (McKendry, 2002a). The general properties of these two groups of biomass are shown in Table 3 and Table 4.

Table 3. Proximate analysis of typical biomass material (wt %)

Biomass type	Ash	Moisture	Volatile material	Fixed carbon
Woody (McKendry, 2002a)	1	20	82.00	17.00
Herbaceous (Vassilev et al., 2010)	5.1	12.0	66.0	16.9

Table 4. Ultimate analysis of typical biomass material (wt %)

Biomass type	C	H	O	N	S
Woody (Rutberg et al., 2011)	50.25	6.09	43.35	0.20	0.10
Herbaceous (Vassilev et al., 2010)	49.9	6.2	42.6	1.2	0.15

The calorific value of biomass is an expression of the energy content released when the material is burned in air. It is available in two forms namely higher heating value (HHV) and lower heating value (LHV). The values for typical woody and herbaceous biomass are shown in Table 5. The form and the actual amount of energy recovered from biomass material usually depend on the conversion method (McKendry, 2002a) discussed in Section 2.1.

Table 5. Calorific value of typical biomass material (MJ/kg)

Biomass type	HHV	LHV
Woody (Reed et al., 1988)	20.90	20.40
Herbaceous (Wright et al., 2006)	18.12	17.21

2.4.5 COMPOSITION OF SELECTED BIOMASS TYPES USED IN THIS STUDY FOUND IN LITERATURE

The proximate and ultimate analysis of Napier grass, peach pips, bamboo and pine tree are shown in Table 6 and Table 7.

Table 6. Proximate analysis of selected biomass material

Biomass type (and references)	Ash (%)	Moisture (%)	Volatile material (%)	Fixed carbon (%)	LHV (MJ/kg)
Nappier grass (TC et al., 2002; Lee et al., 2010)	9.68	9.43	72.58	8.38	18.00
Peach pips (Parikh et al., 2005)	1.10	-	79.10	19.80	19.42
Bamboo (Channiwala and Parikh, 2002)	1.95	11.50	86.80	11.24	20.55
Pine tree (Cuiping et al., 2004)	0.89	8.61	76.50	14.45	19.38

Table 7. Ultimate analysis of biomass material used in this study

Biomass type (and references)	C	H	O	N	S	Cl
Nappier grass (Lee et al., 2010)	42.40	5.98	45.32	1.71	0.09	0.24
Peach pips (Parikh et al., 2005)	49.14	6.34	43.52	0.48	0.02	-
Bamboo (Channiwala and Parikh, 2002)	55.8	4.8	38.1	1.3	-	-
Pine tree (Cuiping et al., 2004)	49.41	7.67	42.19	0.1	0.05	-

2.4.6 BIOMASS THERMAL CHARACTERISATION

The thermal behaviour of biomass is an important characteristic. Thermal analysis is a technique in which the mass and/or energy content of a solid material is measured as a function of temperature whilst the material is subjected to a controlled temperature programme (Inczedy

et al., 1998). There are several techniques used to conduct thermal analysis of solid material. These techniques (i.e. thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetric (DSC), etc.) are usually applied when characterising biomass (Yang et al., 2007; Stenseng et al., 2001).

2.4.6.1 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is a method of thermal analysis in which a mass loss of a material is measured as a function of increasing temperature (with constant heating rate) or as a function of time. Thermal properties of biomass have been investigated using TGA analysis. The results obtained during TGA play a significant role when computing the kinetics of biomass (Bassilakis et al., 2001; Mansaray and Ghaly, 1999; Kumar et al., 2008; Slopiecka et al., 2012; Wongsiriamnuay and Tippayawong, 2010; Hui et al., 2010).

Characteristics of biomass differs per type. Pyrolysis of biomass takes place in different stages illustrated in Figure 16. The moisture content is removed first from the material at ~ 100 °C. This is followed by the removal of volatile materials in a second stage at temperatures between 250 - 450 °C. From Figure 16 it can be seen that a fraction of char and ash is left at the end. If the process is carried in the presence of air char will burn leaving the ash as the final residue (Reed et al., 1988).

The three stages of biomass pyrolysis happen due to the presence of three major components of biomass discussed in section 2.4.2. The weight percentage of these components in a specific biomass influence its thermal behaviour. When taking into consideration the water evolution stage, the biomass pyrolysis could sometimes be said to happen in four stages namely: the dehydration, hemicellulose decomposition, cellulose decomposition and finally the lignin decomposition (Yang et al., 2007). However, in most cases the hemicellulose and cellulose are said to decompose during active pyrolysis (Gašparovič et al., 2010) hence the pyrolysis of biomass is sometimes said to be divided into three stages.

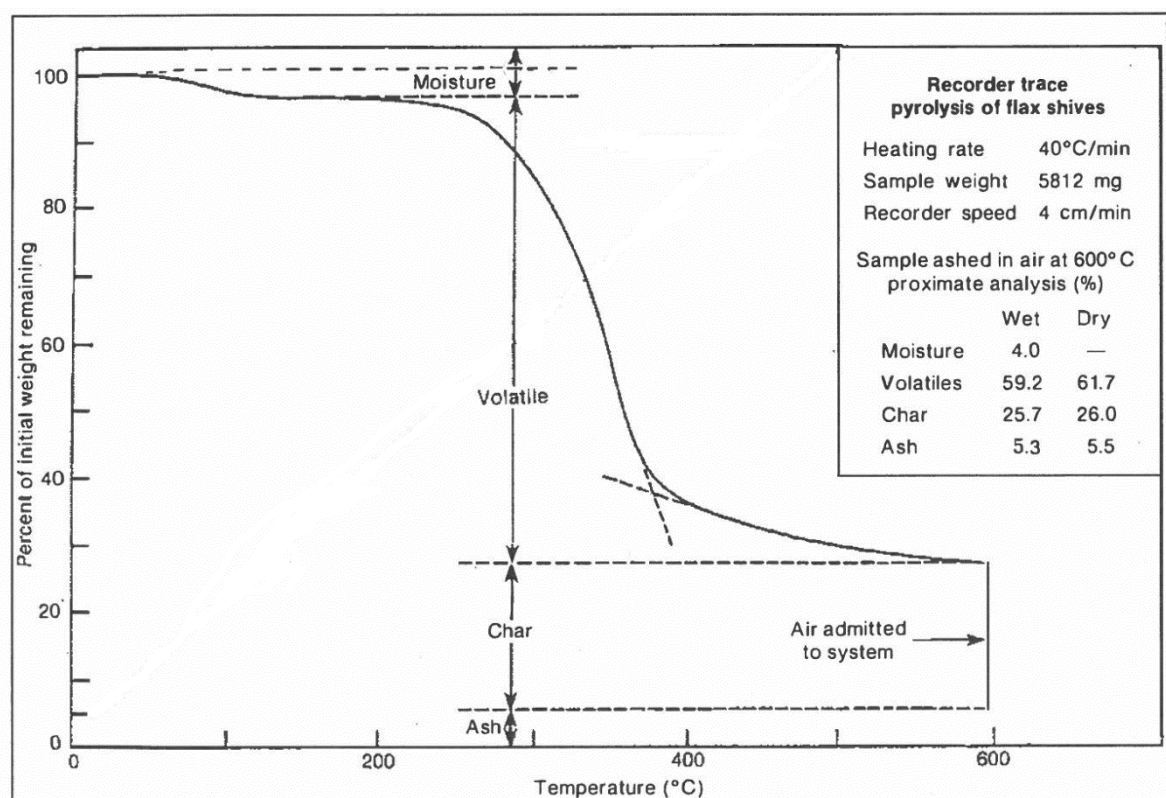


Figure 16. TGA curve of a general biomass sample in the absence of air
(Reed et al., 1988)

Each type of biomass produces slightly different quantities of char, volatiles and ash. Knowledge of these quantities, as well as the temperature dependencies of the reaction and associated weight losses, are useful in understanding gasifier operation and design (Reed et al., 1988)

3 DESCRIPTION OF EXPERIMENTAL EQUIPMENT

3.1 TGA-FTIR INSTRUMENT

The Perkin-Elmer TGA-FTIR hyphenated system (TGA 4000 and Spectrum 100) (Figure 17) was used for the characterisation of the biomass samples. This instrument can reach a maximum temperature of 1000 °C and a maximum heating rate of 200 °C/min. The instrument uses an alumina pan as a sample holder. The sample size that can fit in to the pan depend on the sample density. It is advisable to have the samples in a powder form. The samples were placed into a pan using a spatula to avoid contamination with moisture from human skin. A pair of tweezers was used to carefully hold the pan and place it into the TGA furnace. Prior to biomass characterisation the TGA was calibrated using a metal ball with a mass of 56 mg. Calcium hydroxide powder was then used as a reference sample.

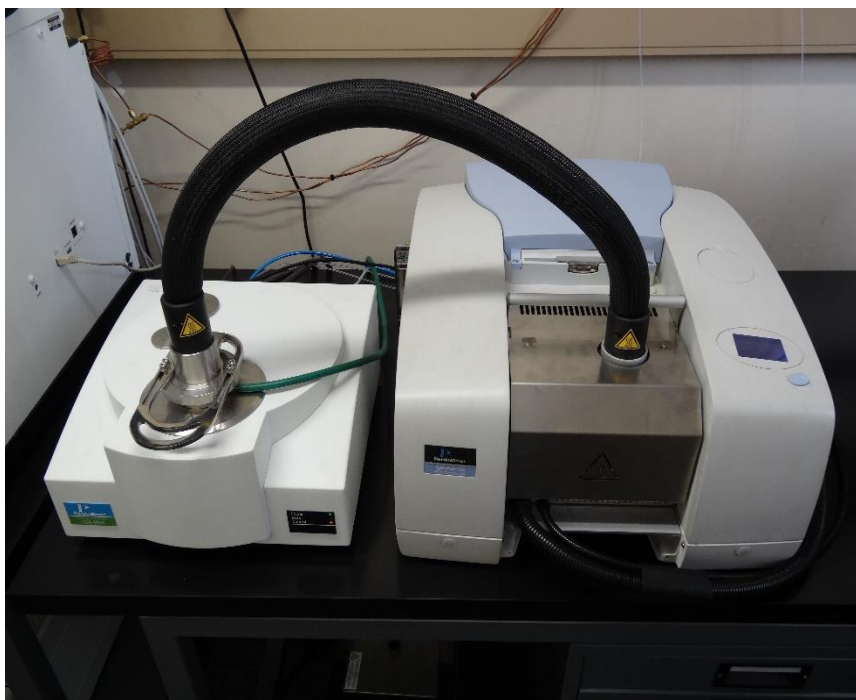


Figure 17. PerkinElmer TGA-FTIR instrument

3.2 PLASMA GASIFICATION SYSTEM

The plasma gasification system which was used for the biomass gasification experiments is shown in Figure 18. The system consists of four main components which are the plasma reactor (consisting of the plasma torch, quench probe, feeding pipe and the glass view part), knockout vessel, filter trap and the sampling point. The main utilities of the system are the cooling water from the cooling towers which are placed outside the laboratory under covered roof with open sides, plasma power supply and a ventilation system connected to the building's ventilation system.

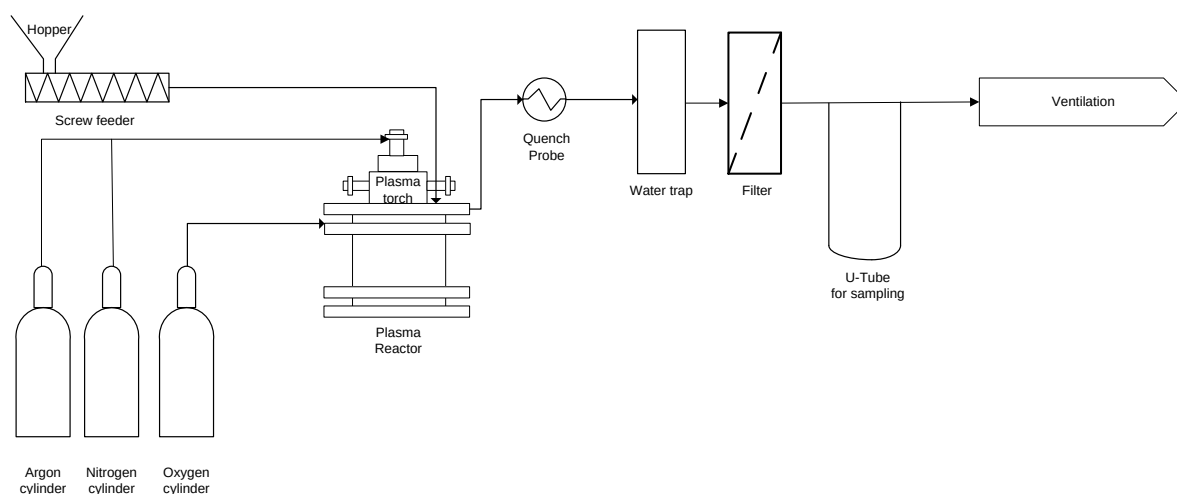


Figure 18. Laboratory scale plasma gasification system

3.2.1 PLASMA REACTOR

The plasma reactor is the heart of the gasification system (Figure 19). It consists of a stainless steel chamber, the ceramic crucible fitted inside the reactor chamber (the crucible is fitted to prevent heat loss to the walls of the reactor). Between the stainless steel chamber and the ceramic crucible there is a fine sand to further reduce heat loss. The outside walls of the reactor and the bottom flange are water cooled. The ceramic lid is placed on top of the ceramic crucible before covering the reactor with a stainless steel lid to ensure that more the heat supplied into the reactor is contained inside the ceramic crucible. The lid of the reactor contains four holes.

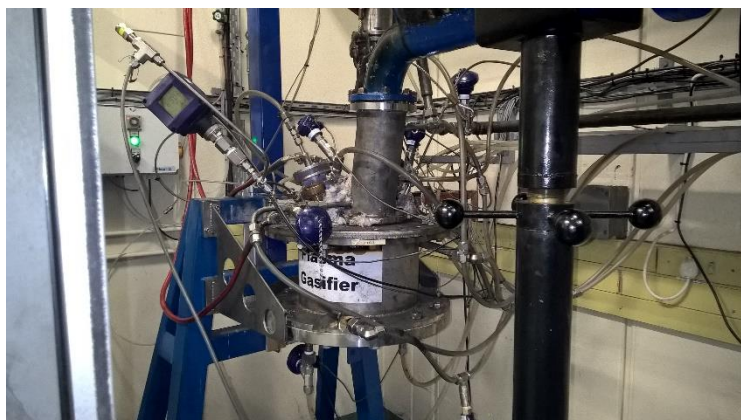


Figure 19. Plasma gasification reactor

One hole is for fitting the plasma torch (Figure 20) which is the main component of the plasma reactor. The plasma torch consists of the anode and the cathode which are mainly made of tungsten or copper. The torch is operated by means of a 30 kW plasma power supply (Figure 21). The power supplied into the system can be changed by adjusting the current settings depending on the required operating temperature. In this study the power varied between 13-16 kW.



Figure 20. Plasma torch



Figure 21. A 30 KW plasma power supply

The second hole on the reactor lid is fitted with a quench probe (Figure 22). The specialised heat exchanger has a 68 mm outer pipe fitted with a 42.5 mm inner probe. Both the outer and the inner probe are water cooled. The product gases of the gasification process exit through the quench probe. The gas is cooled to $\sim 40^\circ\text{C}$ before it enters the knockout vessel.

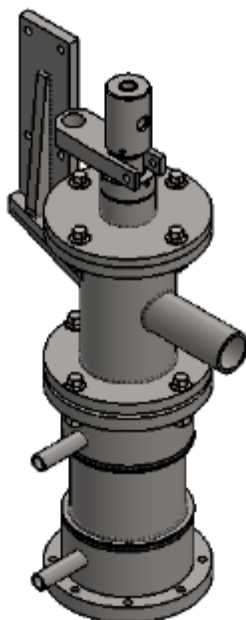


Figure 22. Quench probe

The third hole of the reactor lid is fitted with a feeder pipe attached to the feeding hopper (Figure 23). The pipe is 100 mm in diameter and it is also cooled with water. This is done shield thermal radiation from the feeder pipe to prevent pre-gasification.



Figure 23. Feeding hopper

The fourth hole is a view port sealed with a transparent quartz glass. This glass is used to view the inside of the reactor during operation. Also this glass is used for monitoring the temperature of the reactor by using an optical pyrometer in case the type R thermocouple breaks.

The lid also has a nozzle which is used for introducing the reagent directly into the reactor. The other option is to introduce the reagent through the plasma torch.

3.2.2 KNOCKOUT VESSEL

Water is one of the products of the gasification process. Any water vapour available in the product gas will condense after being cooled through a quench probe. The knock out vessel (Figure 24) is used to separate water and any available particulates from the syngas. The gas flow straight into the top of the vessel through a 40 mm pipe. The water and the particulates precipitate at the bottom of the vessel while the syngas flows through a pipe at the side of the vessel into a filter trap. The vessel has a 200 mm OD, and with a 50 mm throat.



Figure 24. Knockout vessel

3.2.3 FILTER

After the knockout vessel the syngas flows through a filter trap (Figure 25). The filter is fitted with a filter bag used to filter the fine solid ash present in the gas. It also has a pot below the bag where any particulates that weren't trapped by the knockout pot can accumulate.



Figure 25. Filter

3.2.4 GAS SAMPLING POINT

The system currently has no inline analytical instrumentation. A U-tube (Figure 26) is used to take gas samples after the filter for offline analysis. There is a valve before the filter which when controlled manually it creates a difference in pressure which enable the gas to flow through the U-tubes before being sent into the ventilation system.



Figure 26. U-tube

4 TGA EXPERIMENTS

TGA experiments were conducted at the laboratories of the Fluoro-materials Group at the University of Pretoria. This study was carried out to investigate the decomposition mechanisms and reaction kinetics of different biomass materials.

4.1 MATERIALS

Biomass samples used in this work were Napier grass (*Pennisetum pupureum*), peach pips (*Prunus persica* (L.) Batsch), bamboo wood (*Bambusa balcooa*) and pine wood (*Pinus patula*). All samples were sourced from local suppliers of forestry products, except the bamboo, which was taken from the University of Pretoria's botanical garden. Nitrogen gas (>99.999%) was obtained from African Oxygen Ltd, and used as received

4.2 SAMPLE PREPARATION

The biomass samples were prepared by first cutting the material into small pieces and then by milling using a Retsch mill (Type SR 200, Model 70546). The samples were further sieved in order to obtain a fine fraction.

4.3 THERMOGRAVIMETRIC ANALYSIS

The TGA-FTIR analysis was performed using a Perkin Elmer TGA 4000 coupled to a Perkin Elmer Spectrum 100 FTIR spectrometer. The gases evolved from the TGA were transferred to a heated infrared cell (kept at 250 °C) via a heated stainless steel transfer line (kept at 250 °C). The IR cell was fitted with KBr single crystal windows and had a beam path length of 10 cm. For each TGA experiment, approximately 20 mg of sample was placed in an alumina crucible. Thermograms were recorded from ~25 °C to 950 °C at three different heating rates, viz.: 20, 100 and 200 °C/min under nitrogen atmosphere flowing at a rate of 20 ml/min, then kept isothermal for 15 minutes. The end temperature is close to the operating temperature of gasification system. The FTIR spectrometer was set to scan from 4000 cm⁻¹ to 550 cm⁻¹ at a rate of one spectrum every 6 seconds with frequency resolution of 1 cm⁻¹.

4.4 RESULTS AND DISCUSSION

4.4.1 PYROLYSIS UNDER NITROGEN

The TGA-FTIR results for the different biomass which were tested under a nitrogen atmosphere are discussed below.

4.4.1.1 BAMBOO MATERIAL

The TGA along with the corresponding differential thermogravimetric (DTG) curves for bamboo at heating rates of 20, 100 and 200 °C/min are shown in Figure 27 and Figure 28.

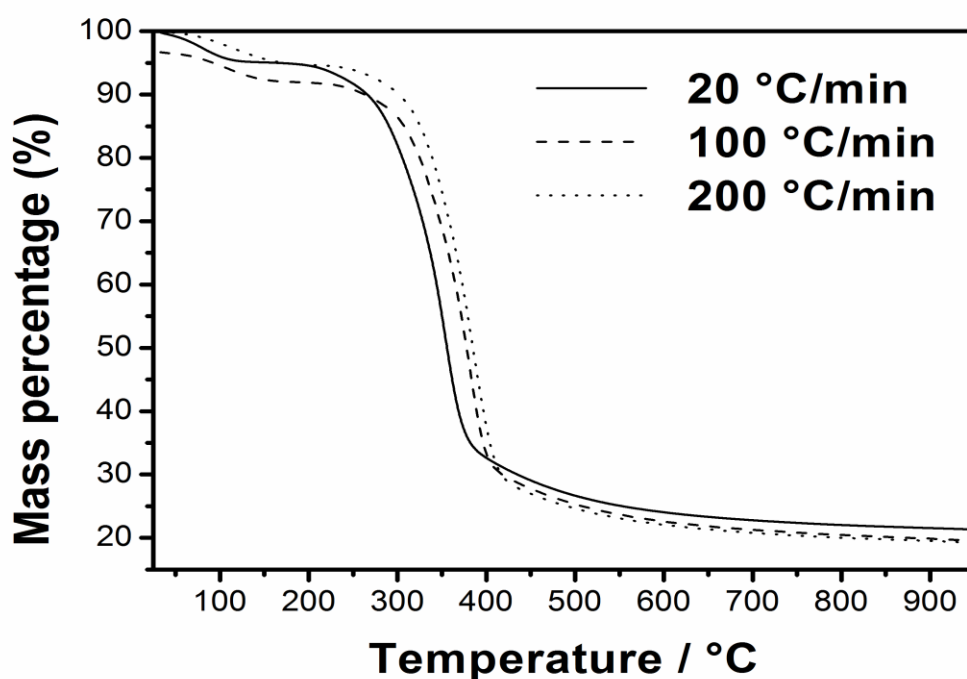


Figure 27. TGA curves of bamboo at 20, 100 and 200 °C/min under nitrogen.

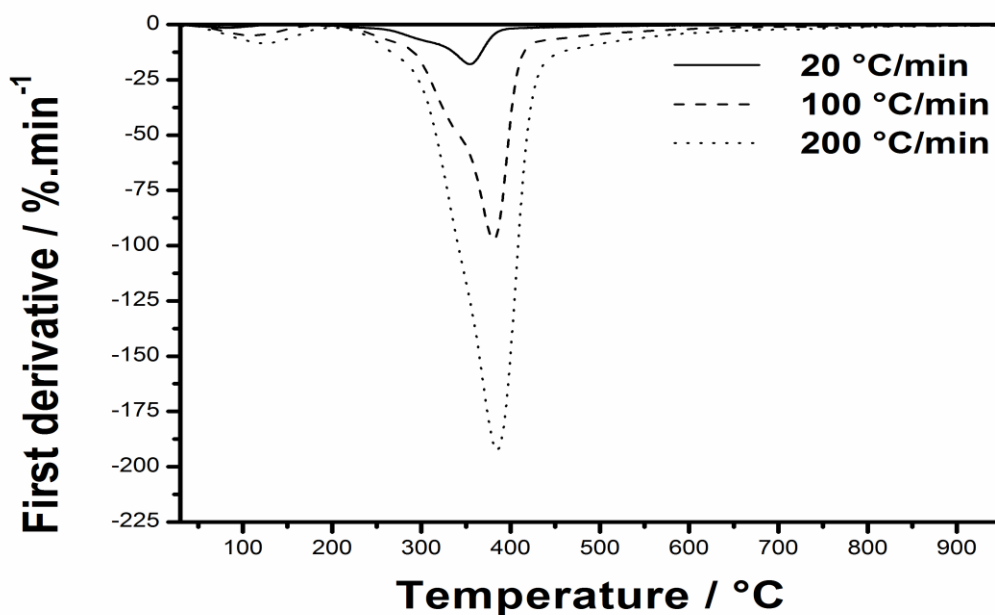


Figure 28. First mass derivative (DTG) curves of bamboo heated at 20, 100 and 200 °C/min under nitrogen.

It is clear from the TGA and DTG curves that the bamboo decomposition follows the trend of a typical biomass pyrolysis experiment as shown in Figure 29 (Gašparovič et al., 2010).

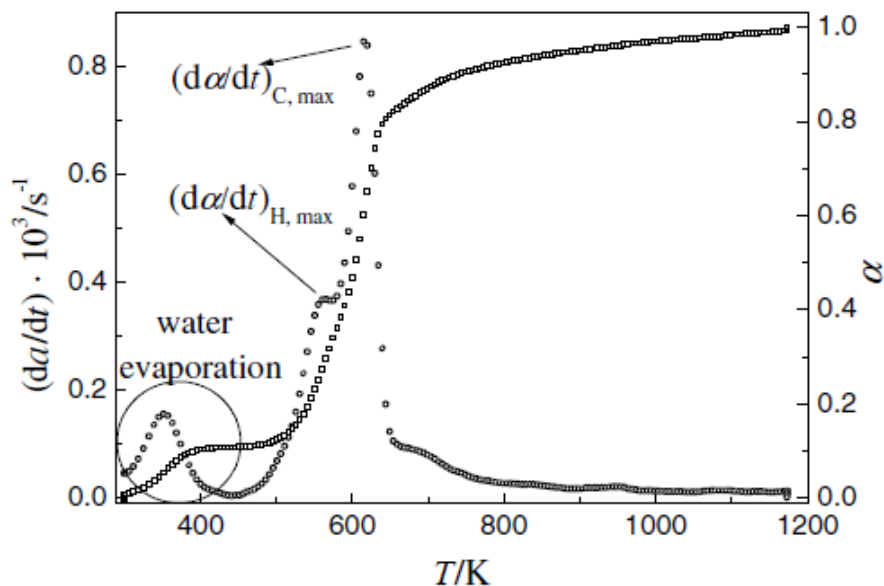


Figure 29. Typical TGA and DTG analysis for biomass material (Gašparovič et al., 2010).

The pyrolysis of biomass material occurs in three stages as indicated by the point of inflection.

This is due to the decomposition of its three main components, viz. hemicellulose, cellulose and lignin (Yang et al., 2007). The first stage is predominantly dehydration, occurring at temperatures below ~ 200 °C for bamboo (Figure 27 and Figure 28). The dehydration temperatures differ for each heating rate. The maximum dehydration temperatures was 81 °C for a heating rate of 20 °C/min, 110.7 °C for the 100 °C/min and 123.4 °C for 200 °C/min (Figure 28). The maximum dehydration rates were 1.417, 4.918 and 8.828 wt %/min for the 20, 100 and 200 °C/min respectively.

The second stage comprises active pyrolysis. The decomposition of hemicellulose and cellulose stages are grouped together in this stage. The hemicellulose decomposition takes place first (mainly in the temperature range 220-315 °C) followed by the decomposition of the cellulose between 314-400 °C (Yang et al., 2007; Gašparovič et al., 2010; Mui et al., 2008). The hemicellulose decomposition of the bamboo material is indicated by the slight shoulder in the DTG curve in Figure 28 (which is similar to that in Figure 29). This shoulder is clearly visible for the heating rates of 20 and 100 °C/min. The decomposition temperatures obtained in this case fall within temperature ranges mentioned in the literature; but it was noticed that as the heating rate was increased so did the temperature range of decomposition.

The shoulder in the DTG curves for bamboo ranged fell in the range 250-312 °C for the heating rate of 20°C/min and 280-348 °C for the heating rate of 100°C/min. This shoulder which is associated with hemicellulose decomposition was not visible at the heating rate of 200 °C/min. Instead a sharp smooth peak was obtained at temperatures between 290 and 440 °C. This sharp curve is associated with the decomposition of the cellulose and it can be said to be the maximum decomposition rate for the whole material. The maximum decomposition temperatures (maximum peak associated with cellulose decomposition) for the 20 and 100 °C/min were 353.7 °C and 380.67 °C respectively. The maximum decomposition rates obtained were 17.9, 97.4 and 192 %/min for the heating rates of 20, 100 and 200 °C/min respectively.

The third stage is termed passive pyrolysis. Lignin (which is more thermally stable) decomposes here, in a wide range temperatures from 160 to 900 °C (Yang et al., 2007). Based on the temperature range at which lignin is said to decompose, it is clear that it decomposes in both active and passive pyrolysis regions but without noticeable peaks (Slopiecka et al., 2012). It is during this stage that the final weight conversion happened at a rate between 1.84 and 1.57

%/min for the heating rate of 20 °C/min, 7.9 and 0.166 %/min for the 100 °C/min and 19.9 and 0.400 %/min for the 200 °C/min.

4.4.1.1.1 EFFECT OF HEATING RATE

The heating rate is known to have an effect on the process. This is observed in Figure 27 & Figure 28. As the heating rate increases the curve shifts towards high temperatures. Hence the dehydration temperature obtained at a heating rate of 200 °C/min was higher than that at 20 and 100 °C/min. The heating rate also affects the start and the end temperatures of each stage (i.e. dehydration, active and passive pyrolysis stages). In short it can be concluded that as the heating rate was increased, firstly the TGA curve shifted towards high temperatures, secondly the maximum decomposition rate increased and finally the conversion increased (though the deference in conversion was slight for the heating rate of 100 and 200 °C/min). The shift of the curves towards high temperature is explained on the basis of heat transfer limitation. For low heating rates, more time is available for the sample to reach thermal equilibrium. It should also be noted that the temperature is measured below the sample holder, not in the sample. Thus a small difference between the recorded and the actual temperature is expected. The difference is greater for faster heating rates. In addition chemical kinetic effects are more pronounced at slower heating rates. These effects cause the curves to shift to the right (Slopiecka et al., 2012). The effect of the heating rate on gases released is discussed on the next section.

The char residues which remained were found to be 21.5, 19.6 and 19.4 % for the 20, 100 and 200 °C/min (Figure 28). Thus it can be concluded that higher pyrolysis rates lead to more effective gasification.

4.4.1.1.2 FTIR RESULTS

An inline FTIR instrument was used to analyse the gases released during pyrolysis. Ideally the main product of the gasification process should be hydrogen (H₂) and carbon monoxide (CO) with some carbon dioxide and hydrocarbons like methane. The TGA characterisation experiments does not correspond exactly with what is happening inside a gasifiers. It merely gives an indication as to what to expect. Therefore gases released during TGA experiments are not exactly what will be released during our plasma gasification.

Figure 30, Figure 31 and Figure 32 shows the FTIR spectra (4 spectra per heating rate) for bamboo. The first graph for each heating rate (82 °C for 20 °C/min, 107 °C for 100 °C/min and 117 °C for 200 °C/min) correspond to the dehydration stage. It can be seen from each spectrum that mostly water peaks appear here. There are noticeable water peaks at wave numbers of ~ 3600 and 1500 cm^{-1} . These peaks validate what was observed from the TGA results discussion (water evaporation during the first stage of the decomposition process as seen in the DTG curves Figure 28). The effect of heating rate is observed here as well. The higher the heating rate, the higher the observed dehydration temperatures and the higher the absorption units of the peaks including that of carbon dioxide which was observed at this stage at a wave number of 2380 cm^{-1} . It is considerably smaller than the other CO_2 peaks obtained during active pyrolysis (especially during higher heating rates). During active pyrolysis, the CO_2 peak is immediately noticed (second and third spectrum from different heating rates). A second CO_2 peak is observed at a wavenumber of 670 cm^{-1} . The other noticeable peak at 1800 cm^{-1} belong to aldehydes. Though it is relatively small compared to other peaks, the carbon monoxide peak (which is the peak of interest) is observed during active pyrolysis at wave number 2150 cm^{-1} .

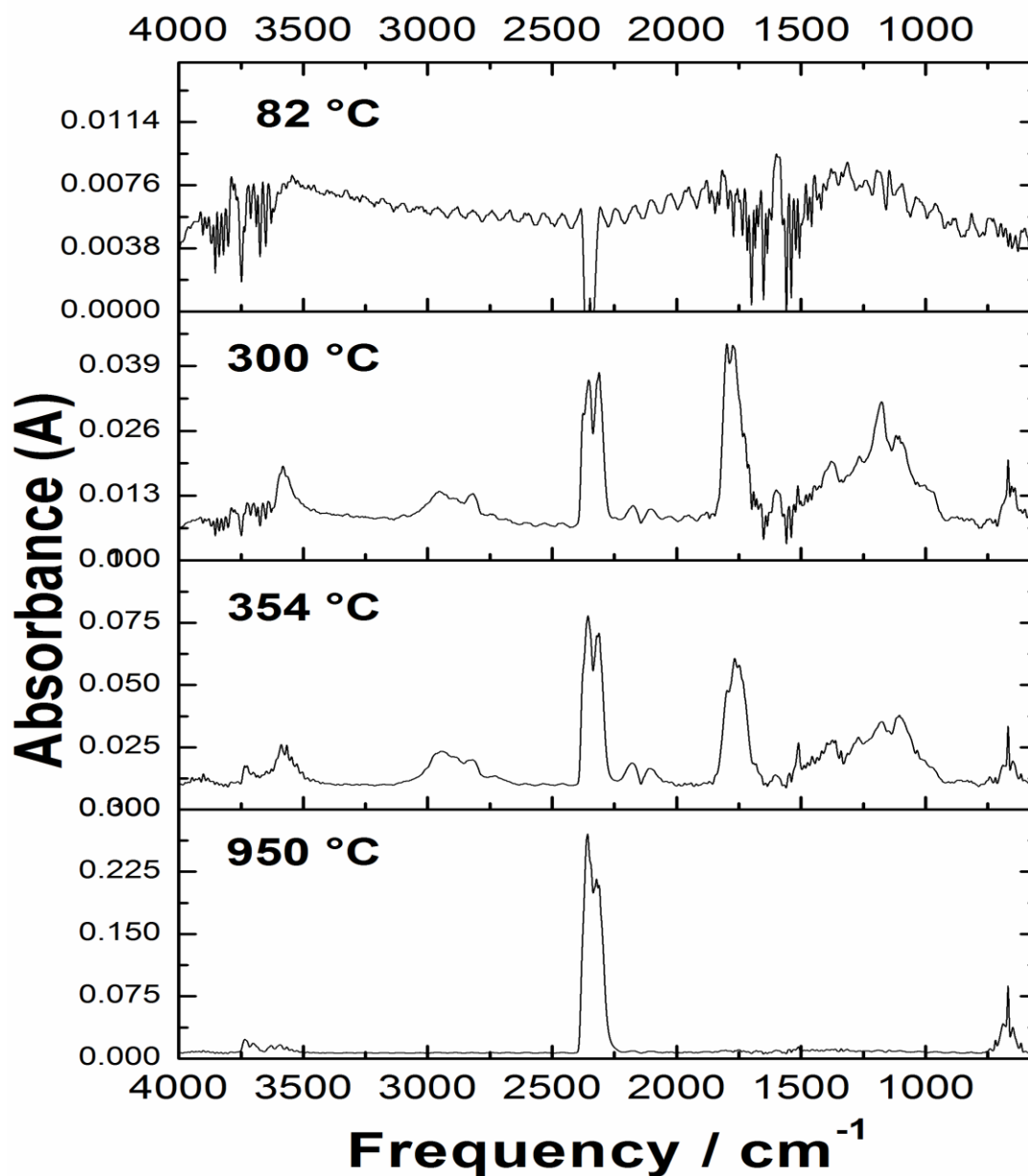


Figure 30. FTIR spectra of bamboo heated at 20 °C/min under nitrogen.

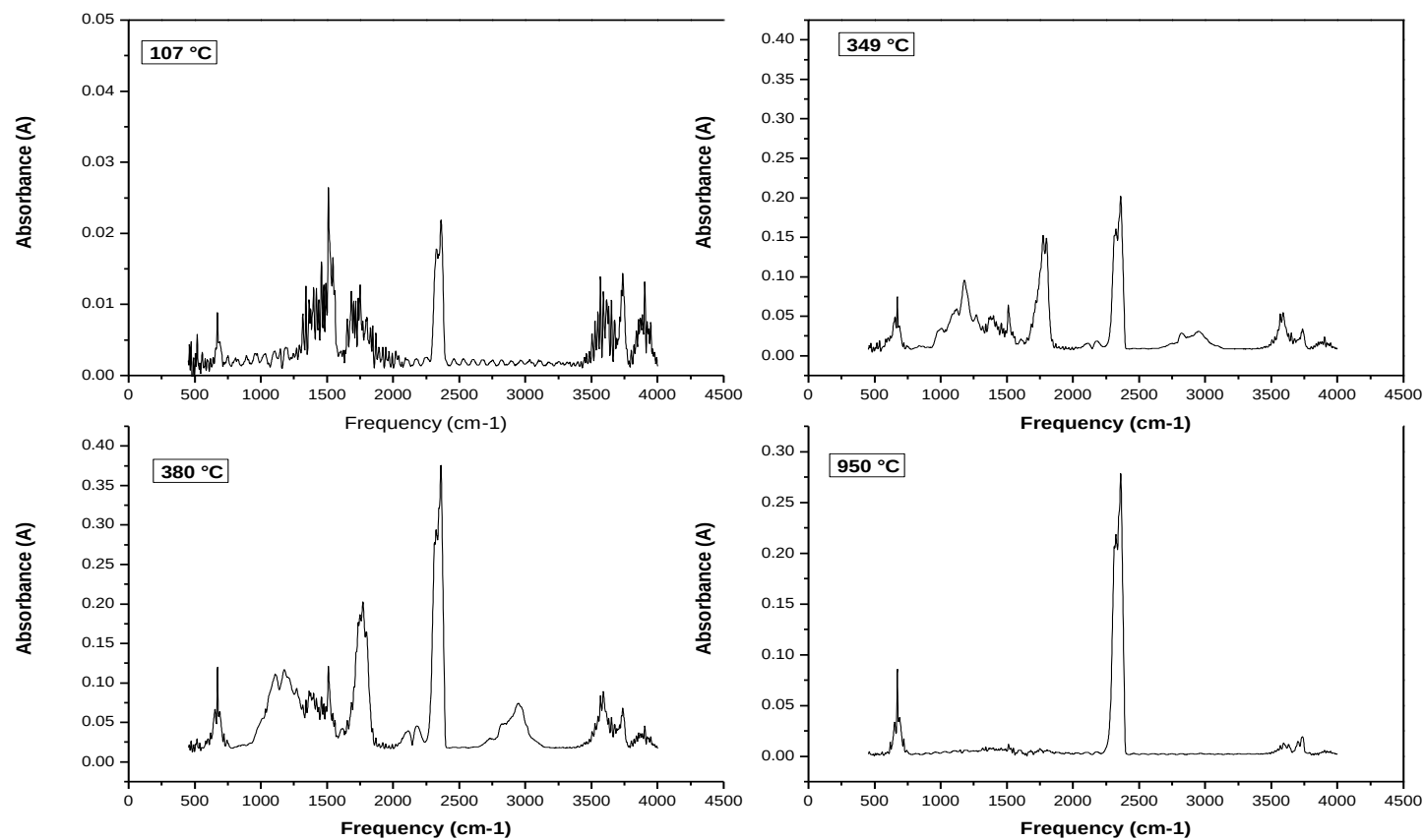


Figure 31. FTIR spectra for bamboo heated at 100°C/min under nitrogen.

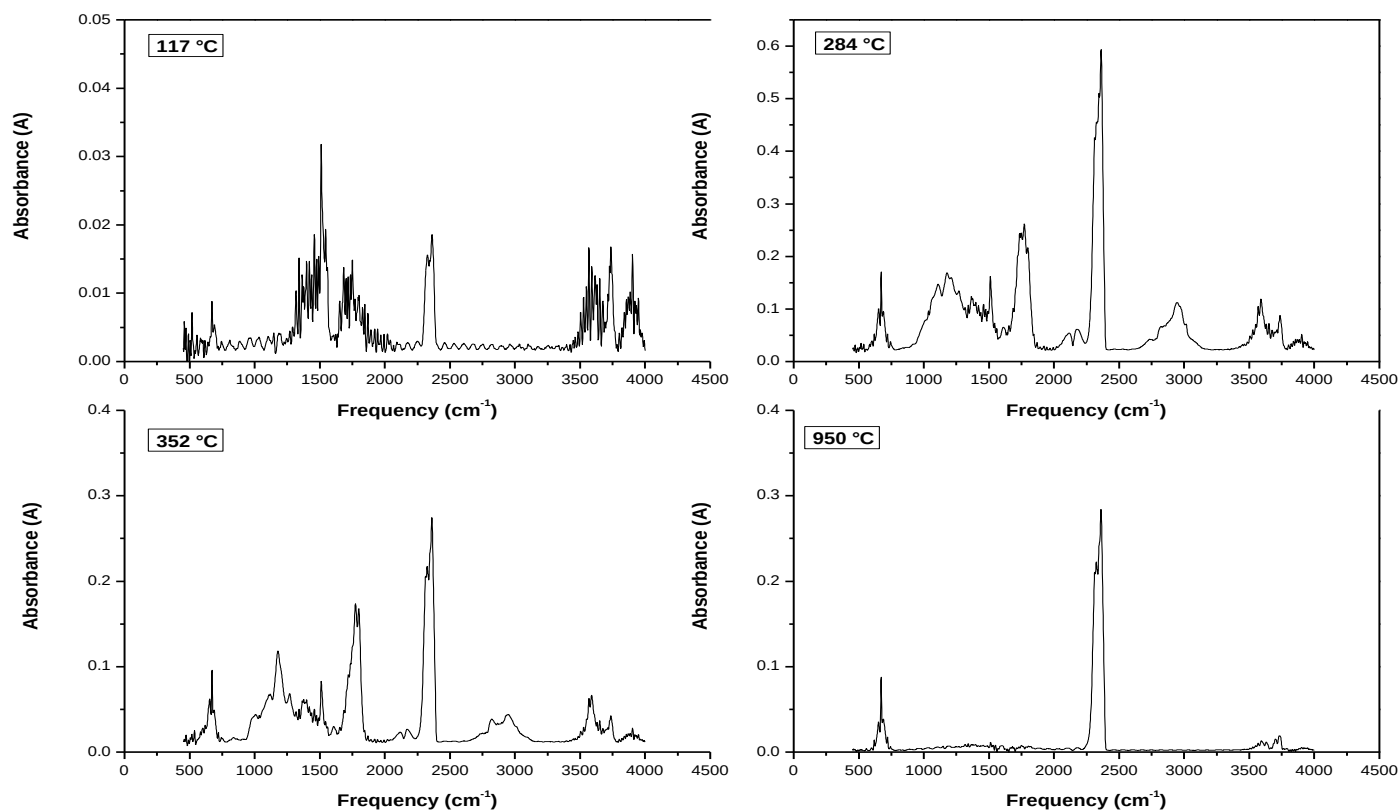


Figure 32. FTIR spectra of bamboo heated at 200°C/min under nitrogen.

A methane peak was clearly observed at 3000 cm^{-1} while other group of alkanes were observed at 1200 cm^{-1} . Methane and other hydrocarbons are known to be the main product of fast pyrolysis operated at temperatures up to $500\text{ }^{\circ}\text{C}$ with short residence time ($\sim 1\text{ sec}$). Therefore their presence during the TGA decomposition of biomass material is expected.

As mentioned earlier, the heating rate also affects the peak quantities of the gases released. The high the heating rate, the higher the peaks. For examples, the CO_2 peak has an absorption unit of up to 0.09 for the $20\text{ }^{\circ}\text{C}/\text{min}$, 0.4 for the $100\text{ }^{\circ}\text{C}/\text{min}$ and up to 0.6 for the $200\text{ }^{\circ}\text{C}/\text{min}$. This is expected as at slower heating rates there is more time for the evolving gases to pass through the gas line and lower concentrations will be observed.

4.4.1.2 COMPARISON BETWEEN FOUR MATERIALS

The TGA-FTIR results for pine tree, peach pips and Napier grass are shown in the Appendix A. The behaviour of these materials during pyrolysis is similar to that of bamboo discussed above, but with noticeable difference.

The maximum decomposition rates obtained during active pyrolysis for the heating rate of $20\text{ }^{\circ}\text{C}/\text{min}$ is 12.5, 17.9, 18.9 and $19.6\text{ wt \%}/\text{min}$ for peach pips, bamboo, Napier grass and pine wood respectively. The pine tree showed to have high decomposition rate as compared to the other three materials. The same trend happened under $100\text{ }^{\circ}\text{C}/\text{min}$. Pine tree had the highest decomposition rate of $99.5\text{ wt \%}/\text{min}$ while peach pips had the lowest decomposition rate of $66.85\text{ wt \%}/\text{min}$. However when the heating rate was increased to $200\text{ }^{\circ}\text{C}/\text{min}$ Napier grass seemed to decompose at the fastest rate of $266.8\text{ wt \%}/\text{min}$ as observed in Figure 34.

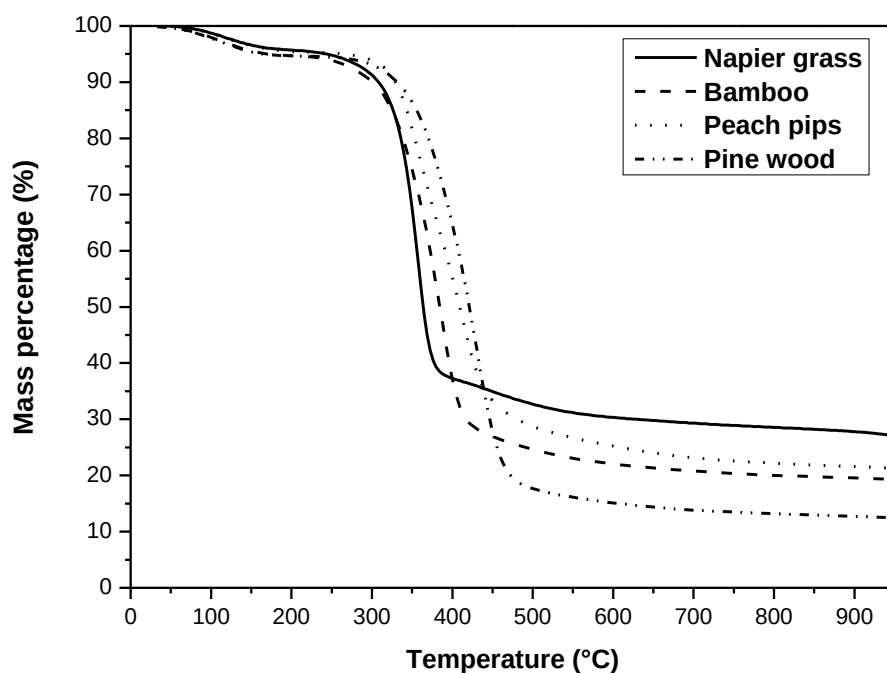


Figure 33. TGA of Napier grass, pine wood, bamboo and peach pips heated at 200 °C/min under nitrogen.

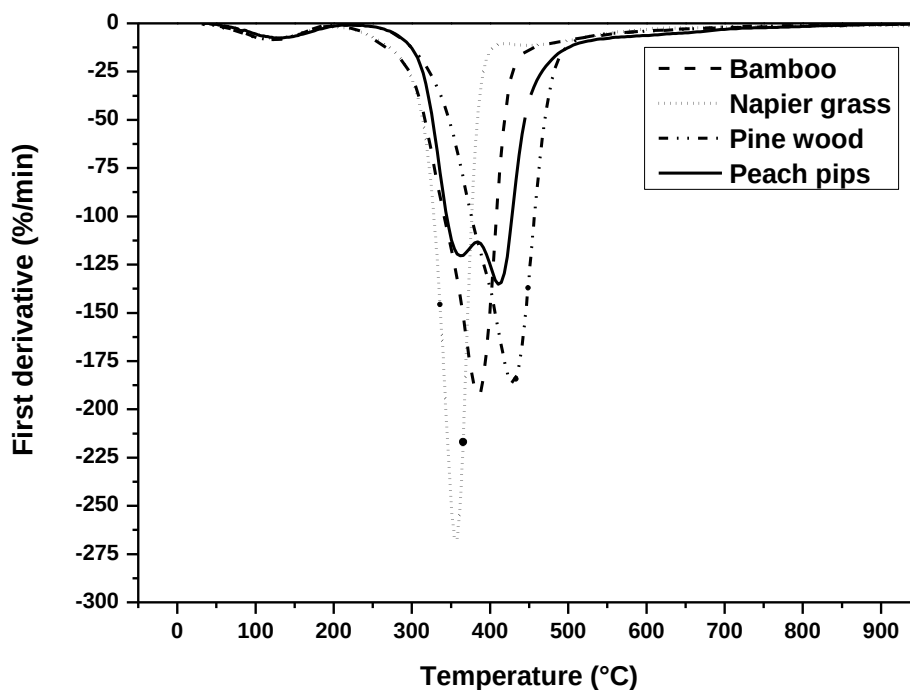


Figure 34. DTG of Napier grass, pine wood, bamboo and peach pips heated at 200 °C/min under nitrogen.



Although Napier grass decomposed at a fastest rate, it had low conversion (Figure 33). The residues remaining at the end of the process were 12.4, 19.5, 21.2 and 26.6 weight percentage for pine, bamboo, peach pips and Napier grass respectively. These conversion correspond to those in the literature for most biomass materials under nitrogen atmospheres (Kumar et al., 2008).

The same heating rate effect that was observed on bamboo was also observed on the other three materials. At high heating rates higher conversion was achieved and the materials decomposes at a faster rate. However it should be noted that some materials decompose faster than the others as discussed above.

The FTIR spectra (shown in the Appendix A) for the other three materials show similarities to FTIR spectra of bamboo. At low temperatures (the first stage of pyrolysis) the volume of volatiles released were low. As the temperature is increased, the peaks height start to increase, resulting in clearer and sharper peaks. Even though the peak heights at low temperatures are small, the water peaks can still be identified in all materials. As discussed previously, this stage is due to dehydration, hence water peaks are expected. The peak identifications are discussed in detail under the discussion of bamboo material in Section 4.5.

4.4.2 OXYGEN ATMOSPHERES

4.4.2.1 TGA AND DTG RESULTS OBTAINED UNDER OXYGEN

As mentioned earlier, results obtained from TGA characterisation were used as a guideline as to what to expect when gasifying the biomass in a plasma system. The same four material studied previously were also characterised in a TGA-FTIR instrument under oxygen. The conditions were kept the same as under nitrogen atmospheres. The analyses were also done at three different heating rates namely 20, 100 and 200 °C. The resulting TGA and DTG curves are shown in the Appendix C, D, and E.

Figure 35 and Figure 36 compare the TGA and DTG results for pine, bamboo, Napier grass and peach pips at a heating rate of 200 °C/min under oxygen atmospheres.

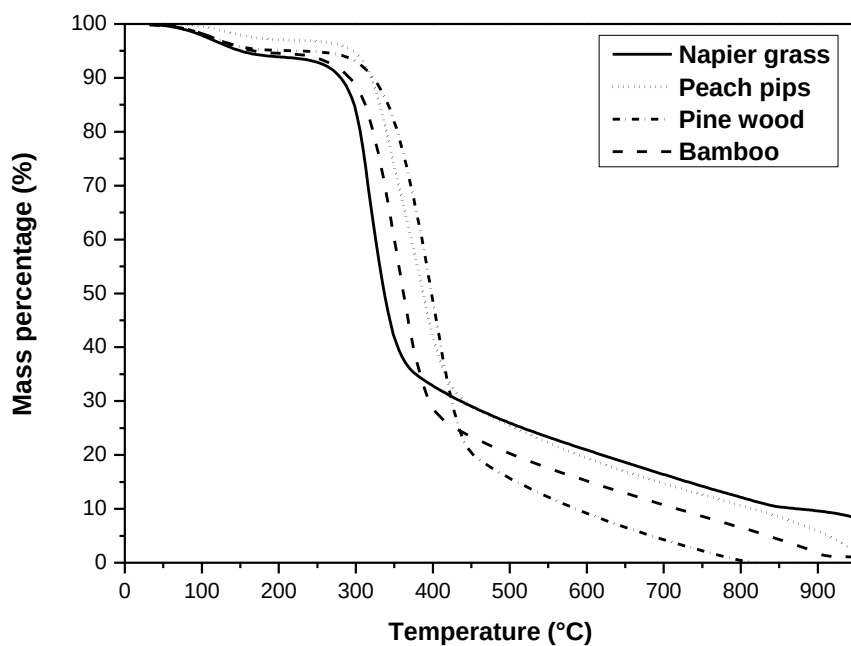


Figure 35. TGA of Napier grass, pine wood, bamboo and peach pips at a heating rate of 200 °C/min under oxygen.

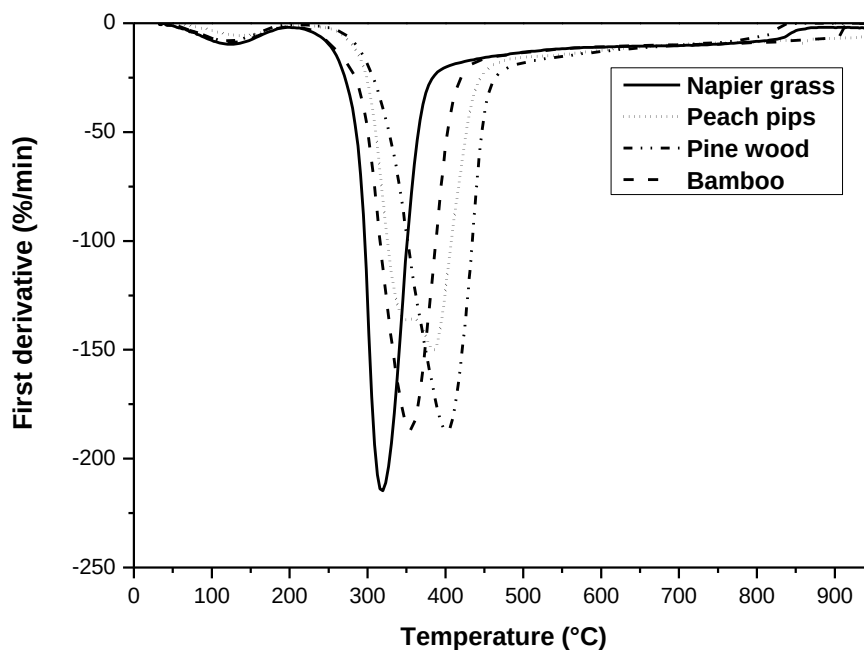


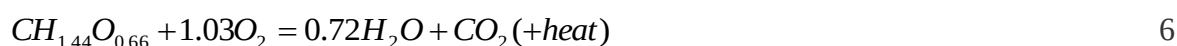
Figure 36. DTG of Napier grass, pine wood, bamboo and peach pips at a heating rate of 200 °C/min under oxygen.

It is observed from Figure 35 that the conversion achieved under oxygen is high compared to that under nitrogen; obviously since combustion now takes place. For all materials conversion was above 90 %. Napier grass was still found to have low conversion (~92.8%) compared to the other three materials. Pine tree was found to have the highest conversion (~99 %) followed by peach pips (~98.8 %) and bamboo (~98 %). Napier grass was still decomposing at a highest rate when compared to other materials (Figure 36).

The effect of the heating rate observed under oxygen is the same as under nitrogen. The TGA curves shifted towards high temperatures as the heating rate was increased. However, the effect of heating rate on conversion was not significant. If one wanted to make a distinction it could still be noticed that the residues remaining after pyrolysis were a little bit less for the heating rate of 200 °C/min compared to other heating rates (i.e 20 & 100 °C/min). The decomposition rate also increased as the heating rate increased. The decomposition rate achieved at a heating rate of 200 °C/min were 214.7 %/min for Napier grass, 187.5 %/min for pine, 186.8 %/min for bamboo and 149.9 %/min for peach pips.

4.4.2.2 FTIR RESULTS OBTAINED UNDER OXYGEN ATMOSPHERES

In Chapter two pyrolysis was defined as a thermal decomposition occurring in the absence of oxygen. Once the organic material decomposes in the presence of oxygen the process is called combustion and the product of combustion is water and carbon dioxide according to this reaction of a typical biomass sample (Equation 6).



Once the biomass is partially combusted the process is called gasification and the resulting products are mainly a mixture of carbon monoxide and hydrogen, referred to as syngas. When the TGA analysis is conducted under oxygen, the amount of oxygen is not controlled according to the gasification stoichiometry. The FTIR results (Figure 37 to Figure 40) shows that the resulting products during TGA experiment under oxygen is mostly carbon dioxide at wave number ~2380 and ~670 cm⁻¹) and water (at wave number ~3600 and ~500 cm⁻¹). This is observed especially as the operating temperature increases. However peach pips material behaved differently for identical gas flow rates. Other pyrolysis gases (discussed in Section 4.4.1) are more visible in the FTIR results for peach pips (Figure 40).

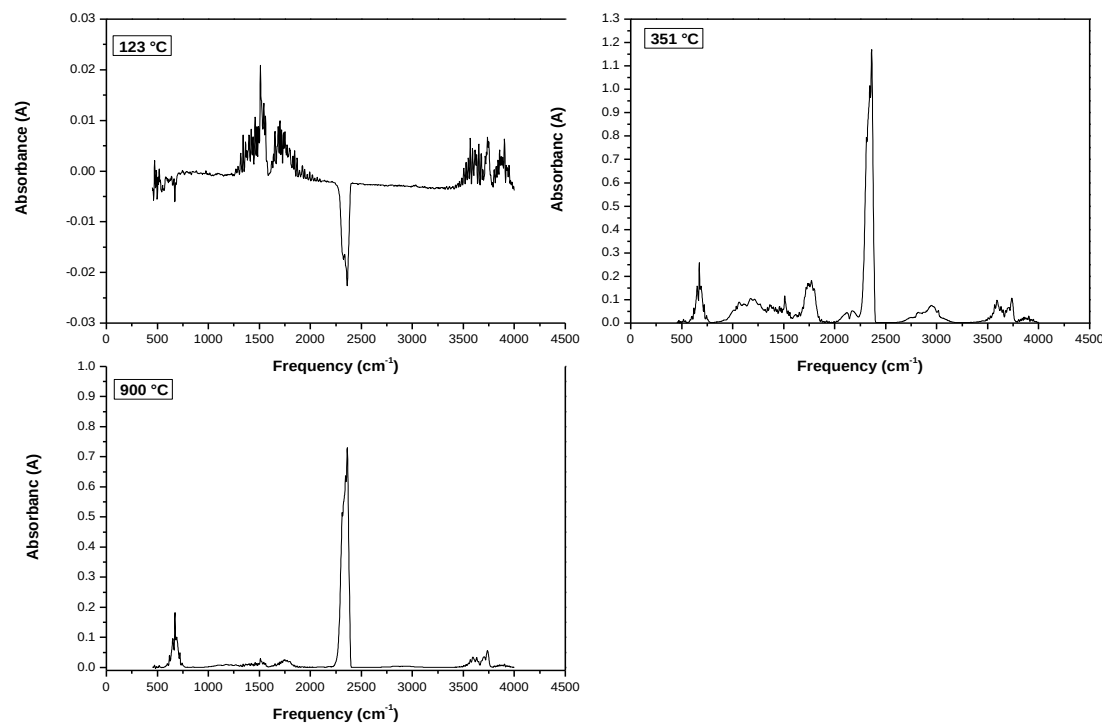


Figure 37. FTIR spectra of bamboo at a heating rate of 200 °C/min under oxygen.

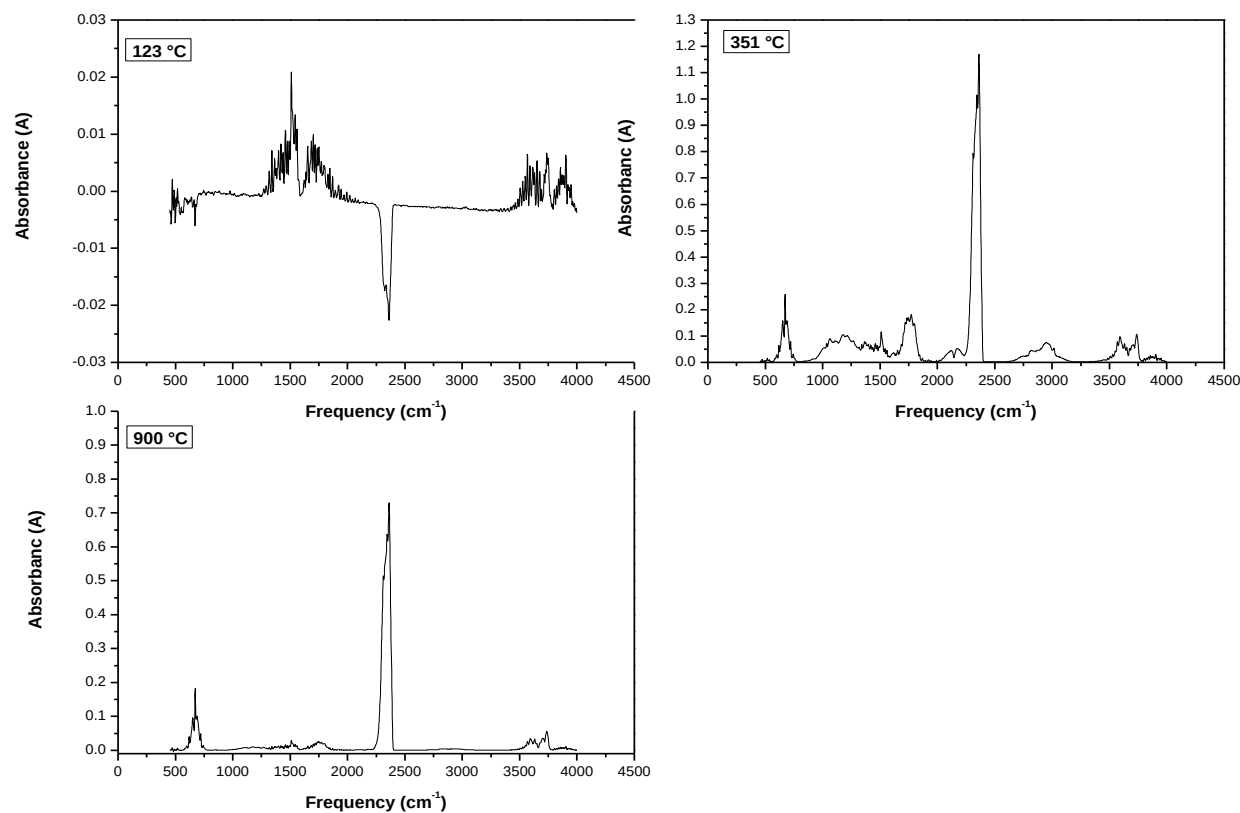


Figure 38. FTIR of pine wood at 200°C/min under oxygen.

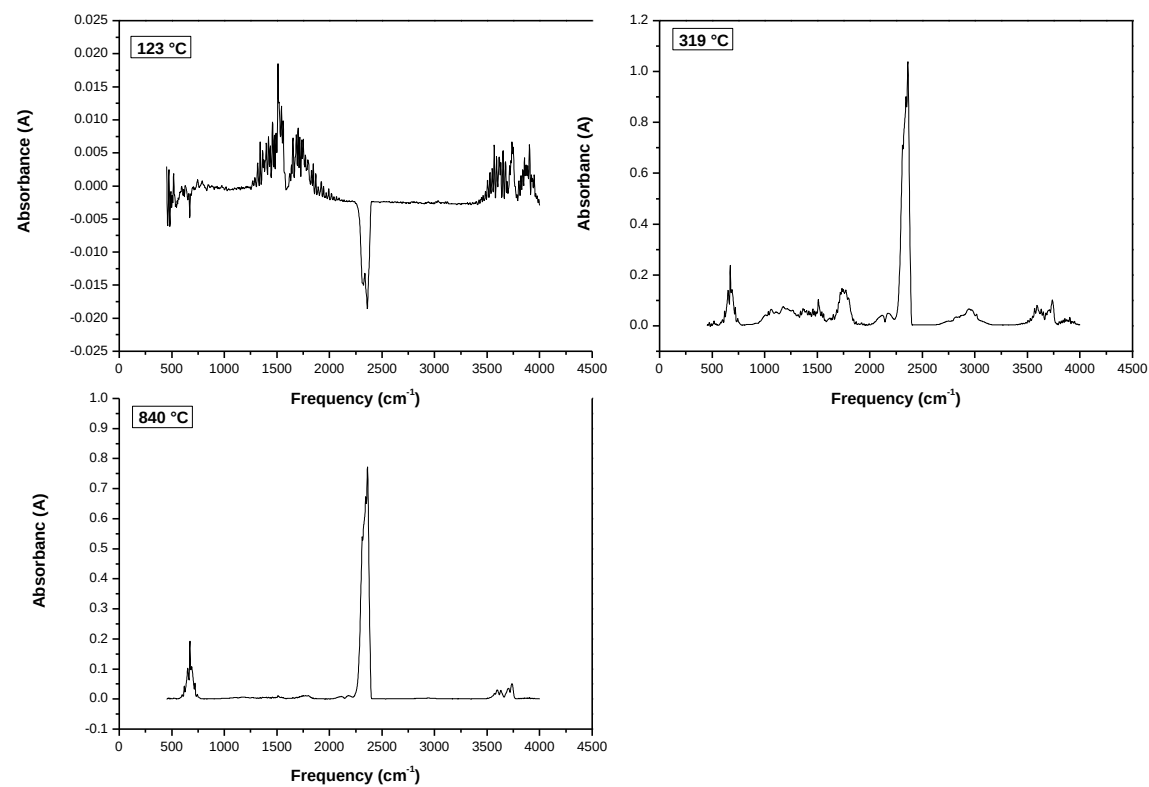


Figure 39. FTIR spectra of Napier grass at a heating rate of 200°C/min under oxygen.

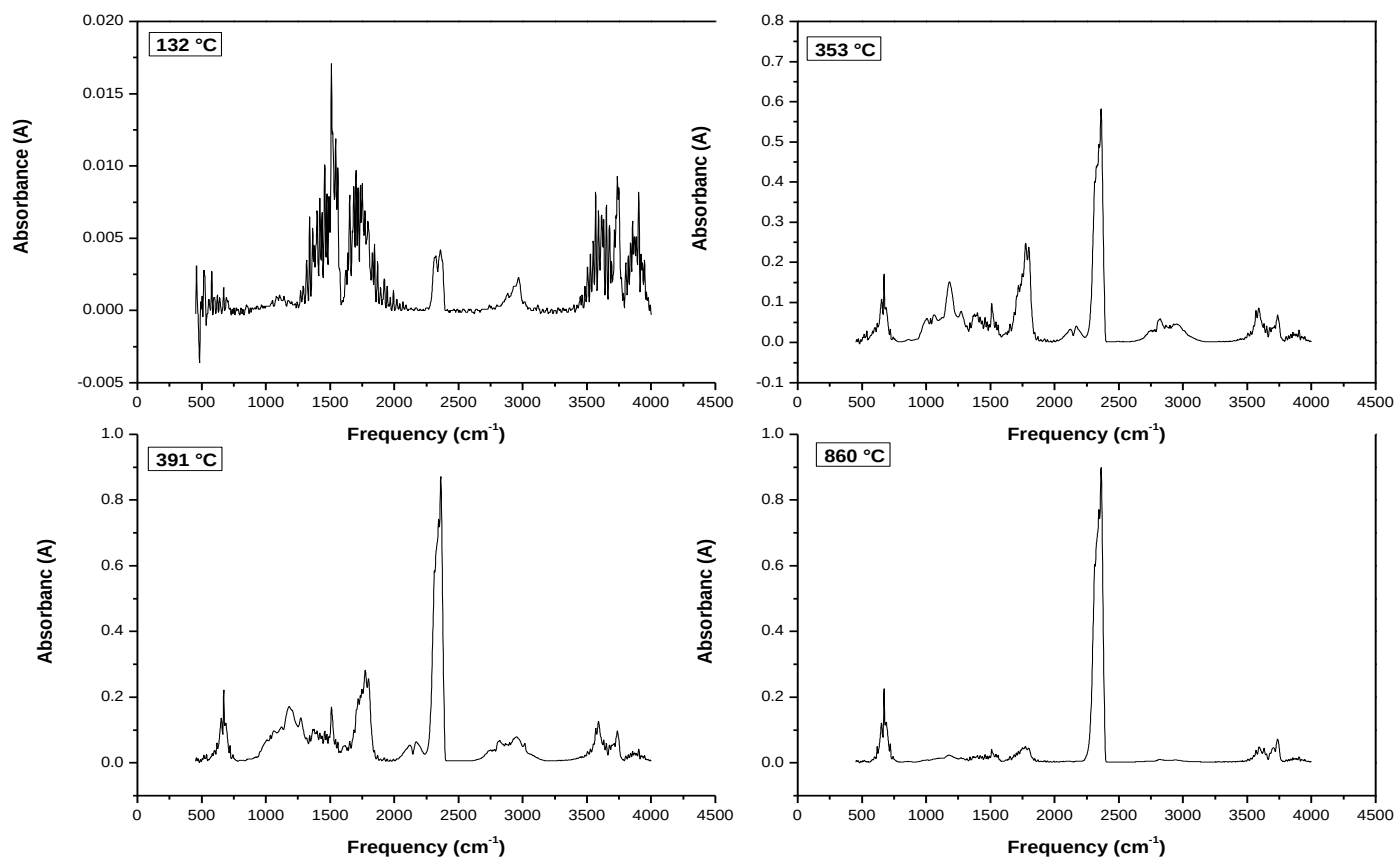


Figure 40. FTIR spectra of peach pips at a heating rate of 200°C/min under oxygen.

4.4.3 KINETIC MODEL DEVELOPMENT

The kinetic parameters can be calculated using either model fitting or model-free (isoconventional) methods (Khawam and Flanagan, 2006). The isoconventional method is widely used in the field of biomass pyrolysis due to its ability to calculate activation energy values without model assumptions (Gašparovič et al., 2010; Wongsiriamnuay and Tippayawong, 2010; Vyazovkin and Wight, 1999). Model-free methods require a set of experimental tests at different heating rates. They do not yield a frequency factor (A), only an activation energy (E_a) (Khawam and Flanagan, 2005). The model fitting method estimates the full kinetic triplet, i.e. the model, its parameters, along with A and E_a . A model fitting method was chosen for this study. The approach taken is as follows (Vyazovkin et al., 2011): The rate can be parameterised in terms of three major variables, i.e. the temperature T , the extent of conversion α , and pressure P according to Equation 7:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) h(P) \quad 7$$

Here t is time and α represent conversion. In most areas of thermal analysis, pressure effects are ignored. Similarly, pressure effects were neglected in this study, and the two-variable form of Equation 8 was used

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad 8$$

The extent of conversion α is defined as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad 9$$

Here m_0 is the initial mass and m_t is the final mass of the sample.

The factor $k(T)$ in Equation 8 is the rate constant; and represents the temperature dependence, expressed by the Arrhenius equation:

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad 10$$

R is the universal gas constant. The model $f(\alpha)$ can in general take three forms, viz.:



accelerating, decelerating, or sigmoidal. In most biomass kinetic studies the reaction model is expressed in term of the deceleration model (Gašparovič et al., 2010; Mui et al., 2008) where the rate has a maximum at the beginning of the process and decreases continually as the extent of conversion increases. Only those kinetic methods that are capable of treating all three types of the conversion dependencies can be regarded as reliable (Vyazovkin et al., 2011). The Sestak-Berggren equation, (Equation 11), which accommodates all three functionalities, is an example of such a model (Brown et al., 2000; Perez-Maqueda et al., 2006).

$$f(\alpha) = \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p \quad 11$$

Here n , m and p are constants. Substitution of Equations 10 and 11 into 8 gives:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p \quad 12$$

Application of the chain rule to the left-hand term of Equation 8, and division by the heating rate, $\beta = dT/dt$, yields

$$\frac{d\alpha}{dt} = \frac{1}{\beta} A \exp\left(\frac{-E_a}{RT}\right) \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p \delta T \quad 13$$

The kinetics parameters can be estimated from Equation 14 by direct fitting of the equation to each thermogram. The rate of expression was found to be mathematically uncomplicated, and a simple Euler integration was used for curve fitting, viz.

$$\alpha_{i+1} = \alpha_i + \frac{1}{\beta} A \exp\left(\frac{-E_a}{RT_i}\right) \alpha_i^m (1 - \alpha_i)^n [-\ln(1 - \alpha_i)]^p \delta T \quad 14$$

Here i refers an individual step along the thermogram. The fitting process comprised computation of model values for each step on the thermogram, for $0.05 < \alpha < 0.95$, and iteratively adjusting the parameters n , m and p , A and E_a to minimize the i.e. the sum of the square of the differences (SSD) between computed and experimental step values.

Biomass pyrolysis was found to be a three-step process, each with its own model and model parameters. In order to handle this three-step process, the procedure above had to be modified. For the Sestak-Berggren equation to fit the model, it was found necessary for α to have a large range of values, as close to 0 - 1 as possible. Each thermogram thus had to be split into three



discreet thermal events, each with its own α , in the range $0.05 < \alpha < 0.95$, defined as:

$$\alpha_i = \frac{m_{0,j} - m_j}{m_{0,j} - m_{0,j+1}} \quad 15$$

The zero subscript refers to the initial value for the j^{th} thermal event.

4.4.3.1 KINETIC COMPUTATION

The kinetic parameters for all the cases investigated are listed in Figure 8 to Figure 11. The extent of conversion for these materials heated at 200 °C/min, for the total reaction as well as for the individual thermal events, is presented graphically in Figure 41 to Figure 44.

Table 8. Kinetic model parameters for the thermal decomposition of peach pips.

Peach pips									
β (°C/min)	20			100			200		
Stages	1	2	3	1	2	3	1	2	3
E_a (kJ/mol)	16.97	20.63	25.80	11.31	13.08	9.91	9.44	12.05	4.43
A (min ⁻¹)	208.78	55.11	50.19	89.89	60.94	20.10	85.59	69.81	27.38
m	0.00	0.05	0.00	0.03	0.05	0.28	0.03	0.05	0.454
n	1.12	1.01	2.19	1.11	0.49	1.84	1.42	0.00	2.12
p	0.46	0.63	0.00	0.61	0.72	0.00	0.68	0.66	0.018
SSD	3.80	3.20	29.70	0.23	0.70	4.31	0.65	0.48	1.57

Table 9. Kinetic model parameters for the thermal decomposition of Napier grass.

Napier grass									
β (°C/min)	20			100			200		
Stages	1	2	3	1	2	3	1	2	3
E_a (kJ/mol)	13.67	23.80	29.13	13.18	15.95	16.214	10.70	12.95	10.7
A (min ⁻¹)	98.04	55.70	44.95	157.80	62.71	21.4	158.44	67.76	21.1
m	0.03	0.50	0.00	0.03	0.05	0.00	0.03	0.05	0.19
n	1.78	0.31	3.64	1.11	0.26	4.24	1.37	0.27	4.57
p	0.57	0.49	0.00	0.56	0.63	0.00	0.73	0.62	0.136
SSD	6.80	4.62	129.81	0.53	1.19	3.74	0.89	1.02	1.44

Table 10. Kinetic model parameters for the thermal decomposition of pine wood.

Pine wood									
β (°C/min)	20			100			200		
Stages	1	2	3	1	2	3	1	2	3
E_a (kJ/mol)	16.41	26.44	19.542	14.84	19.13	56.34	12.83	14.94	9.66
A (min ⁻¹)	210.05	52.40	20.55	267.19	64.99	81884.	238.03	60.95	26.84
m	0.05	0.05	0.00	0.07	0.05	0.00	0.19	0.05	0.00
n	1.19	0.33	2.72	1.00	0.41	3.5	1.03	0.53	2.60
p	0.45	0.47	0.00	0.46	0.54	0.00	0.44	0.61	0.00
SSD	5.47	1.57	27.65	0.50	0.30	1.37	0.27	0.12	1.18

Table 11. Kinetic model parameters for the thermal decomposition of bamboo.

Bamboo									
β (°C/min)	20			100			200		
Stages	1	2	3	1	2	3	1	2	3
E_a (kJ/mol)	13.29	26.81	3.16	11.60	19.12	10.7	10.46	15.14	10.9
A (min ⁻¹)	102.22	57.29	0.34	110.29	69.39	6.92	115.14	76.11	25.4
m	0.03	0.05	0.00	0.03	0.05	0.00	0.03	0.05	0.00
n	2.00	0.21	1.41	1.15	0.32	2.4	1.12	0.39	2.78
p	0.55	0.32	0.00	0.60	0.50	0.00	0.65	0.57	0.00
SSD	11.96	2.97	26.65	6.90	0.59	1.05	0.30	0.29	1.5

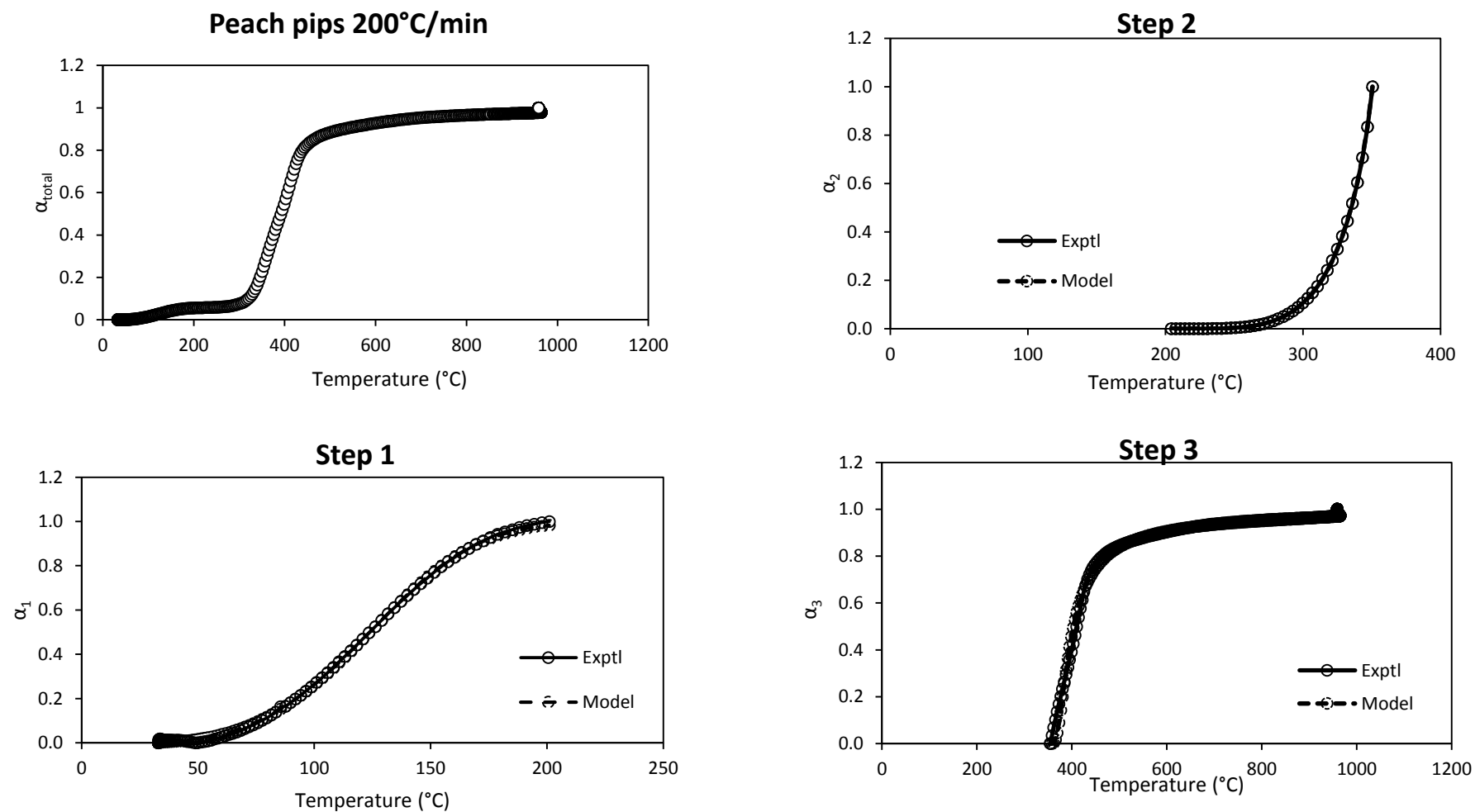


Figure 41. Experimental and predicted α -T curves of peach pips at a heating rate of 200 °C/min under nitrogen atmospheres.

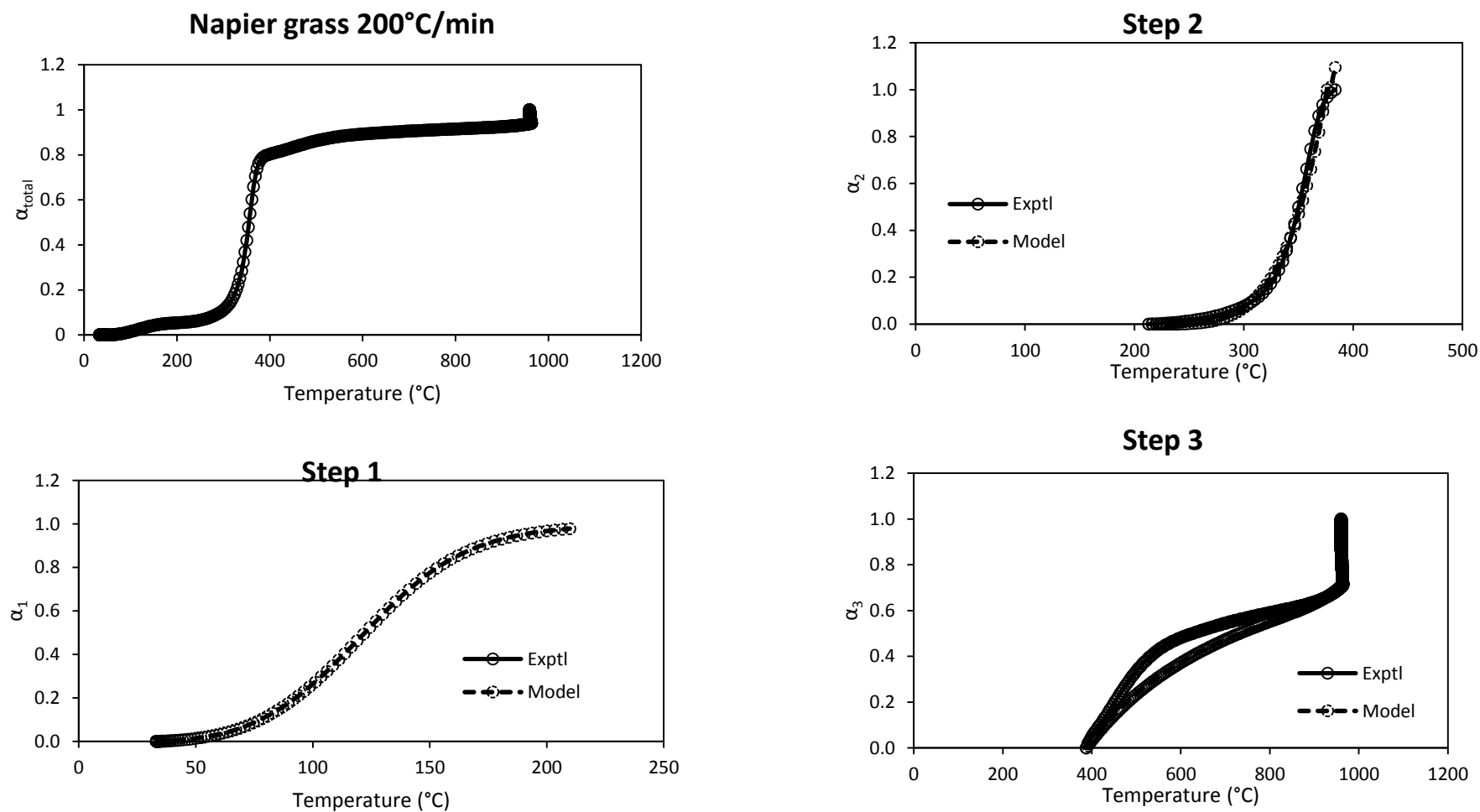


Figure 42. Experimental and predicted α -T curves of Napier grass at a heating rate of 200 °C/min under nitrogen.

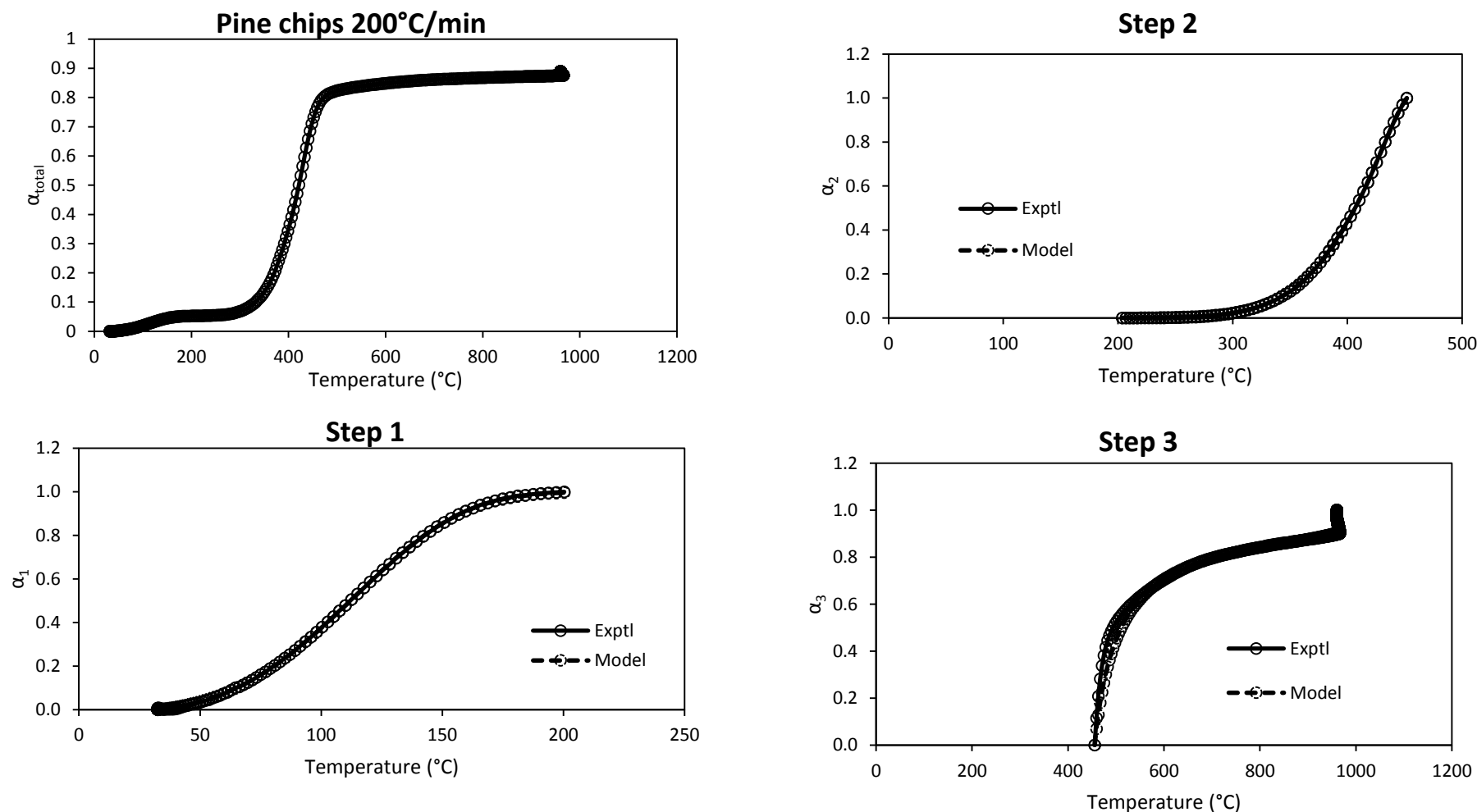


Figure 43. Experimental and predicted α -T curves of pine wood at a heating rate of 200 °C/min under nitrogen.

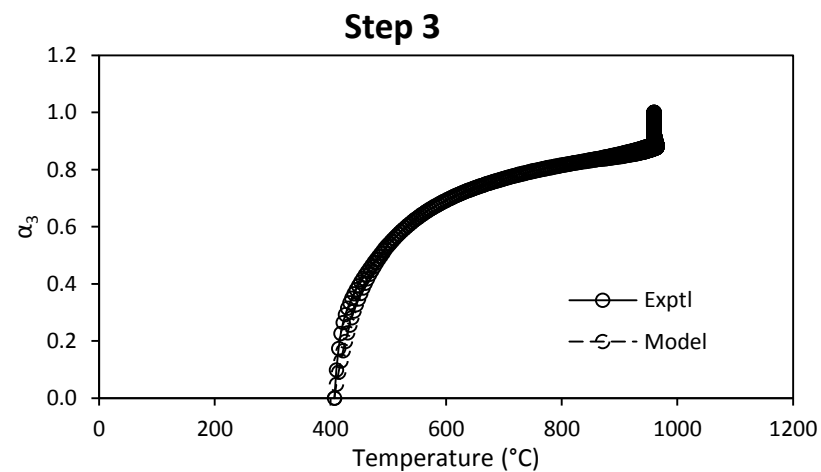
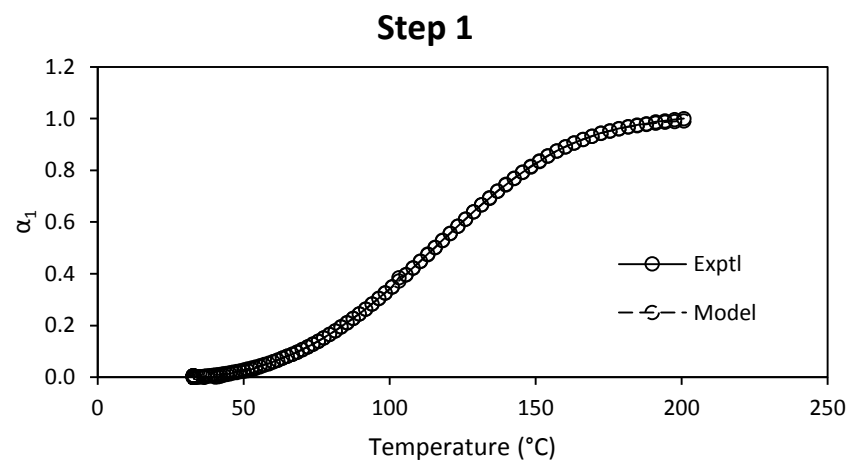
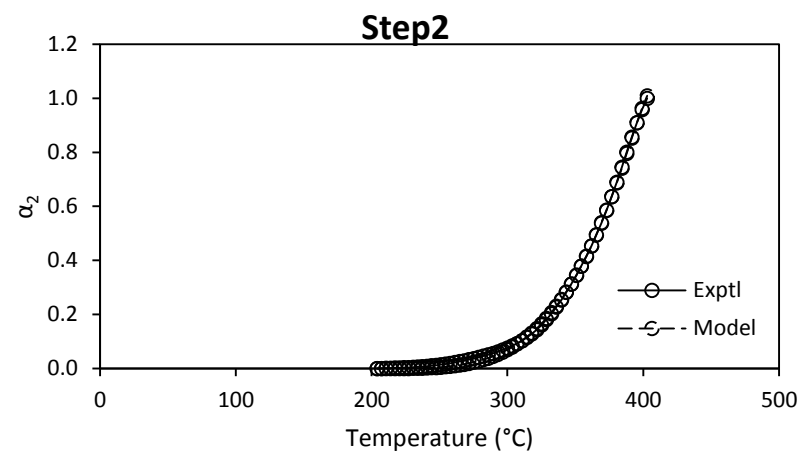
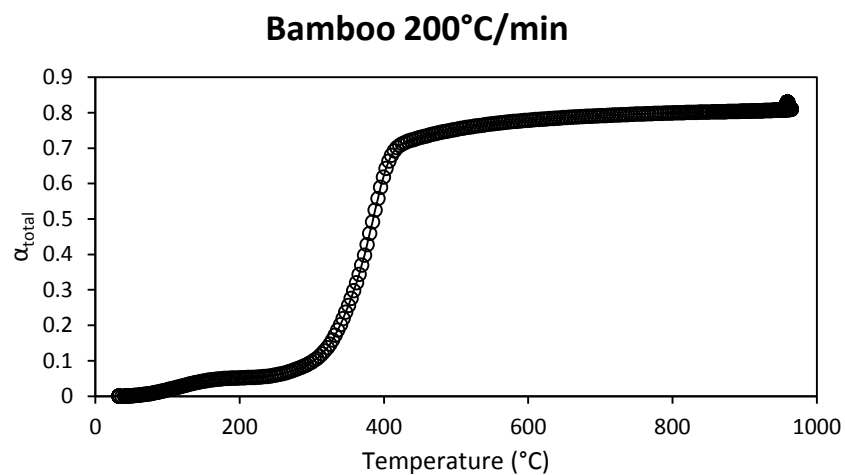


Figure 44. Experimental and predicted α -T curves of bamboo at a heating rate of 200 °C/min under nitrogen.

Visually the model is a reasonable fit in all cases. The trend for the magnitude of the activation energy is that it is smallest for the first dehydration stage, possibly because the event may be driven by heat transfer effects rather than pure chemical kinetics, and that all values decrease as the heating rate increases.

4.5 CONCLUSION

The results indicated that at temperatures above 950 °C, under nitrogen and with a high heating rate (200 °C/min), almost 80 wt % of the bamboo and peach pips materials were converted to gas. The conversion efficiency of pine wood was found to be higher (~ 88 wt %.) while Napier grass was found to have the lowest conversion efficiency of ~ 73 wt %. The low conversion efficiency on Napier grass can be contributed to a higher ash content in most grasses (mostly as silicon compounds). It was observed that the decomposition rate of Napier grass was higher than those of other three materials. As expected, oxygen influenced the pyrolysis process significantly. It was observed that the conversion efficiencies for the 4 samples generally increased with oxygen. The bamboo, peach pips, pine wood results obtained under oxygen (using similar conditions as for nitrogen) indicated that ~ 99 wt % conversion efficiency was achieved. Napier grass was found to have a conversion efficiency of ~ 93 % under oxygen.

Three different heating rates were evaluated. The conversion efficiencies as well as the decomposition rates increased as the heating rate increased.

The DTG curves indicated that in all cases pyrolysis happens in three distinct stages, namely dehydration (at temperatures ~ 120 °C), active pyrolysis (temperatures between 220 and 400 °C) associated with hemicellulose and cellulose decomposition, and finally the passive pyrolysis stage (in a wide temperature range, from 160 to 900 °C) associated with lignin decomposition. FTIR results confirmed this hypothesis. The gases released during active pyrolysis were a high concentration of CO₂ along with small concentrations of CO, CH₄ and aldehydes. The gas released during passive pyrolysis was mainly CO₂. The FTIR results obtained under oxygen indicate that combustion took place. The main products found were CO₂ and H₂O.

5 PLASMA GASIFICATION EXPERIMENTS

A set of biomass plasma gasification experiments were conducted where the effects of operating temperature, feed rate, and the addition of oxygen were tested. Each experimental run lasted for an hour.

5.1 METHOD

5.1.1 MATERIAL PREPARATION

Pine wood chips and peach pips chips (Figure 45 and Figure 46) were prepared for the plasma gasification experiments. The samples were shredded into a homogeneous particle size to enable them to flow through the screw feeder. For the purpose of the ultimate analysis, the materials were milled down to fine powder samples and were subsequently tested. The samples were not dried before analysis.



Figure 45. Pine wood chips



Figure 46. Peach pips

The peach pips were available in the laboratory before the study. Pine chips were generated from standard transporting wooden pallets. Napier grass was received from a local farm in Brits, North West Province, South Africa.

A number of attempts at feeding bamboo was made. The system kept on blocking due to the nature of this material after shredding. The material was found to be very fluffy and therefore most of the sample passed through the gasifier too quickly for adequate gasification. This was probably due to the high turbulence generated by the plasma jet. This material subsequently blocked the quench probe, resulting in pressure build up inside the reactor and ending the

experiment prematurely. This problem was also found when feeding Napier grass. It was concluded that the system was not suitably designed for feeding chipped bamboo and Napier grass. The plasma gasification work was therefore carried out on only two materials, viz. peach pips and pine chips.

5.1.2 ULTIMATE ANALYSIS

A general chemical formula for biomass is $C_xH_yO_z$. In order to determine the values of x, y and z for each material, an elemental analysis (ultimate analysis) was done. The ultimate analysis was done on all four materials at the University of Free State. Although Napier grass and bamboo materials were excluded from the experimental gasification, they were analysed in order to do the theoretical comparative study as explained earlier. Table 12 shows the ultimate analysis of the four materials.

Table 12. Ultimate analysis of four biomass material (molar %)

Biomass	C	H	O*	N
Bamboo	29.87	46.00	24.12	0
Napier grass	27.35	44.00	28.41	0.24
Peach pips	31.9	45.36	22.64	0.08
Pine tree	29.77	46.52	23.71	0

*Oxygen was determined by difference

5.1.3 SCREW FEEDER CALIBRATION

The screw feeder had to be calibrated for each material. When calibrating the materials, a specific mass was loaded into the hopper. There is no specification from the suppliers for the mass for the optimum mass of material inside the hopper for calibration, and for this reason the same mass material was measured for comparative reasons. A bucket was placed at the outlet of the hopper. Initially the speed was set at 15.7 rpm and the screw feeder motor was started. Once the material started to fall into the bucket the timer was started and after 5 min the screw feeder motor and the timer were stopped. The material was weighed and the mass recorded. This process was repeated for three more speed settings, i.e. 24.3, 33.0, and 54.5 rpm. The

recorded mass per time interval was plotted against the screw feeder motor speed (Figure 47 and Figure 48). A linear relationship was found and the fitted equation was then used to calculate a speed setting for a required mass flow rate.

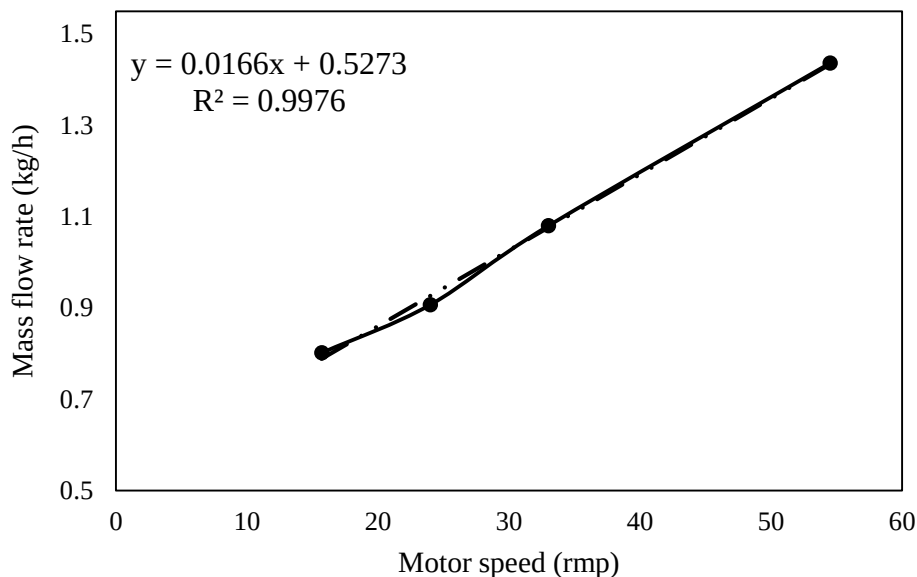


Figure 47. Screw feeder calibration curve for pine wood chips

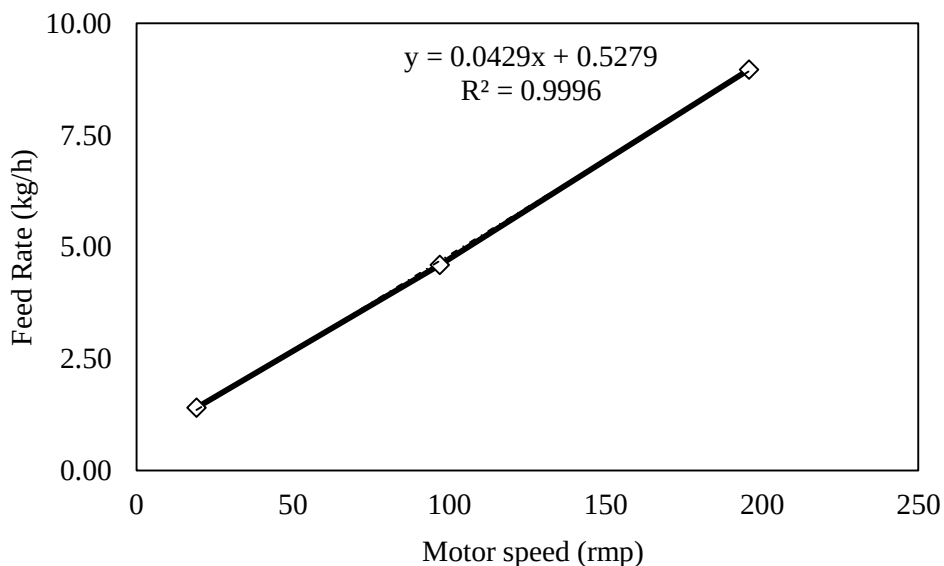


Figure 48. Screw feeder calibration curve for peach pips

5.1.4 LEAK TESTING

The plasma gasification system was tested for any leaks prior to gasification experiments. After filling the hopper with sufficient material for at least three experimental runs, the whole system was tightly sealed to make sure that there were no leaks. The leak test was then done by pressurising the system with nitrogen gas up to a pressure of 1.5 bar absolute. This was above the operating pressure of the system. A pressure drop was monitored for 5 minutes. If there was no pressure drop it indicated that the leak rate was small enough to proceed with experimentation safely. The nitrogen was then flushed out of the system into the building ventilation by opening the isolation valve after the filter (Figure 25).

5.1.5 PLASMA POWER SUPPLY START UP

Prior to starting the plasma power supply, the cooling water was switched on and the water flow was recorded. The supply of the plasma gases into the torch was automatically controlled by the control system of the custom built plasma power supply. The start-up procedures were pre-set into the controller of the power supply. By pressing the start button the start-up phases in Table 13 were automatically executed.

Table 13. Plasma power supply start up procedure

Phase no.	Description
1	This is a purging phase for argon or nitrogen to ensure that the air is flushed out of the plasma torch. This phase lasts for 5 seconds.
2	After purging the lines argon is introduced into the torch for few seconds. The plasma is started during this phase.
3	After the torch is running, stable nitrogen is slowly introduced into the torch while argon is slowly reduced at the same time. An increase in nitrogen and decrease in argon happens in parallel until the argon flow is completely stopped.
4	This is an operating phase. The argon flow is now at zero and the torch operates at a nitrogen flow rate of ~3 kg/h.

The voltage reading depended on the nitrogen flow and is typically between 90 and 100 V. The current setting is determined by the required temperature of experimentation. A significant drop in voltage indicates that the torch is faulty and the experiment would need to be stopped immediately.

5.1.6 BIOMASS FEEDING

It is very important to ensure that the self-cleaning action of the quench probe is working properly before feeding the biomass into the gasifier. If the quench probe is not functioning properly the product gas from the reactor is not be cooled sufficiently and results in a prolonged reaction time which in turn results in the formation of long chain hydrocarbons, not the ideal products for the purposes of this study.

There is a thermocouple installed in the reactor for reactor temperature monitoring. As backup, a Minolta Land Cyclops optical pyrometer was used to monitor the reactor temperature. The pyrometer was focused through a quartz sight glass as described in Chapter 3. Once the reactor had reached the desired operating temperature (900, 1000 and 1100 °C), the biomass material feed was started. The screw feeder was set at a desired speed (the feed rates used were 1.00, 1.25 and 1.50 kg/h) according to the calibration curve for the specific material.

5.1.7 SYNGAS SAMPLING

A sampling station was situated outside the gasification containment area as discussed in Chapter 3. Gas samples were taken every 10 minutes during the course of an experiment. The gas samples were trapped in the U-tubes (Figure 26) and properly labelled. After each experimental run these samples were analysed offline by a gas chromatograph (GC).

5.1.8 GASIFICATION EXPERIMENTAL PROCEDURE

5.1.8.1 TEMPERATURE EXPERIMENTS ON PEACH PIPS

The operating temperature is reported to have a significant influence on gasification processes (Abdoulmoumine et al., 2014; Dufour et al., 2009; Berrueco et al., 2015b; Guo et al., 2014). The volume of syngas is said to increase with an increase in temperature resulting in a decrease in char and tar content. At high temperature the tar cracking reaction (Equation 16) is favoured

which further leads to high conversion to gas with low to no tar production (Berrueco et al., 2015b; Guo et al., 2014; Septien et al., 2012)

$$C_p H_q (tar) = C_x H_y + C + H_2 + CO \quad 16$$

In order to test the effects of temperature on the plasma gasification process, three different operating temperatures were investigated in three different experimental runs. The temperatures were 900, 1000 and 1100 °C. It should be noted that these are the initial reactor temperature before feeding. During the experimental run the glass hole which was used to monitor the reactor temperature became dark making it difficult read the temperature using a pyrometer (the actual temperature readings are shown in Table 14). During experimentation the reactor temperature was the only variable, with a constant feed rate of 1.25 kg/h and a constant equivalence ratio (defined as the ratio of actual oxidant supplied to stoichiometric oxidant required for complete combustion, on a dry ash free (daf) basis) of zero. In most studies the effect of temperature is tested with an ER between 0.25 and 0.3. The electrical power input into the plasma torch to reach a reactor temperature of 900, 1000 and 1100 °C were 12.7 ± 1.4 , 12.8 ± 1.8 and 13.3 ± 2.1 kW respectively.

5.1.8.2 FEEDING RATE EXPERIMENTS ON PEACH PIPS

High feed rates result in high gas yields, but lead to lower gas quality and high tar yield (Guo et al., 2014). In this study the feed rate was evaluated to determine its effect on biomass conversion as well as syngas concentration. Three different feed rates of 1.0, 1.25 and 1.5 kg/h were tested. A feed rate of 1.0 kg/h corresponded to the minimum setting of the feeder. When a feed rate of >1.5 kg/h was used, the feed material filled the plasma reactor, preventing efficient gasification process. Therefore the feed rate tests were limited to this range. The tests were done using a constant temperature of 1000 °C (the initial reactor temperature) with an equivalence ratio (ER) of zero. The residue remaining after every experimental run were measured and compared. The quality of the syngas was also analysed for each experimental run.

5.1.8.3 EQUIVALENCE RATIO EXPERIMENTS ON PINE WOOD CHIPS

The equivalence ratio quantifies the oxygen feed into the process (Guo et al., 2014). It is defined as the ratio of actual oxidant supplied to stoichiometric oxidant required for complete combustion on a dry ash free (daf) basis (Equation 17).

$$ER = \frac{\left[\Phi_{m, oxy} / \Phi_{m, fuel} \right]_{actual}}{\left[\Phi_{m, oxy} / \Phi_{m, fuel} \right]_{stoich}} \quad 17$$

where $\Phi_{m, oxy}$ is the oxygen flow rate and $\Phi_{m, fuel}$ is the biomass flow rate. In general, full gasification occurs at an $ER \sim 0.25$. By way of illustration see point G in Figure 49. The exact temperature value may not be realistic for plasma processes, since the illustration is from general gasification literature.

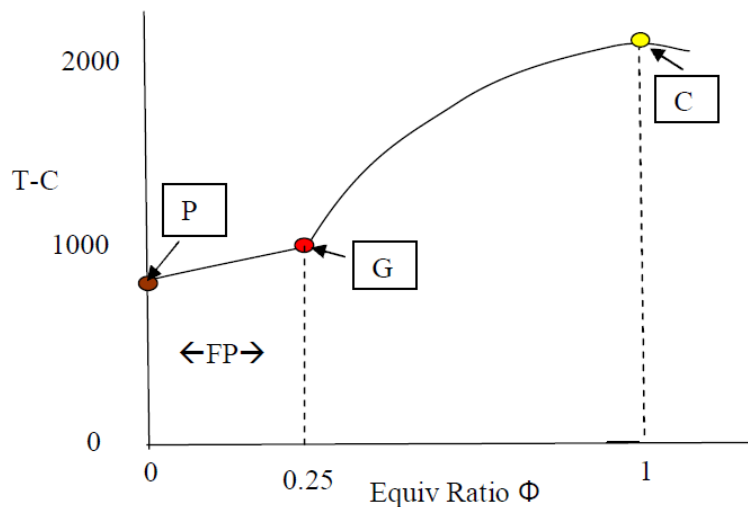


Figure 49. The equivalence ratio diagram (Reed and Desrosiers)

The effect of equivalence ratio on biomass plasma gasification was studied by varying the amount of oxygen flow into the reactor in three sets of experiments. Biomass composition is required when calculating the equivalence ratio. In this case the chemical formula of pine wood was calculated from the ultimate analysis in Table 12 and was found to be $CH_{1.6}O_{0.8}$. The stoichiometric oxygen/fuel ratio was determined from a complete combustion reaction (Equation 18).



From Equation 18, one mole of oxygen is required for every formula unit of pine wood. One kg/h of pine wood is equal to 0.0379 kmol/h. An oxygen flow rate of 1.21 kg/h is therefore required for a complete combustion. Therefore the stoichiometric oxygen/fuel ratio is 1.2.

The H₂ and CO yields are favoured at an ER of ~ 0.25 (Guo et al., 2014; Reed and Desrosiers; Reed et al., 1988; Abdoulmoumine et al., 2014). In this study the actual amount of oxygen used were 0.303, 0.606 and 2.12 kg/h. Pine wood feedstock flow rate was kept constant at 1.25 kg/h in all three cases resulting in the actual oxygen/fuel ratios of 0.24, 0.48 and 1.7. From Equation 17 the ER was calculated and found to be 0.2, 0.4 and 1.4. The temperature (the initial reactor temperature) was kept constant at 1000 °C. The results obtained from these three different ER were compared.

5.2 RESULTS AND DISCUSSIONS

The analytical results for the gasification experiments indicated that approximately 50 % mole nitrogen was measured, obviously due to the fact that nitrogen was used as a plasma gas. As mentioned earlier, the presence of nitrogen in syngas is undesirable because it dilutes the fuel gas concentration and reduces the calorific value. In this study, the results obtained were simply normalised for nitrogen. It should also be mentioned that in some instances the results also contained small amounts (< 1%) of methane, acetylene, oxygen and carbon dioxide. These minor products were not considered further. In cases where the percentage of these components increased to > 1% the results were considered and are included and discussed here.

5.2.1 EFFECT OF GASIFICATION TEMPERATURE

5.2.1.1 CONVERSION EFFICIENCY

The effect of gasification temperature was studied on peach pips. The main objective was to investigate how biomass conversion efficiency and syngas composition were affected by the gasification temperature at an equivalence ratio (ER) of zero, i.e. with no additional oxygen feed.

In order to determine conversion efficiency achieved, the particulates remaining after each temperature test were collected from the reactor, the gas outlet pipe, the knock-out pot, and the filter (Chapter 3). These particulates were weighed and total conversion efficiency was calculated by subtracting the total remaining particulates from the total biomass fed into the system. The conversion efficiency (in wt %) was then plotted against the operating temperature (Figure 50).

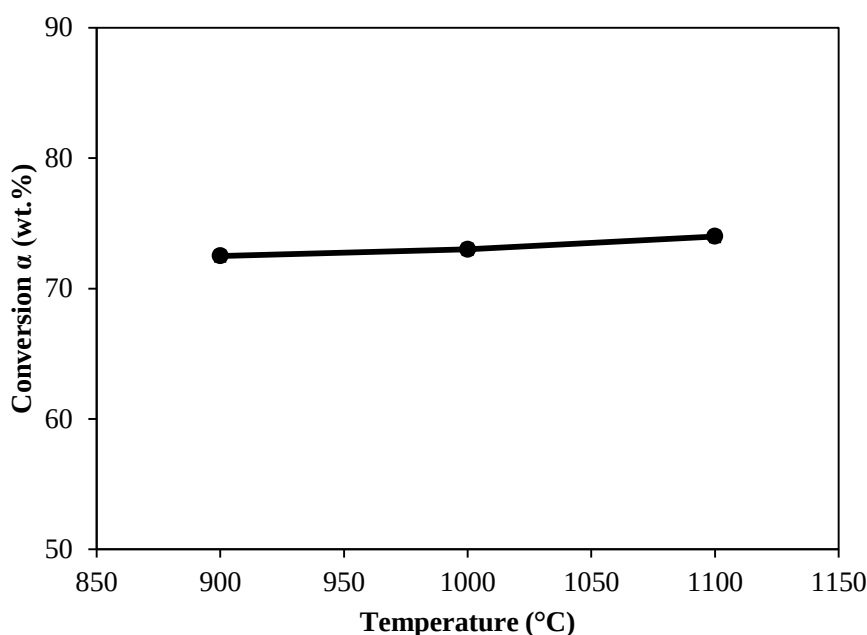


Figure 50. Temperature vs conversion using peach pips as feed

Conversion efficiency slightly increased with an increase in the gasification temperature (Figure 50). This is in agreement with literature. At high temperatures products of endothermic reactions are favoured (Lv et al., 2004). Since the tests were done in the absence of an oxidant, the water-gas and Boudouard reactions, Equation 1 & 5 which are endothermic were favoured, contributing to an increase in H_2 and CO formation and leading to a decrease in char (Berrueco et al., 2015b; Abdoulmoumine et al., 2014). The conversion achieved for the gasification temperatures of 900, 1000 and 1100 °C were 72.5, 73 and 74 % respectively.

5.2.1.2 SYNGAS CONCENTRATION

Figure 51 shows the effect of temperature on CO and H₂ formation. As already explained earlier, components such as CO₂ and CH₄ are not shown in this graph since their concentration were less than 1 % mol. From this observation it is clear that the CO/H₂ ratios were ~ 1 in all three cases (i.e. 1.03 at 900 °C, 1.026 at 1000 °C and 0.98 at 1100 °C). As expected the concentration of H₂ slightly increased from 49 to 51 % mole when the temperature was increased from 900 to 1100 °C. This was due to the water-gas reaction. On the other hand the concentration of CO slightly decreased with an increase in temperature. The trend of CO formation varies in different studies. It was found to increase with temperature between 700 and 800 °C, then remained constant between 800 and 1000 °C in the absence of an oxidant (Dufour et al., 2009). It was found to slightly decrease with an increase in temperature between 700 and 800 °C and sharply increase between 800 and 850 °C at an ER ~ 0.31 (Berrueco et al., 2015b). In another study it was found to increase with an increase in temperature between 800 and 1100 °C when the ER ~ 0.25 (Abdoulmoumine et al., 2014). These variations may have been caused by the possibilities of many reactions during gasification. Depending on the conditions inside the reactor at the point when the samples were taken, one reaction which is favourable or unfavourable to the formation of CO may have taken place.

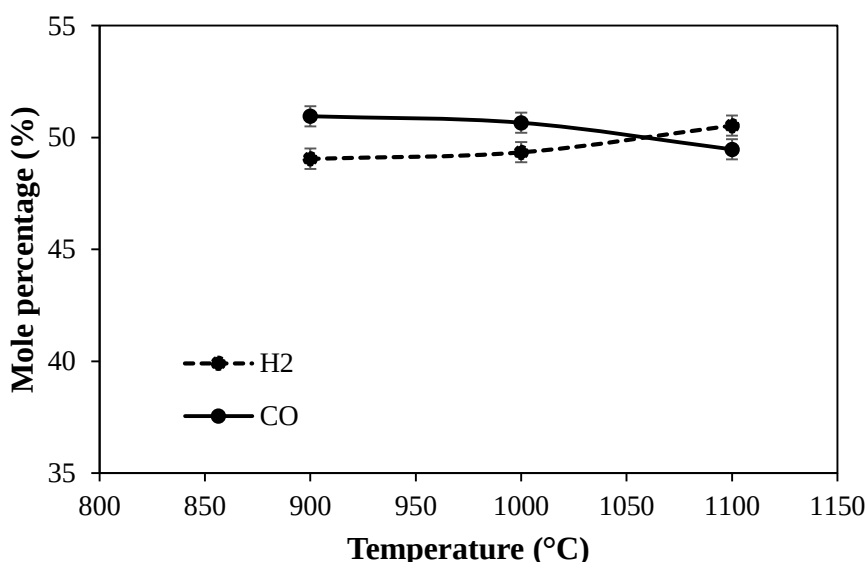


Figure 51. Product yield vs temperature using peach pips

5.2.1.3 ENERGY BALANCE

The mass and energy flows for peach pips gasification under a constant feed rate of 1.25 kg/h and different gasification temperatures of 900, 1000 and 1100 °C are shown in Table 14. From the literature, the calorific value of peach pip was found to be 19.4 kJ/g, producing (6.8 kW for a feed rate of 1.25 kg/h (Parikh et al., 2005).

Table 14. Calorific value of syngas produced from gasification of peach pips at different temperatures

Torch power (kW)	Temperature (°C)	Syngas (kg/h)	H ₂ (mol %)	CO (mol %)	LHV _{syngas} (kW)	LHV _{syngas} (kJ/g)
12.7 ±1.4	912.9	0.910	51	49	4.47	17.68
12.8 ± 1.9	934.7	0.913	51	49	4.48	17.66
13.0 ± 2.1	1097	0.925	49	51	4.46	17.35

It is observed from Table 14 that the calorific values of the syngas obtained at different gasification temperatures were almost equal, at 4.5 kW. Approximately 66% of the energy contained in the feed material was released as syngas. The rest of the energy (~34 %) remain in the solid residues (char). This was in agreement with the mass conversion results.

Roughly 35 % of the energy input into the system as electrical energy to run the torch, is recovered as the chemical energy content of the syngas. Sensible heat losses to the various reactor and torch components are given in Table 15. The torch has a very low energy efficiency. Commercially available non-transfer arc plasma torches have energy efficiencies of ~ 65% (Hrabovsky et al., 2006). In this system the efficiency of the torch was found for be ~ 32 %. The main reason for this was the fact the gasification reactor was not optimised to shield the anode housing from the heat radiation from the reactor. As a result 66 % of the energy supplied into the plasma torch was lost through anode cooling. The sensible heat content of the syngas constitutes 16 % of the energy input, while reactor losses constitute 18 %. Obviously a net

positive amount of energy is desired. To achieve this a careful thermal and mechanical redesign of the system is required.

Table 15: Average power losses to various water-cooled torch and reactor components

Component	Power losses (%)
Cathode	2
Anode	66
Inner quench	10
Outer quench	6
Reactor wall	12
Reactor flange	4

5.2.2 EFFECT OF FEED RATE

5.2.2.1 CONVERSION EFFICIENCY

The effect of feed rate on gas and char yield was investigated for peach pips. In some gasifiers a high feed rate is known to be beneficial for increasing product yield (Guo et al., 2014; Lv et al., 2007). However, it could reduce product quality due to higher gas yield and shorter residence leading to higher tar yield.

The results in Figure 52 shows no clear trend in the range of feed rates investigated. It decreased from 78 wt % to 73 wt % when the feed rate was increased from 1.00 to 1.25 kg/h. It then increased to 78 wt % when the feed rate was increased from 1.25 to 1.50 kg/h. It should be noted that these tests were done in the absence of an oxidant (i.e. ER ~ 0) at a constant reactor temperature (before feeding) of 1000 °C. In general conversion is expected increase with a decrease in feed rate due to the effective mass and heat transfer at lower feeding rates. Due to the turbulent nature inside the plasma reactor, it can be assumed that some very fine particles escape the reactor before they can be gasified. This could have caused the conversion at 1.25 kg/h to be lower than that at 1.50 kg/h. Another scenario could be that the tested feed rates

were too close to one another due to the system limitations already explained.

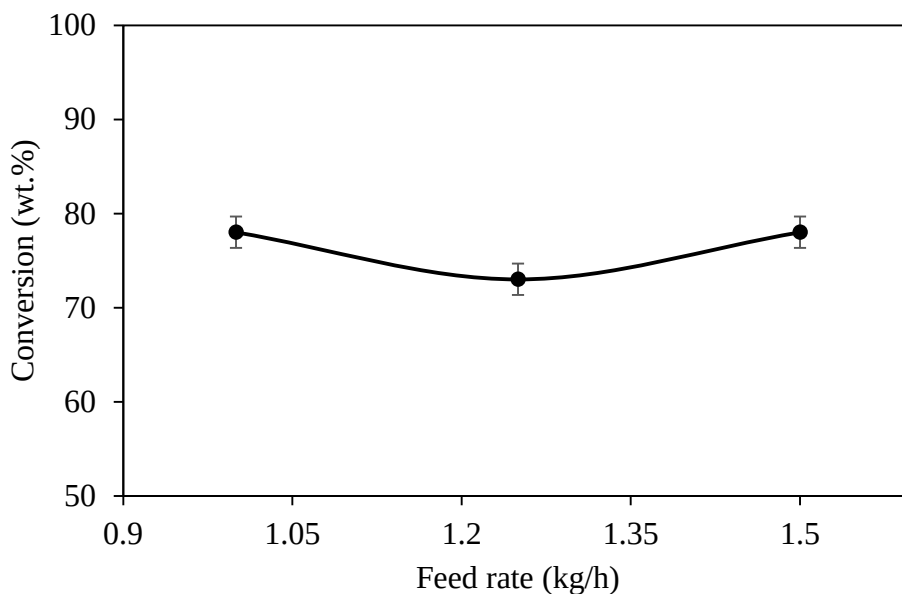


Figure 52. Feed rate vs conversion curve

5.2.2.2 HYDROGEN AND CARBON MONOXIDE CONCENTRATION

The relative H_2 and CO concentrations were also not markedly affected by an increase in feed rate under these conditions. The concentration of these gases were almost constant at all three tested feed rates (i.e. 1.00, 1.25 and 1.50 kg/h) and a CO/H_2 ratio of ~ 1 was achieved in all three cases, Figure 53.

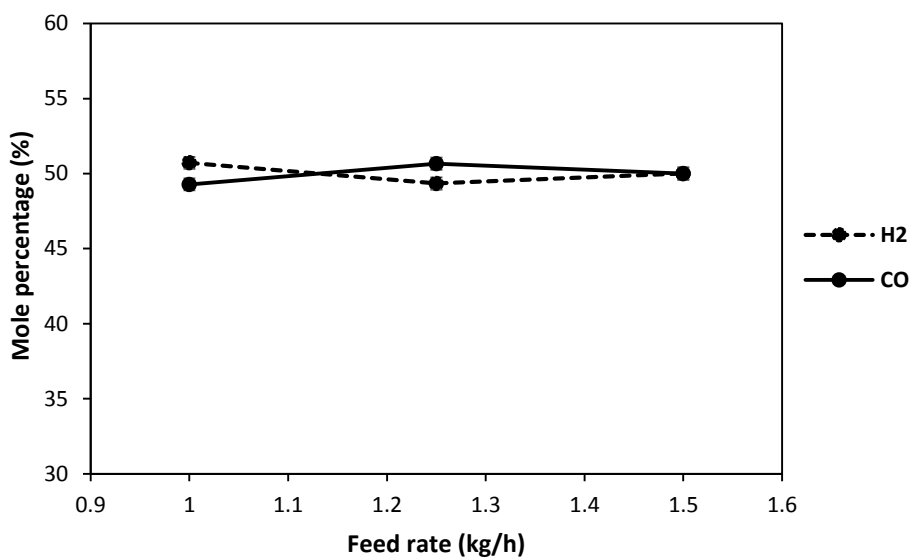


Figure 53. Product yield vs feed rate using peach pips as feed

At a feed rate between 1.00 and 1.25 kg/h, the H₂ concentration slightly decreased from 50.72 to 49.34 % mole. It then slightly increased to 50 % mole when the feed rate was increased to 1.50 kg/h. The CO concentration, on the other hand had an opposite trend to H₂ concentration. It slightly increased from 49.28 to 50.66 % mole between 1.00 and 1.25 kg/h then slightly decreased to 50 % mole at 1.50 kg/h.

5.2.2.3 ENERGY BALANCE

The calorific values of the syngas produced at different feed rates and constant temperature of 1000 °C are shown in Table 16 . The maximum power yields calculated from the enthalpy of combustion of peach pips for the feed rates of 1.0, 1.25 and 1.5 kg/h, are 5.44, 6.80 and 8.70 kW respectively.

Table 16. Calorific values of syngas produced from gasification of peach pips at different feed rates

Feed rate (kg/h)	Syngas (kg/h)	H ₂ (mol %)	CO (mol %)	LHV _{syngas} (kW)	LHV _{syngas} (kJ/g)
1	0.78	51	49	3.85	17.77
1.25	0.91	49	51	4.37	17.36
1.5	1.17	50	50	5.69	17.50

Comparing these values to the syngas energy flow in Table 16 that 70.8, 64.2 and 65.4 % of the energy contained in the feed material was released into the syngas for the feed rate of 1, 1.25 and 1.5 kg/h respectively. A higher energy yield is thus obtained at higher feed rates, but at the expense of conversion efficiency. This suggests that the gasification systems may be more economical at larger scales. The mixture of the syngas and the nitrogen exiting through the quench probe gas was cooled to ~ 29°C.

5.2.3 EFFECT OF EQUIVALENCE RATIO

5.2.3.1 CONVERSION EFFICIENCY

The conversion efficiency of pine wood versus the ER curve is shown Figure 54.

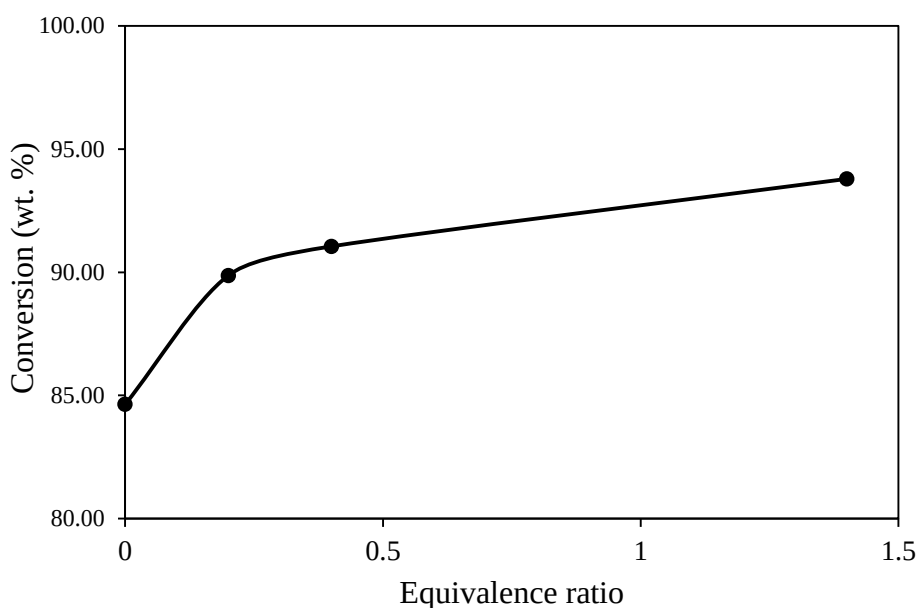


Figure 54. Pine wood conversion vs ER

From the TGA results (Figure 33) pine wood chips were shown to have high conversion even in the absence of oxygen. It is observed in Figure 54 that the amount of residue remaining decreases with an increase in ER, exactly as expected.

5.2.3.2 SYNGAS CONCENTRATION

Figure 55 shows the effect of ER on the main gases produced during gasification of pine wood chips. It is clear from the graph that the H_2 and CO concentrations are high at an ER of zero to 0.2. At 0.2 the CO_2 concentration is ≤ 1 % mole. An increase in equivalence ratio results in a decrease in the concentration of both H_2 and CO. The CO_2 gas starts to increase to ≥ 1 % mole with an increase in ER. These results agree with the literature (Guo et al., 2014).

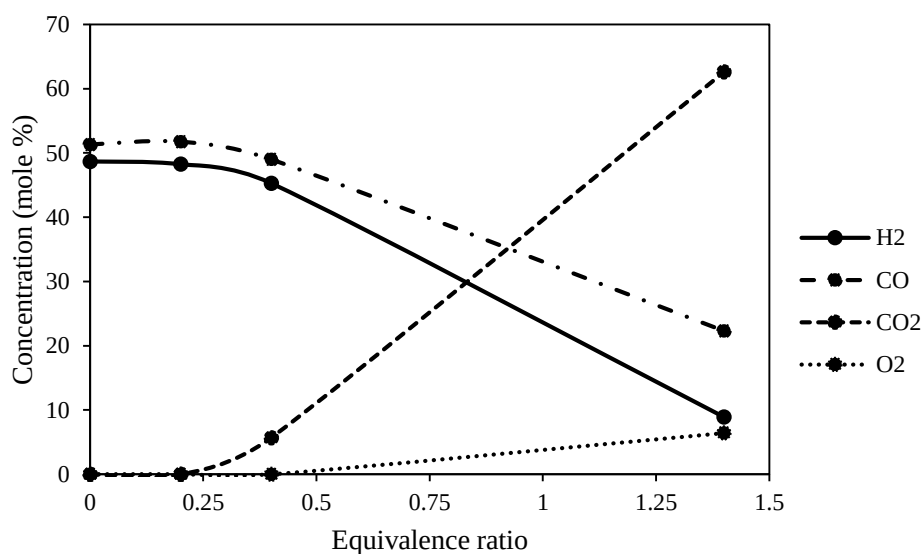


Figure 55. Product yield vs ER

At an ER value of 1, full combustion and maximum concentrations of CO₂ and H₂O are expected as the main products. The gas samples in this study were not analysed for H₂O, and the results were simply normalised with respect to the gases that were analysed for. It is clear at 1 and higher, significant concentrations of CO and H₂ are still present. Mass transfer and kinetic effects are undoubtedly responsible. Nevertheless, the overall observed trend is the expected behaviour.

5.2.3.3 ENERGY BALANCE

The calorific content of syngas produced at different ER values, and a constant temperature and constant feed rate of 1000°C and 1.25 kg/h respectively, are shown in Table 17. Pine wood has a combustion enthalpy of 19.38 kJ/g (Cuiping et al., 2004). Therefore a feed rate of 1.25 kg/h has a maximum energy flow of 6.7 kW.

Table 17 Calorific values of syngas produced for gasification of pine wood at different ER

Equivalence ratio	Syngas (kg/h)	H ₂ (mol %)	CO (mol %)	CO ₂ (mol %)	O ₂ (mol %)	LHV _{syngas} (kW)	LHV _{syngas} (kJ/g)
0	1.06	48.7	51.3	<1	<1	5.04	17.14
0.2	1.12	48.3	51.8	<1	<1	5.31	17.03
0.4	1.14	45.3	49.0	5.7	<1	5.37	16.97
1.4	1.17	8.9	22.3	62.5	6.4	0.77	2.35

It is evident from Table 16 that the calorific value of syngas increased with an increase in ER, up to 0.4. When the ER was increased to 1.4 the caloric value of the syngas decreased significantly to 0.77 kW. This is due to the fact that the combustible gases (CO and H₂) were decreased while the CO₂ was increased. As already mentioned pine wood has high conversion efficiency, leading to the calorific values obtained during the gasification of pine to be higher than that obtained during the gasification of peach pips even at an equivalence ratio of zero. Comparing the enthalpy of combustion of syngas to that of feed material (pine wood) for a feed rate of 1.25 kg/h, it was found that 75.2, 79.2, 80.1 and 11.5 % of the energy contained in the feed material was released to syngas for the equivalence ratios of 0, 0.2, 0.4 and 1.4 respectively.

5.3 CONCLUSION

Initially the plasma gasification system was to be investigated using the four different biomass types. However the test work was carried out using only two materials, viz. peach pips and pine wood chips. This was due to the very light nature and low density of the bamboo and Napier grass. The design of the plasma gasification system was unable to accommodate these low density materials. This resulted in blockages of the system and thereby ending the experiment prematurely. It could be concluded that this system is not desirable for low density material.

The parameters that were evaluated were the gasification temperature, feed rate and the ER. Operating temperatures of 900, 1000 and 1100 °C, feed rates of 1.00, 1.25, and 1.50 kg/h, and the ER values of zero, 0.2, 0.4 and 1.4 were studied. The gasification results indicated that high temperature increased conversion efficiency as the amount of the residue decreased with an increase in gasification temperature. However the product concentrations were not affected by an increase in gasification temperature, the concentration of H₂ and CO were mostly high due to the fact that at high temperatures the water-gas shift and the Boudouard reactions were favoured. The CO/H₂ ratios of ~ 1 were achieved in all three gasification temperatures. However H₂ concentration seemed to increase with an increase in temperature while CO concentration decreased with an increase in temperature.

The tested feed rates were found to have a negligible influence on conversion efficiency as well as on product concentration. Conversion efficiency slightly fluctuated with an increase in feed rate. This could be linked to particle size of the feed stock, but was not confirmed. If finer particles are available in the hopper during the gasification test at a specific feed rate, the finer particles could escape the reactor before being gasified.

The use of oxidant has a significant influence in the overall gasification process as expected. Operating the plasma gasification system with zero ER resulted in a CO/H₂ ratio of ~ 1. A conversion efficiency of ~ 85 % was achieved on pine wood. An ER of 0.2 increased conversion efficiency to ~ 90 % while keeping the CO/H₂ ratio almost the same. A conversion of ~ 91% was achieved when the ER was increased to 0.4. However, the CO₂ concentration started to increase to above 1% mole. At an ER of 1.4, CO₂ production increased significantly to ~ 68 % mol. It can be concluded that an ER between 0.2 and 0.4 is favourable for the biomass plasma gasification process. This agrees with the literature.

The efficiency of converting the electrical energy used for gasification to the chemical energy yield from the syngas, is 30 % to 40 %. The main heat losses is via the torch anode, and thought to be due to the absence of radiation shielding. This may be corrected by a redesign; also the efficiency is expected to increase for larger gasification systems.

6 CONCLUSION AND RECOMMENDATIONS

For both TGA and plasma experimental tests, the highest conversion achieved for peach pips under inert conditions was ~ 78 wt %, while that for pine wood under similar conditions was ~ 85 wt %. The TGA results also indicated the importance of heating rate, with higher heating rates resulting in higher conversion of biomass to gas. High conversion efficiencies were achieved at higher heating rate in all materials. The heating rate with plasma gasification cannot be controlled; however plasma processes are generally known for their high heating rates, which makes them ideal for gasification processes. One would expect higher conversion for the plasma than for the TGA runs. The fact that this was not observed can be ascribed to uncontrolled dwell time of the feed in the reactor, resulting in the conversion reactions not going to completion.

High temperatures favour the product of the endothermic reactions leading to an increase in the formation of CO and H₂. As a consequence the plasma experiments yielded predominantly CO and H₂, except for high ER values. The plasma gasification results indicated an ER between 0.2 and 0.4 to be optimum.

Particle sizes were found to have a crucial role when investigating the effect of feed rate in this system. It is important to use millimetre size particle sizes and avoid the presence of fine particle with low density when testing the effect of feed rate. It was established that low density particles easily escape the reactor without being gasified due to the turbulence inside the reactor.

For this reactor system, the results indicated that more energy has to be put into the gasification process than can be recovered from the combustion of the syngas produced. Overall efficiencies range between 30 and 40 %. The highest energy loss in the system is via the torch anode. More than 60 % of the power is lost this way, resulting in a nominal torch efficiency of ~ 30 %. Non-transferred torches are expected to have efficiencies higher than 60 %. The high anode power losses is most probably attributable to radiative heat impinging on the torch from the gasification reactor chamber.

The main recommendation is that the free-standing efficiency of the torch should be measured, i.e. away from the gasification reactor. If it is indeed low, the torch should be optimised to

obtain an efficiency of at least 60%. If the torch efficiency is not the problem, then a redesign to protect the torch from reactor radiation should be implemented.

7 FUTURE WORK: ORGANIC CHEMICAL WASTE PLASMA GASIFICATION

7.1 CHEMICAL WASTE PLASMA TREATMENT (LiPF₆)

Initially plasma technology at Necsa was developed for waste reduction, especially radiological waste. However, due to the safety issues concerning the handling radioactive material, the technology is being tested on non-radioactive waste such as biomass. However there is other conventional chemical waste generated at Necsa whose disposal is of concern. Generally any chemical waste generated during chemical processes needs to be treated before it can be disposed of in a land fill site. Some chemical waste needs special treatment.

A lot of liquid waste is generated during the production of lithium hexafluorophosphate (LiPF₆) in the fluorine laboratory at Necsa. As a first step towards the treatment of this waste, poly(methyl methacrylate) (PMMA) polymer is used to solidify for solidifying the solution. The solidified waste is carbon rich, therefore converting it to energy through plasma gasification was considered a viable treatment method. This would solve the waste disposal problem while in turn producing syngas. This work was conducted as a preliminary study.

7.1.1 BRIEF BACKGROUND ON LITHIUM HEXAFLUOROPHOSPHATE

Lithium hexafluorophosphate (LiPF₆) serves as an electrolyte in lithium ion batteries. LiPF₆ is used mainly because it is easily soluble in various solvents, has a high electrical conductivity in non-aqueous solution, and has high electrochemical stability. Lithium hexafluorophosphate electrolytes are prepared by dissolving a LiPF₆ organic complex or pure LiPF₆ salt in a suitable electrolyte solvent, such as propylene carbonate.

Lithium hexafluorophosphate waste was produced in the laboratory at Necsa. The LiPF₆ was further dissolved in propylene carbonate in for various tests, including stability as an electrolyte component. This resulted in generation of liquid waste. This waste is very toxic and harmful to the environment, thus needs special treatment and disposal procedures. The plasma waste treatment system was therefore considered and then used as a treatment method.

7.1.2 WASTE SOLIDIFICATION PROCESS

Lithium hexafluorophosphate (LiPF_6) dissolves in several solvents, for example, propylene carbonate, resulting in a LiPF_6 solution which may be classified as waste after use in research facilities. This waste may be dissolved in small pieces of PMMA, such as beads or powders. By controlling the volume of the liquid used and allowing the material to settle for approximately two weeks, solid PMMA encapsulated waste was generated (Figure 56). Poly(methyl methacrylate) used for this purpose was purchased from Sigma-Aldrich.



Figure 56. PMMA encapsulated waste

7.1.3 EXPERIMENTAL METHOD

The screw feeder was calibrated for this specific material. The operating parameters were as follows: a feed rate of 1.00 kg/h and a temperature of 1000 °C in the absence of an oxidant. A solid block of PMMA encapsulated LiPF_6 waste was chopped into smaller piece to enable easy feeding. These pieces were loaded into the hopper. The same operating procedures as in Chapter 5 were followed. The system was operated for an hour. During this process two samples were taken using U-tubes, and submitted analysis.

7.1.4 RESULTS AND DISCUSSIONS

The gas samples were analysed for syngas product using a GC. As for the biomass gasification case, the results were normalised for nitrogen. The normalised results were found to contain 53 % mole H_2 and 47% mole CO . The residues remaining after the tests were ~ 5 wt % in the form of fine ash. The residues were not analysed for traces of lithium due to the lack of an appropriate analytical instrument. Also the column used in the GC couldn't be used for fluorine compounds.



7.1.5 CONCLUSION

The preliminary work that was done to demonstrate the use of plasma gasification as a chemical waste treatment method indicated that the chemical waste (LiPF_6) was successfully treated, and in turn produced syngas. In future more work still needs to be done so that the residues can be analysed for traces of lithium. The gases produced also need to be analysed for fluorine compounds before they can be considered safe to be labelled as syngas.

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APPENDICES

A: TGA-FTIR curves of pine wood under nitrogen

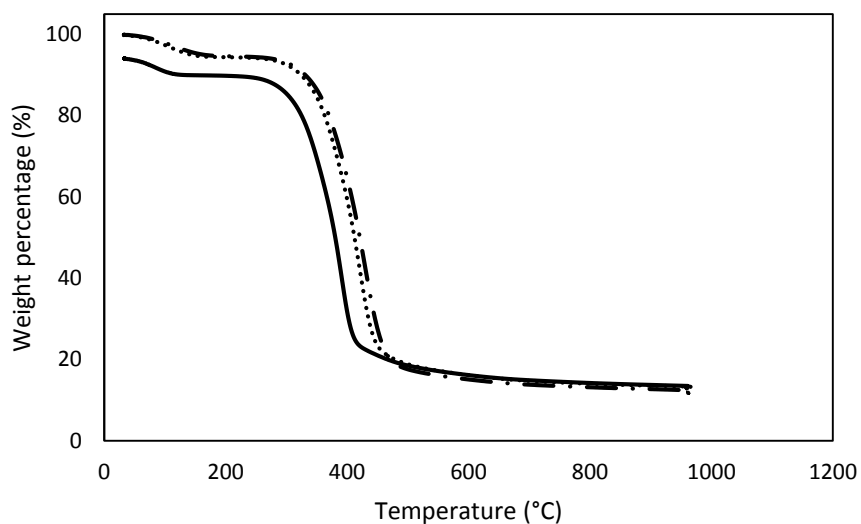


Figure 57. TGA curve of pine wood under nitrogen

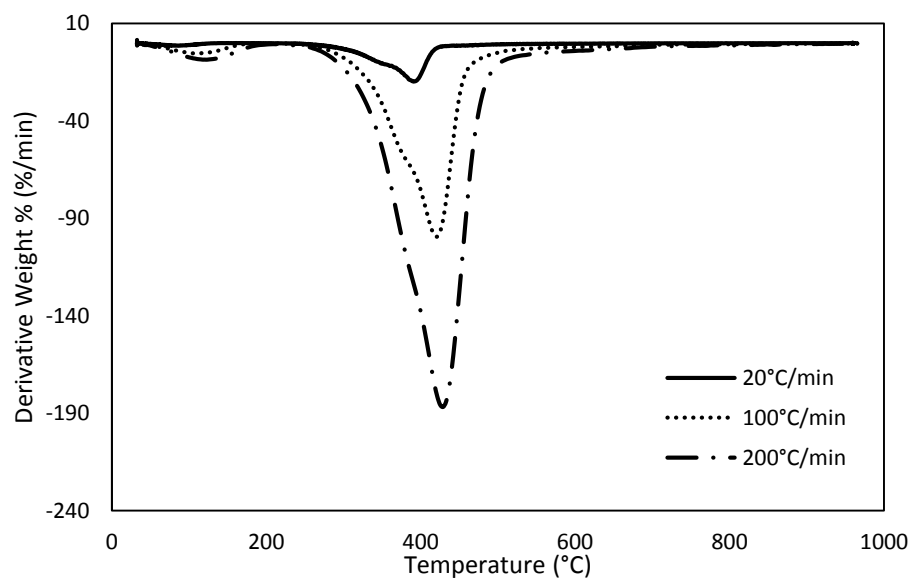


Figure 58. DTG curve of pine wood under nitrogen.

Makaringe

Appendices

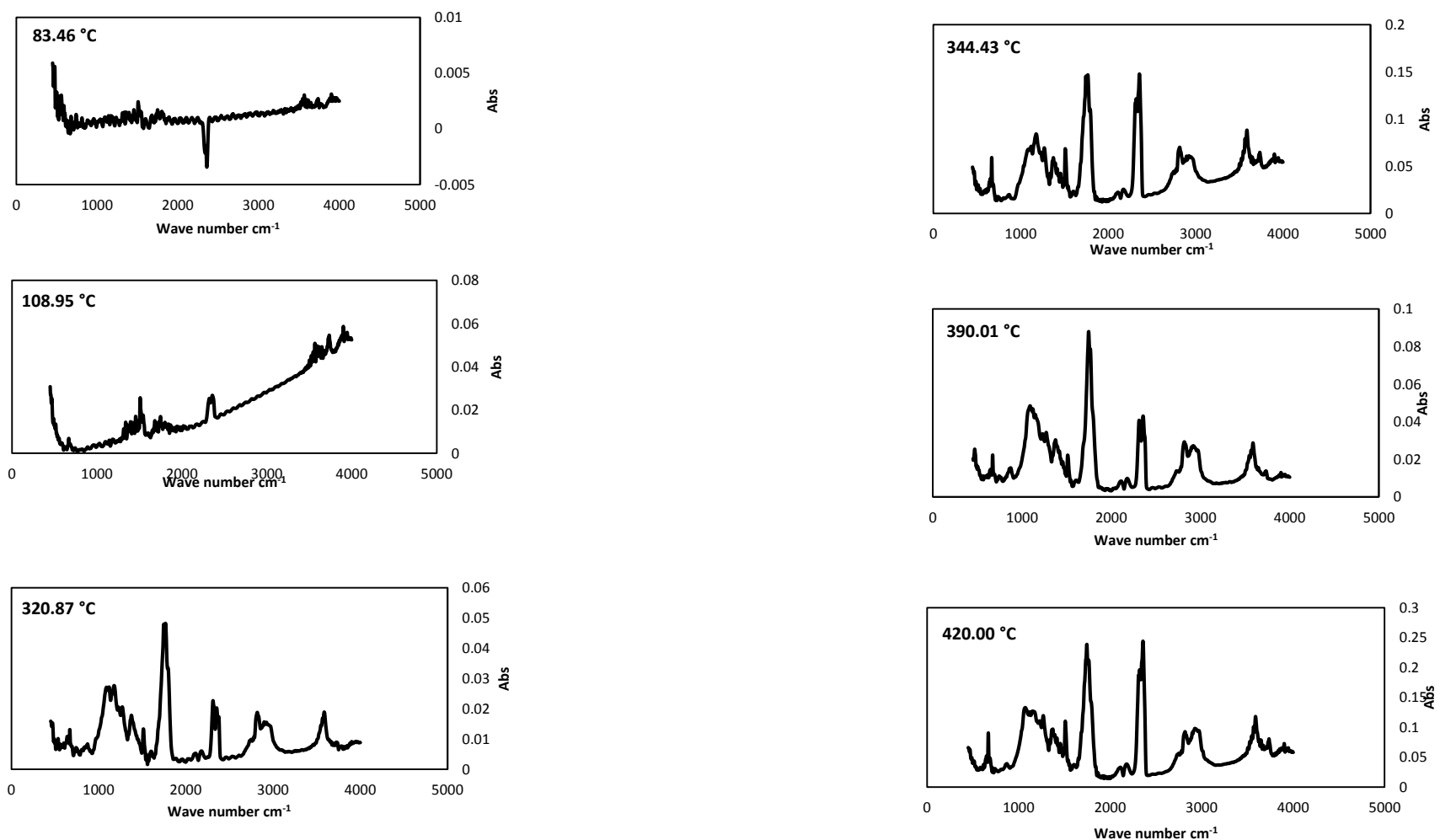


Figure 59. FTIR spectra of pine wood at 100°C/min under nitrogen.

B: TGA-FTIR curves of Napier grass under nitrogen

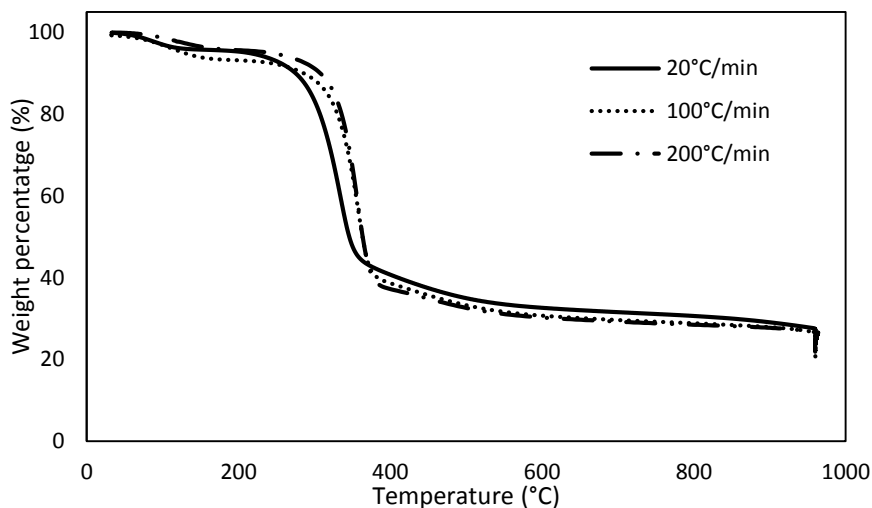


Figure 60. TGA curves of Napier grass under nitrogen

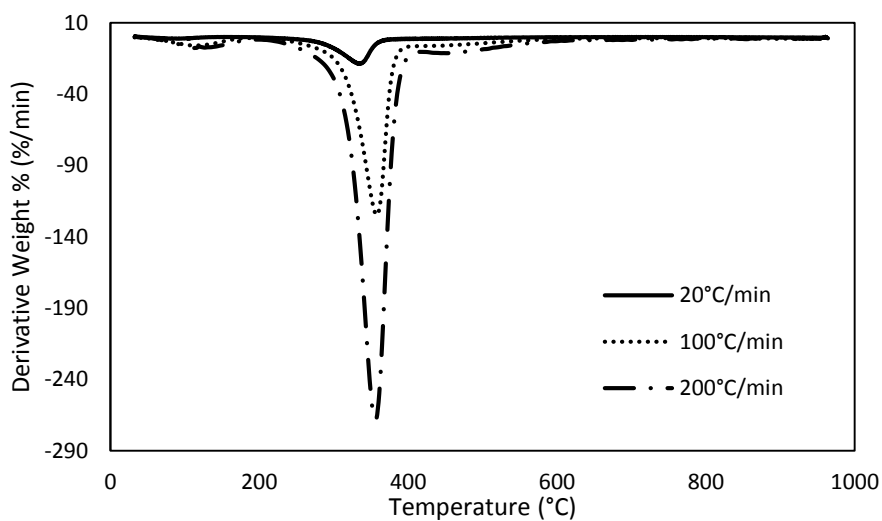


Figure 61. DTG curve of Napier grass under nitrogen.

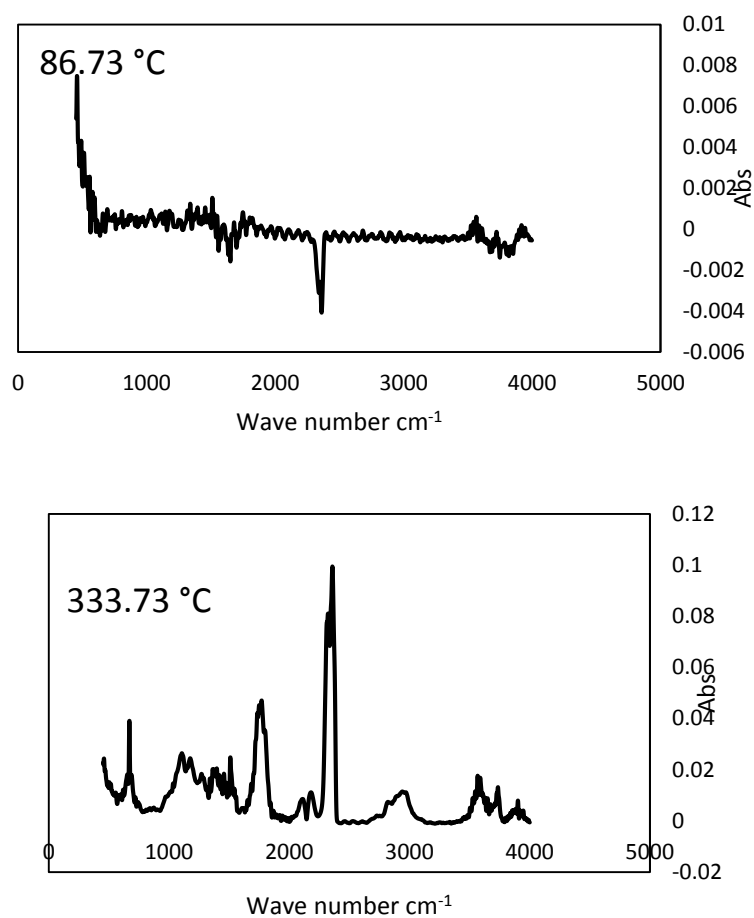


Figure 62. FTIR spectra of Napier grass at 20°C/min under nitrogen.

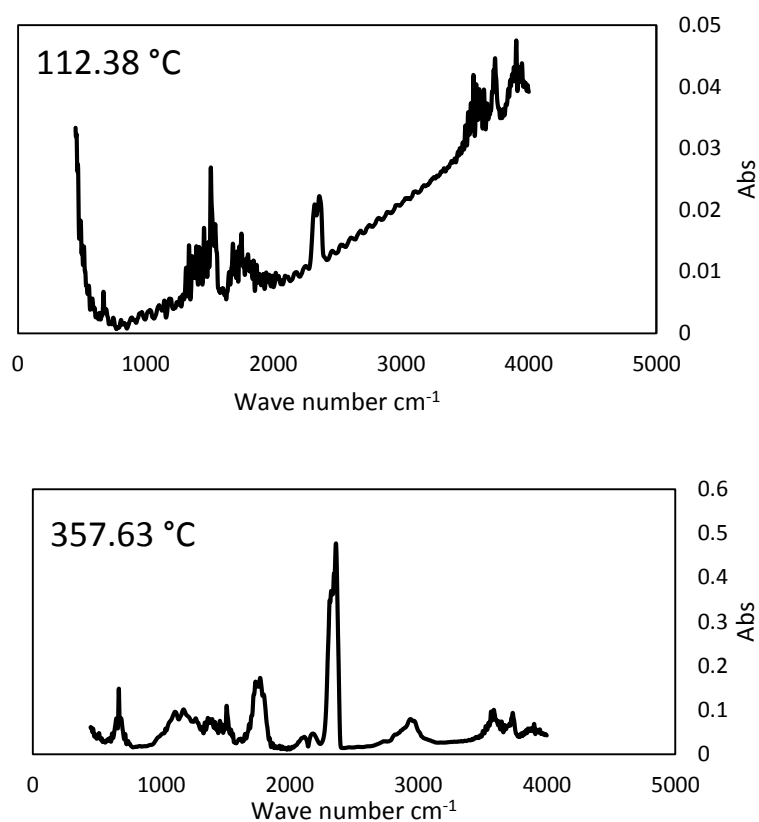
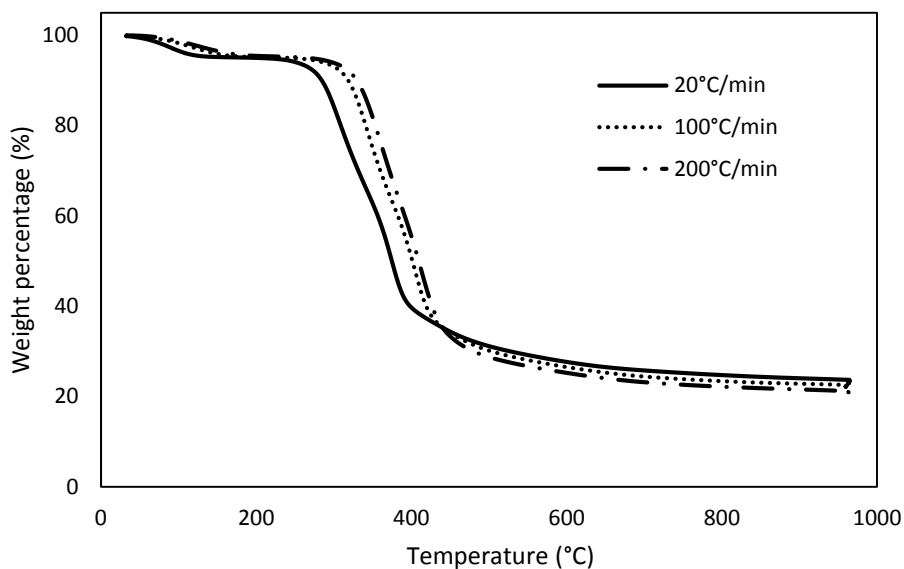
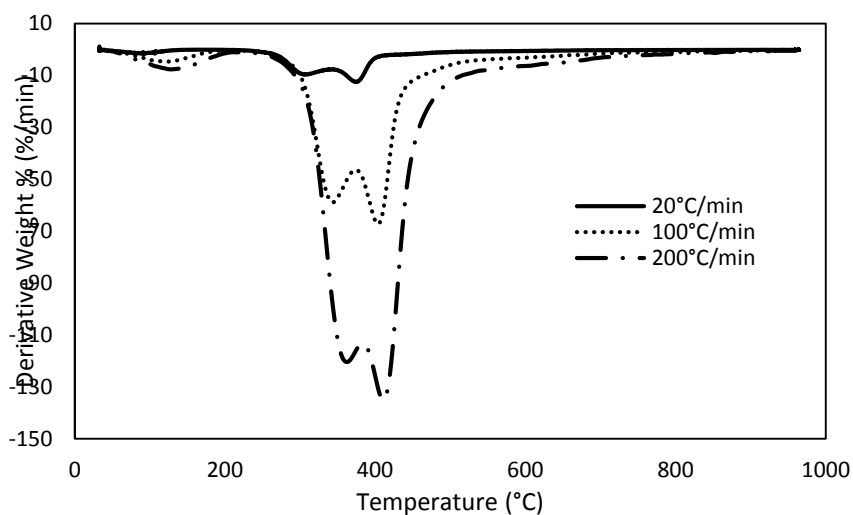


Figure 63. FTIR spectra of Napier grass at 100°C/min under nitrogen.

C: TGA-FTIR curves of peach pips under nitrogen

**Figure 64.** TGA curves of peach pips under nitrogen**Figure 65.** DTG curve of peach pips under nitrogen.

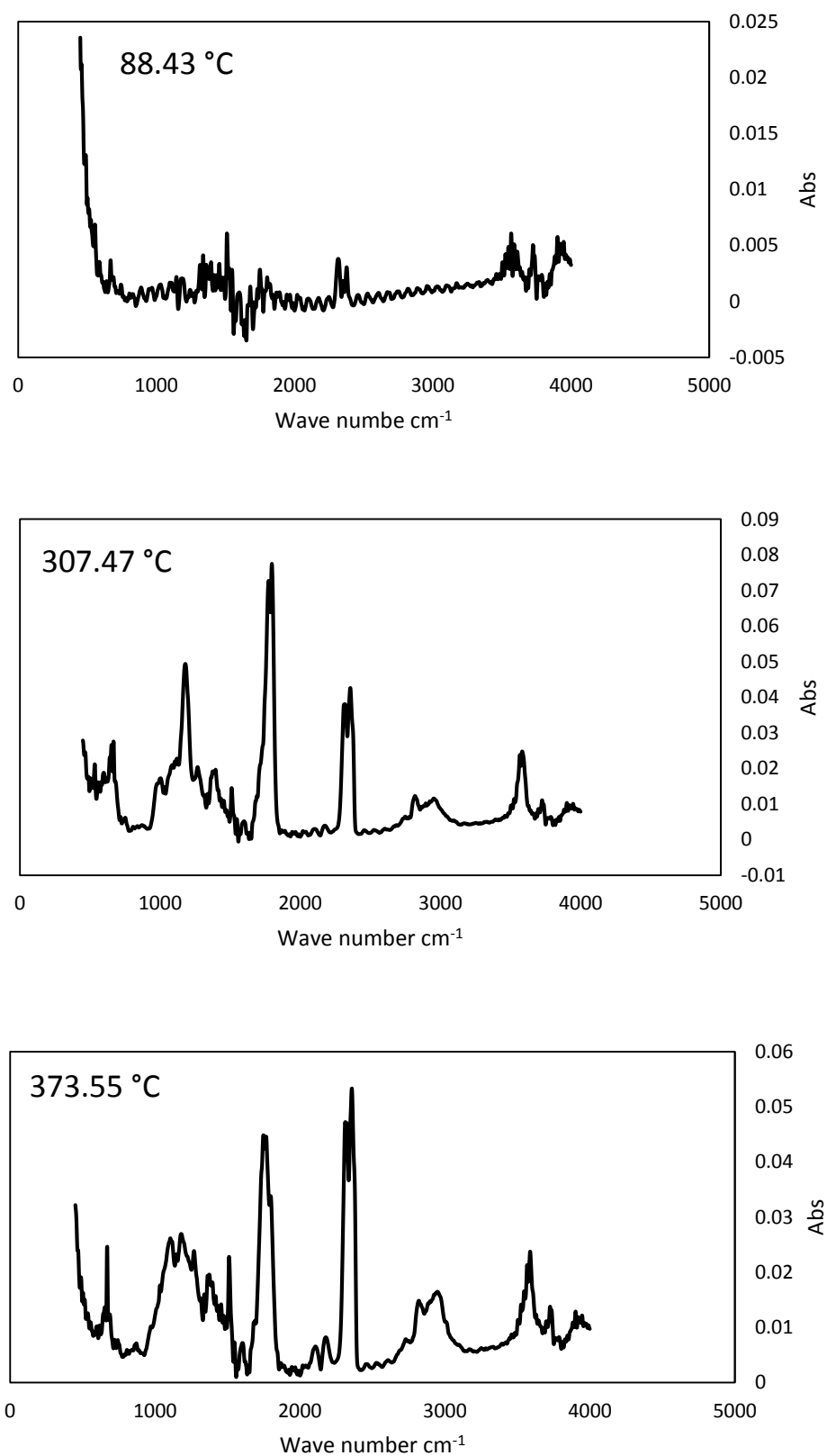


Figure 66. FTIR spectra of peach pips at 20°C/min under nitrogen.

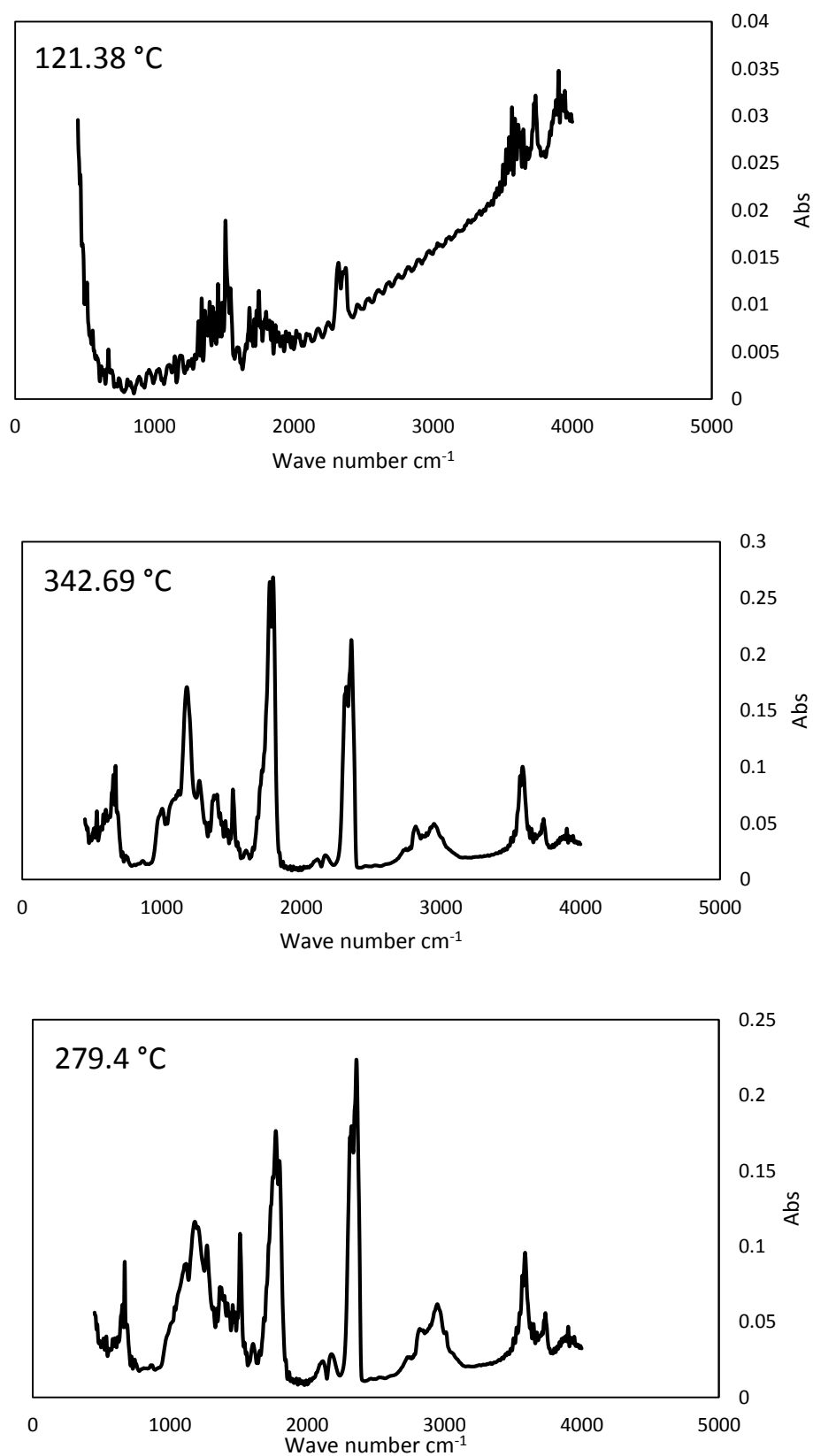
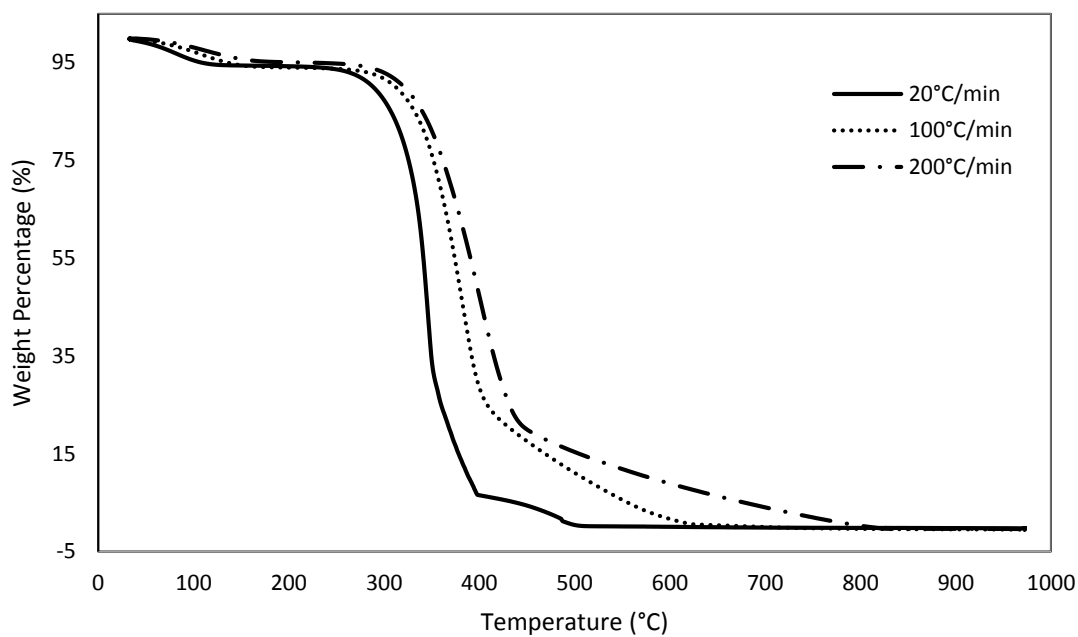
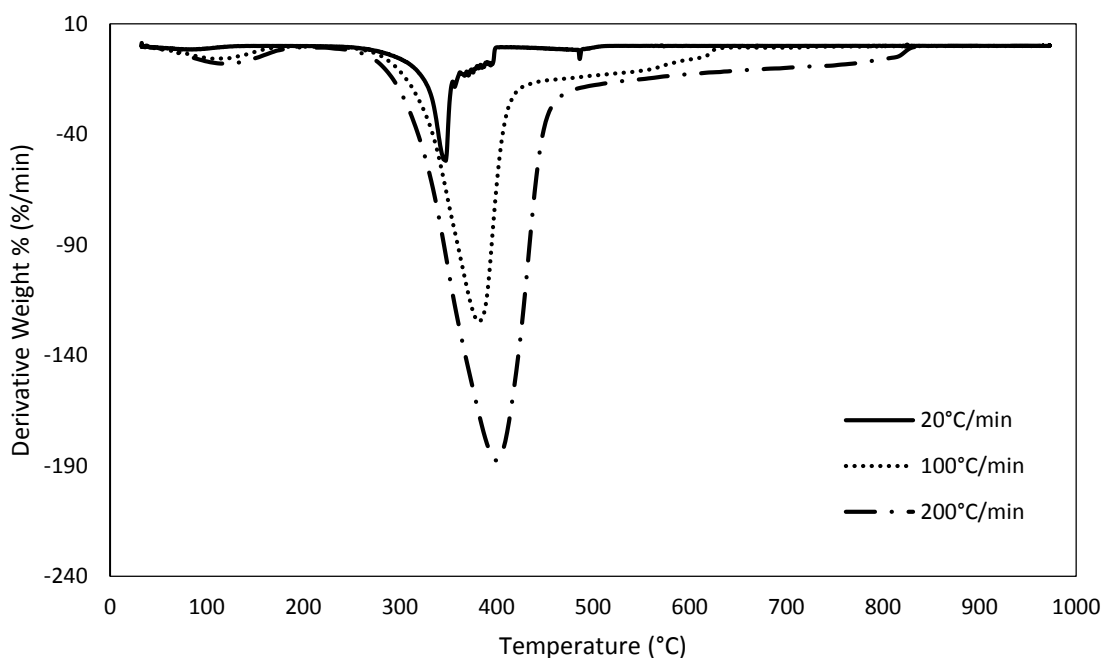


Figure 67. FTIR spectra of peach pips at 100°C/min under nitrogen.

D: TGA-FTIR results curves of pine wood under oxygen**Figure 68.** TGA curve of pine wood under oxygen.**Figure 69.** DTG curve of pine wood under oxygen.

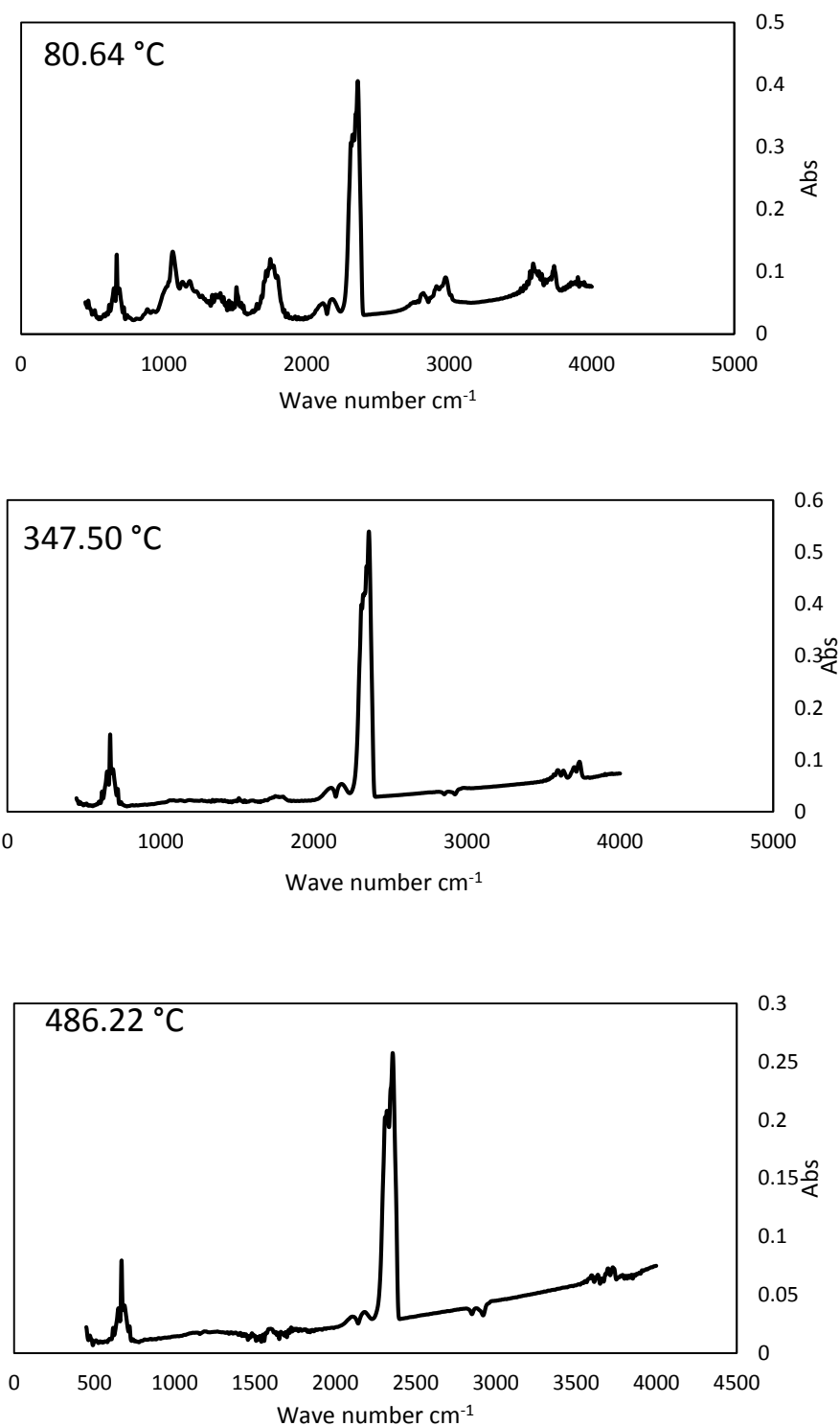


Figure 70. FTIR spectra of pine wood at 20°C/min under oxygen.

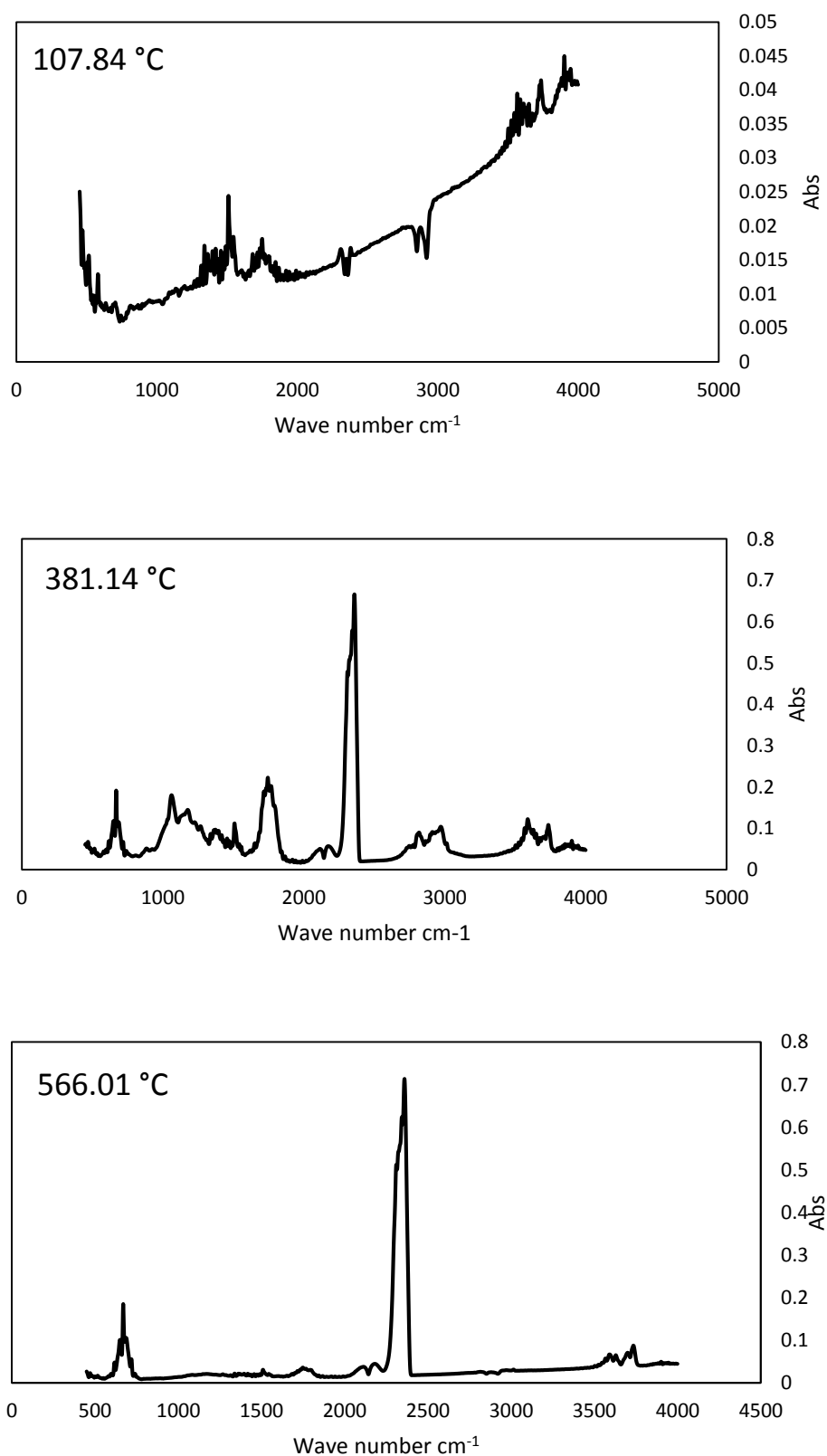
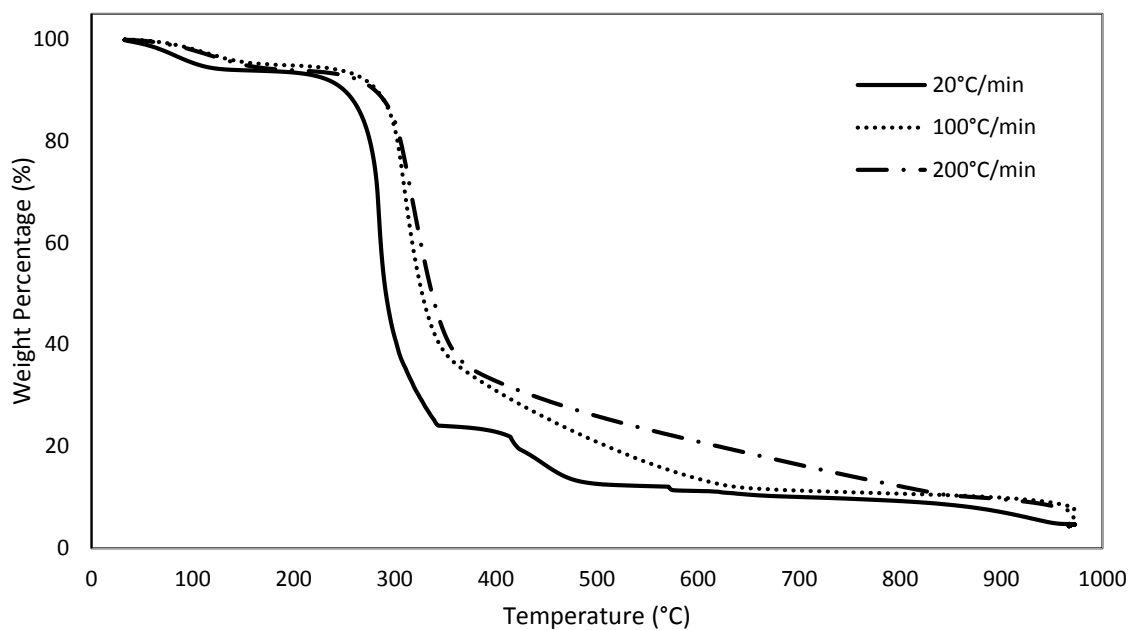
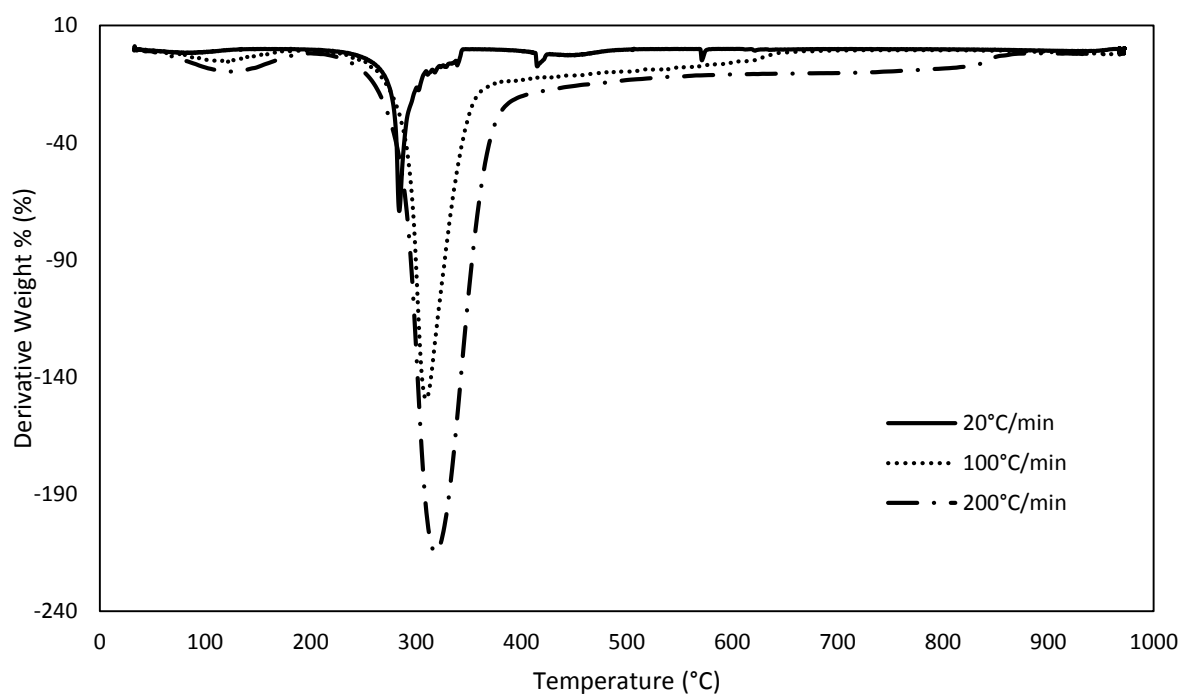


Figure 71. FTIR spectra of pine wood at 100°C/min under oxygen.

E: TGA-FTIR results curves of Napier grass under oxygen**Figure 72.** TGA curve of Napier grass under oxygen.**Figure 73.** DTG curve of Napier grass under oxygen.

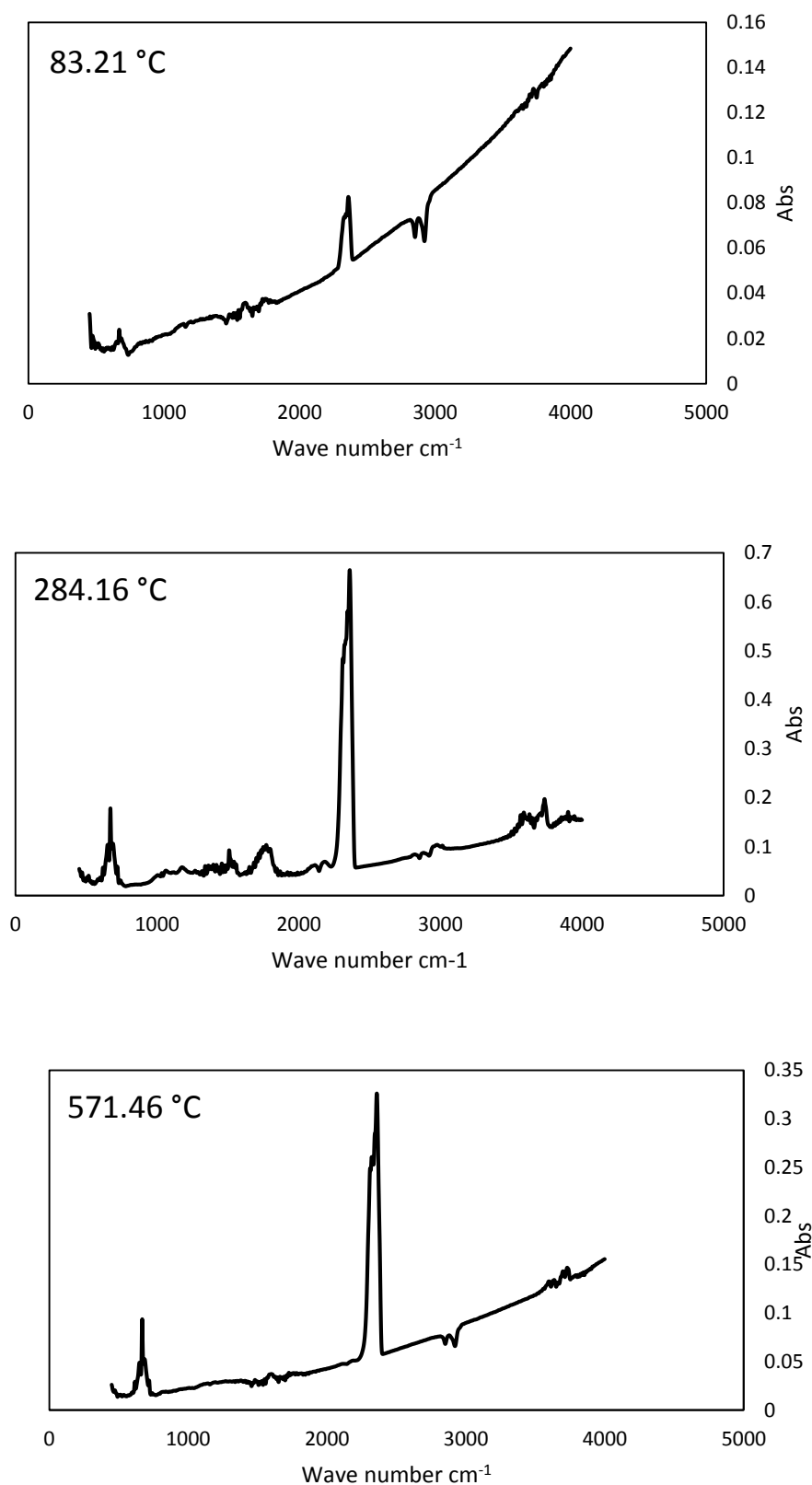


Figure 74. FTIR spectra of Napier grass at 20°C/min under oxygen.

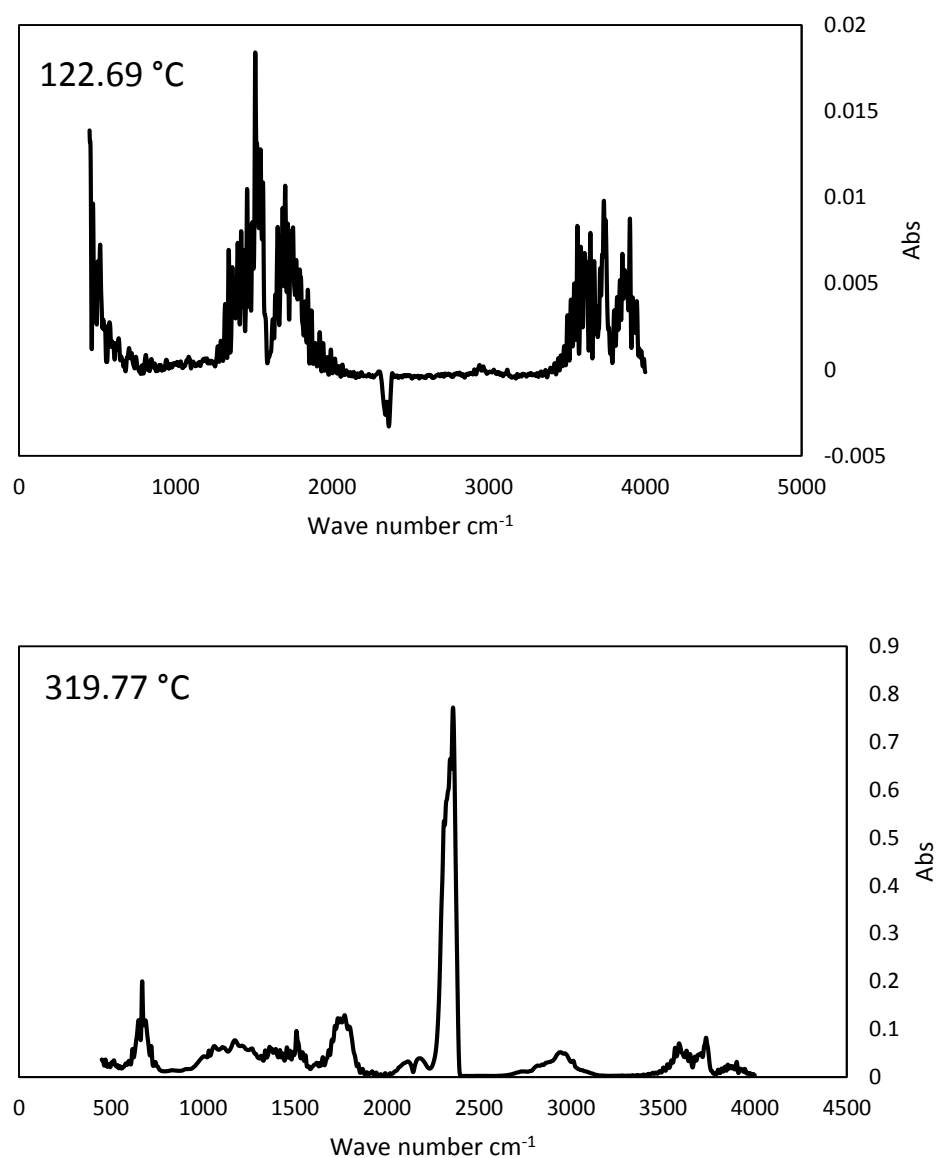


Figure 75. FTIR spectra of Napier grass at $100^{\circ}\text{C}/\text{min}$ under oxygen.

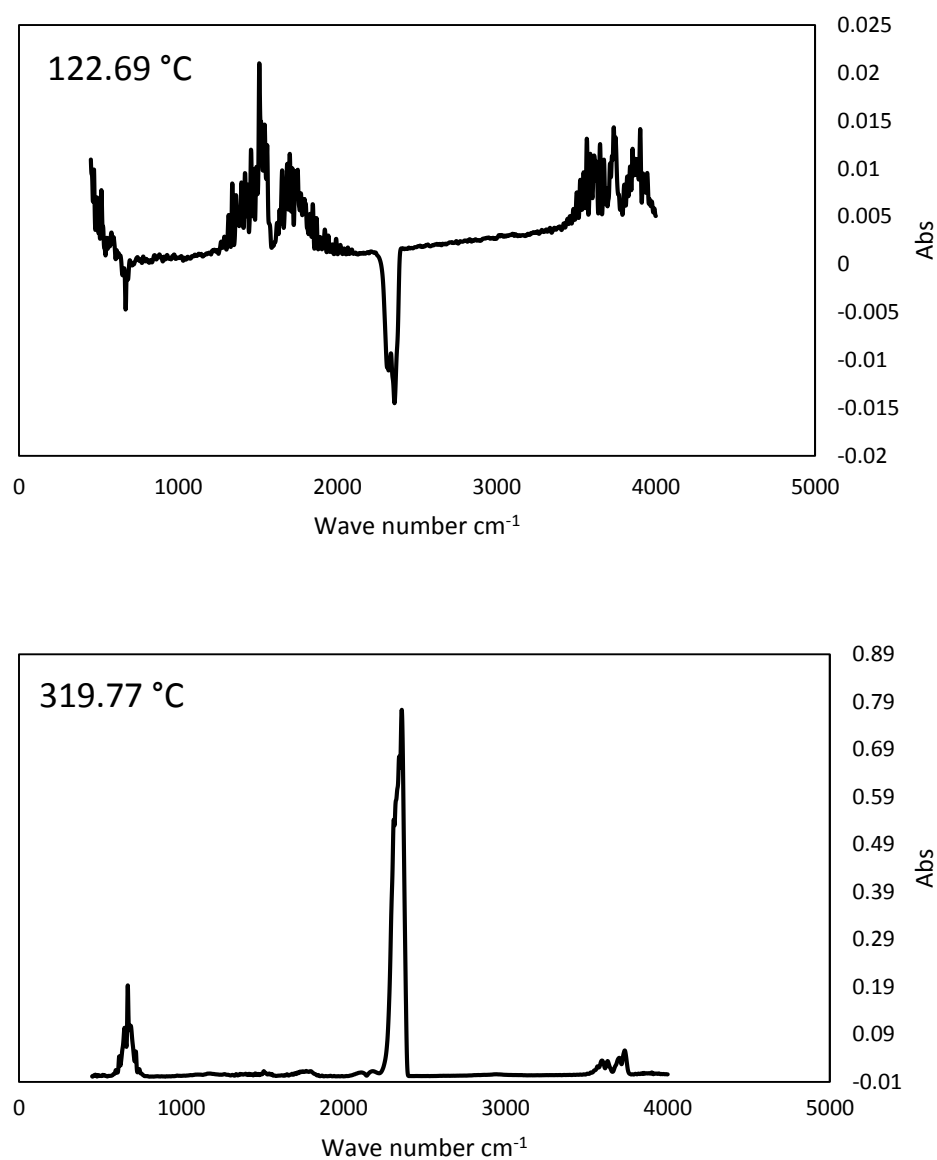


Figure 76. FTIR spectra of Napier grass at $200^\circ\text{C}/\text{min}$ under oxygen.

F: TGA-FTIR results curves of peach pips under oxygen

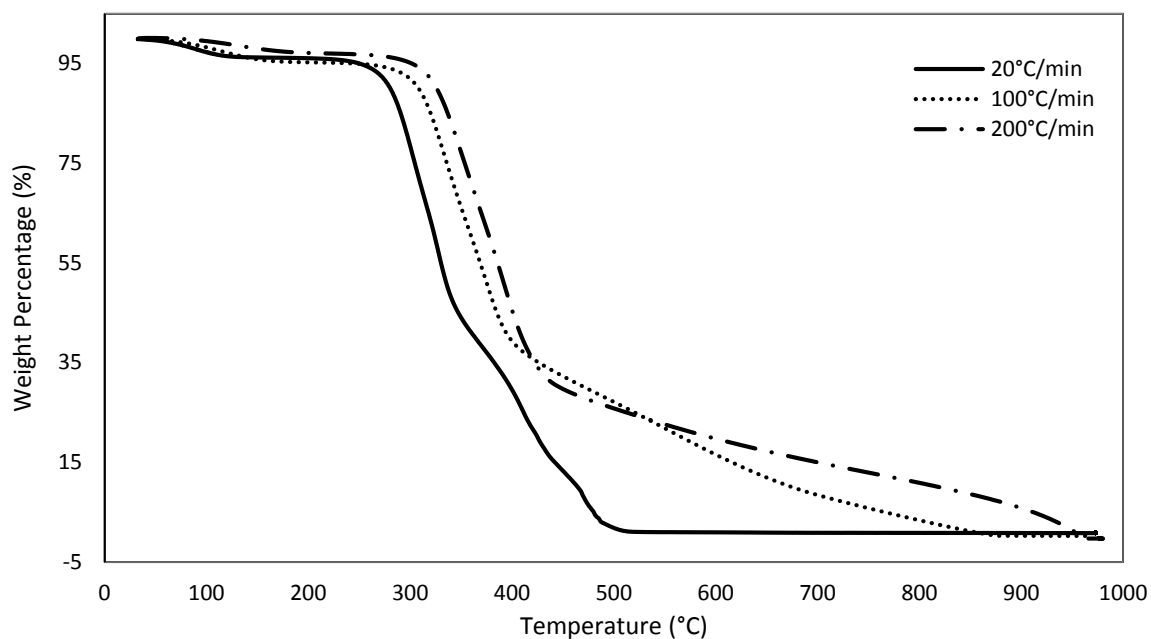


Figure 77. TGA curve of peach pips under oxygen.

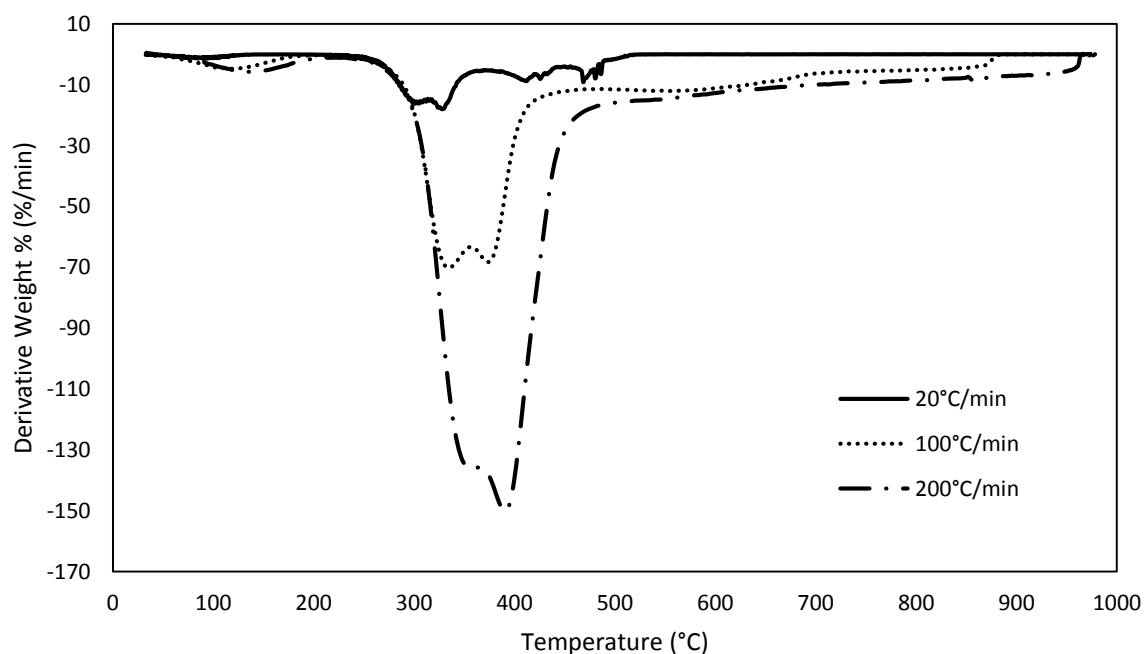


Figure 78. DTG curve of peach pips under oxygen.

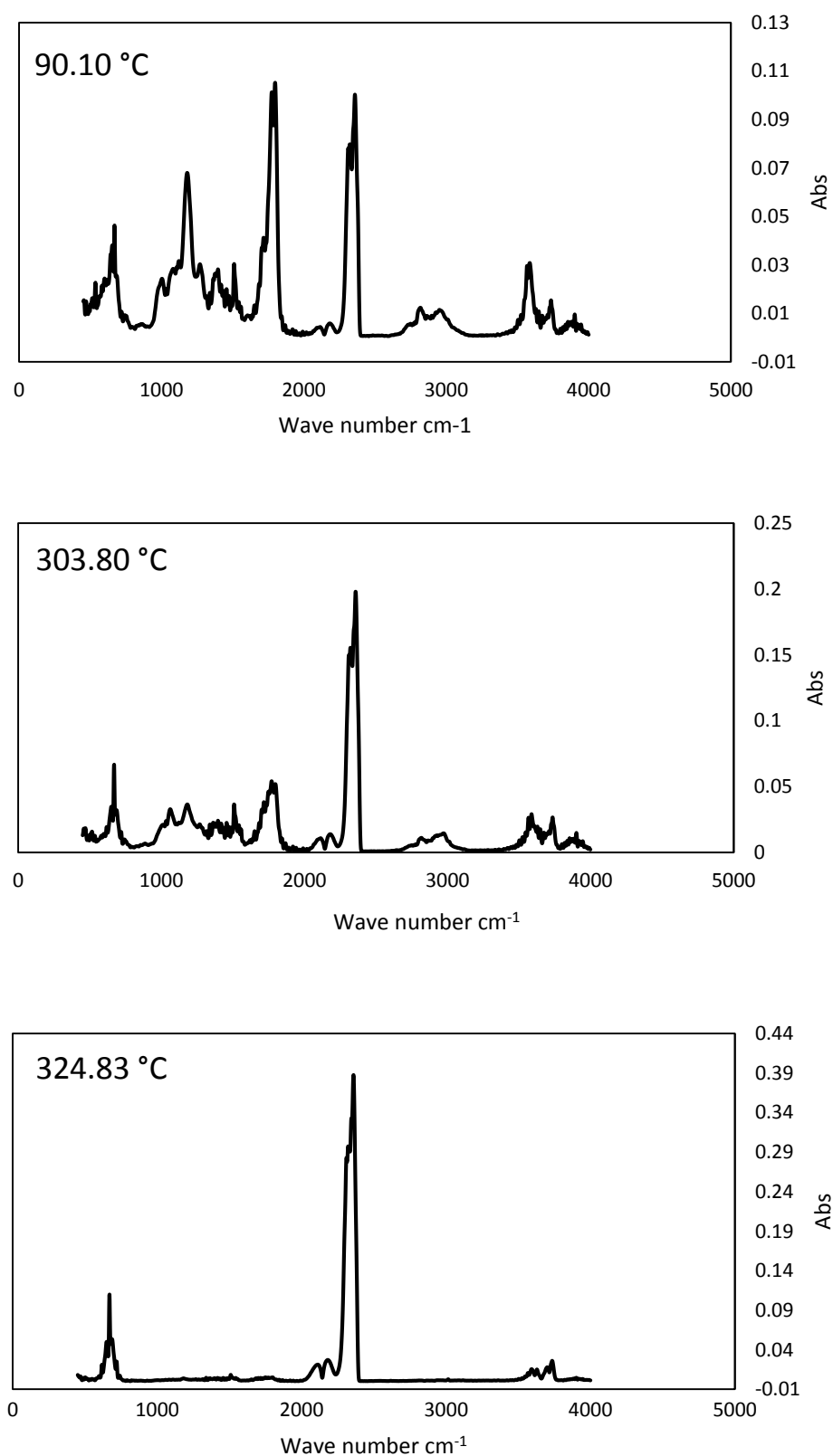


Figure 79. FTIR spectra of peach pips at 20°C/min under oxygen.

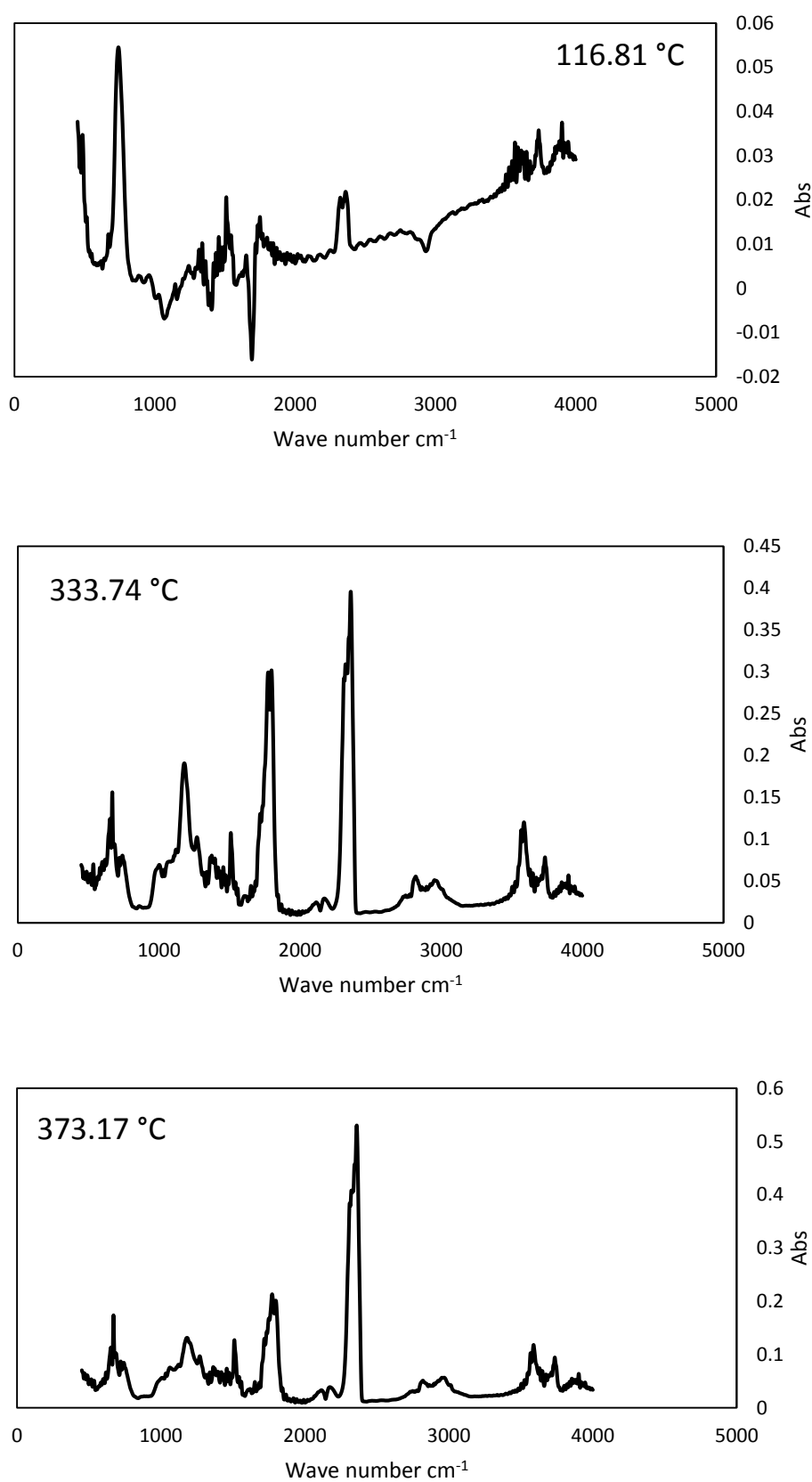


Figure 80. FTIR spectra of peach pips at 100°C/min under oxygen.

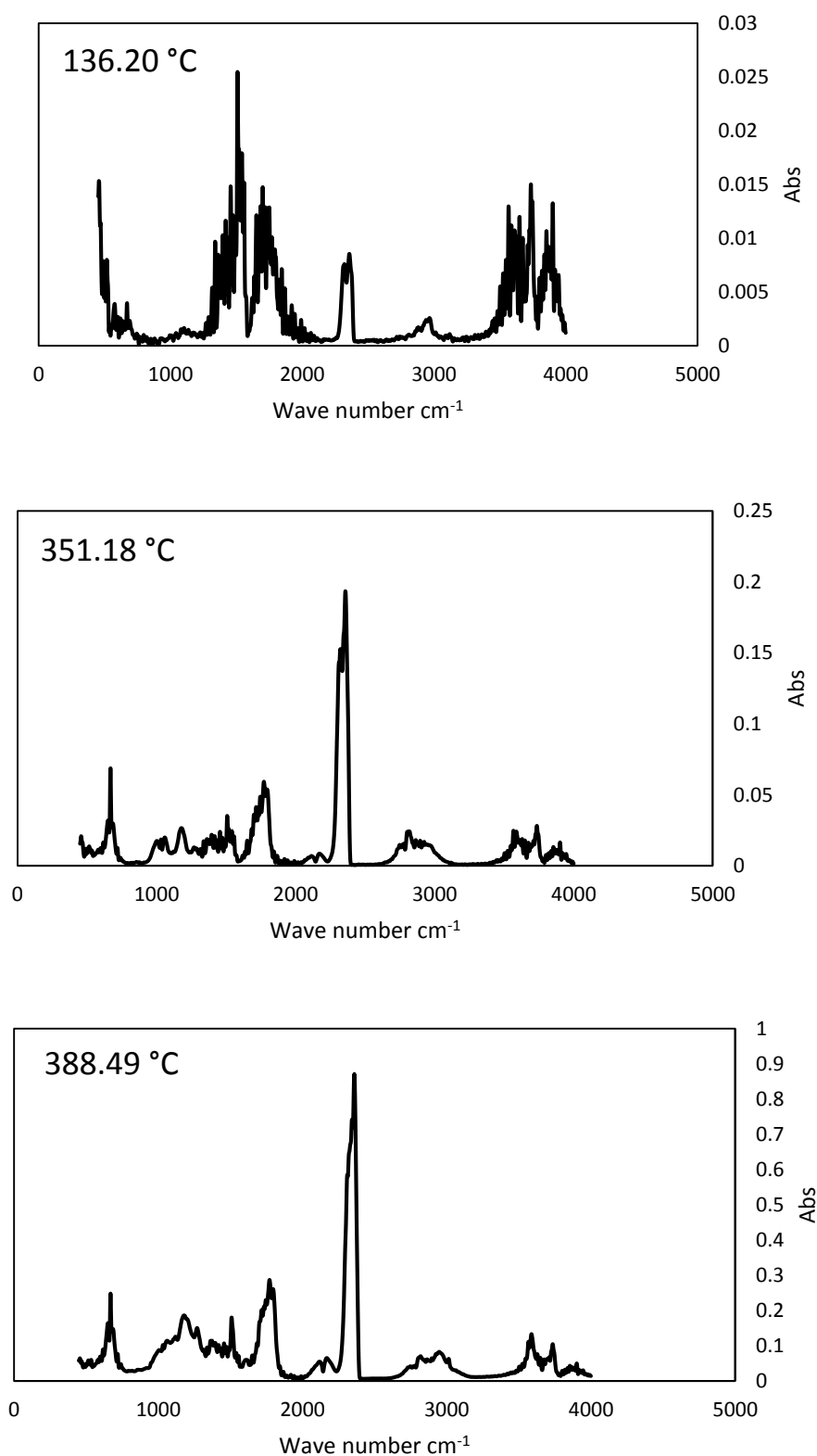


Figure 81. FTIR spectra of peach pips at 200°C/min under oxygen.