

**INVESTIGATION INTO THE CHARACTERISTICS AND POSSIBLE  
APPLICATIONS OF BIOMASS GASIFICATION BY-PRODUCTS  
FROM A DOWNDRAFT GASIFIER SYSTEM**



**University of Fort Hare**  
*Together in Excellence*

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**MASTERS OF SCIENCE IN CHEMISTRY**

**BY**

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## DECLARATION

I, Melapi Aviwe, hereby declare that the entirety of the work contained in this dissertation is my own, original work and that I have not previously in its entirety or in part submitted it at any other university for the sake of obtaining any qualification.

Signature.....

Date.....

## **DEDICATION**

I dedicate the completion of this dissertation to God as well as my family

## ACKNOWLEDGEMENTS

It has been possible to produce this dissertation through the significant contributions many people have made. The contributions are highly appreciated.

Firstly, I would like to thank God 'The Almighty' for the gift of life, with him anything is possible.

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## SUMMARY

Biomass gasification has attracted the interest of researchers because it produces zero carbon to the atmosphere. This technology does not only produce syngas but also the byproducts which can be used for various application depending on quality.

The study conducted at Melani village in Alice in the Eastern Cape of South Africa was aimed at investigating the possible applications of the gasification byproducts instead of being thrown away. Pine wood was employed as the parent feedstock material for the gasifier. Biomass gasification by-products were then collected for further analysis. The studied by-products included tar (condensate), char, soot and resin. These materials were also blended to produce strong materials. The essence of the blending was to generate ideal material that is strong but light at the same time.

The elemental analysis of the samples performed by CHNS analyser revealed that carbon element is in large quantities in all samples. The FTIR spectra showed almost similar results for all the studied samples, since the samples are end products of lignocellulose gasification. The major functional groups observed in all the samples under FTIR included C=C, O-H, C-H, C-O, C-C. Samples under XRD showed amorphous structure as they mostly absorbed within the range of  $10^{\circ}$ -  $35^{\circ}$ . SEM gave the sticky images of resin as well as porous char structures. Char showed a higher heating value of 35.37MJ/Kg when compared to other by-products samples.

**Key words:** Biomass, Gasification, By-products, Blending

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## NOMENCLATURE

XRD	X-ray Diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscope
SCFP	Scrubber Carbon Fine Particles
CO	Carbon monoxide
CH <sub>4</sub>	Methane
O <sub>2</sub>	Oxygen
CO <sub>2</sub>	Carbon dioxide
H <sub>2</sub>	Hydrogen
CCFP	Cyclone Carbon Fine Particles
HHV	Highest heating value
LHV	Lowest heating value



# CHAPTER 1

## INTRODUCTION

### 1.1 BACKGROUND TO THE STUDY

Recently, the interest of researchers towards bioenergy has increased worldwide because biomass is widely available and due to its ability of producing electricity and clean fuels [Hoogwijk *et al.*, 2009]. The hazardous emissions associated with fossil fuels has led to the preference of bioenergy. This bioenergy still remains the primary source of energy for more than half of the world's population, and accounts for 14% of the total energy consumption in the world [Zeng *et al.*, 2007]. The bioenergy production is environmentally friendly due to its zero emissions to the atmosphere.

The composition of biomass is variable depending on the source plant, but the main components are cellulose, hemicellulose and lignin and other components that are often grouped under the name extractives [Malatji, 2009 and Wu *et al.*, 2013]. Biomass depending on the species the ash content varies. Compared to agricultural biomass a woody biomass contains less ash and sulphur [Nemanova, 2014]. A typical biomass contains 0.05 – 0.20 wt. % sulphur on a dry basis, hence it is regarded as low in sulphur [Chmielniak *et al.*, 2003].

Biomass gasification is a thermochemical process whereby solid organic derived, carbonaceous feedstock is converted into a product gas which is known as the syngas. The syngas is composed of combustible hydrogen and carbon monoxide and some other gases.

Biomass gasification by-products are ash, char, tar, water and hydrocarbons. The energy efficiency in case of gasification is higher than that of combustion [Devi *et al.*, 2003].

Biomass gasification process converts carbonaceous materials into charcoal giving gas as a by-product. The process consists of several steps which include material pre-processing, gasification, product gas clean-up and gas utilization [Brar *et al.*, 2012]. The gasification step includes four sub steps that include: heating and drying of biomass feedstock, pyrolysis, oxidation and reduction. The process occurs at high temperatures ranging between 500°C to 1400°C and pressure range that runs from atmospheric pressure to 33bar [Ruiz, 2013]. It occurs in the presence of gasifying agents that can be air, steam or oxygen. A useful gas called syngas is generated by thermochemical gasification of biomass using a gasifying agent, usually air [Corella *et al.*, 2005].

## **1.2 BIOMASS IN SOUTH AFRICA**

Since the beginning of time, humans have been using biomass as an energy source. Biomass is preferred as an energy source because it is reliable and environmentally friendly than fossil fuels and it contributes zero net carbon dioxide when it is used sustainably. Therefore it is very important to develop appropriate and cost-effective technology in order to exploit biomass resources in more efficient ways (UN-Energy, 2005).

Biomass in South Africa has been used as the source of energy especially in rural areas where there is no electricity. It is the cheapest source of energy because it can be freely collected from the forests without having to pay for it. Woody biomass is one of the biomass feedstocks commonly used almost every day as an alternative way for cooking and warming up homes. The highest concentration of woody biomass usage in South Africa is in Limpopo, Eastern

Cape, North West and KwaZulu-Natal [Damm and Ralph, 2008]. The reason is because of the climatic conditions and availability of vast tracks of underdeveloped land.

South Africa has a lot of waste material thrown away by the municipality which can be so much useful in production of synthetic gas via the process of gasification rather than being incinerated. Out of 108 million of waste generated in 2011, at least 97 million tons were discarded [DEA, 2012]. The process is environmentally friendly as it produces zero carbon emission to the atmosphere. The use of biomass gasification turns trash into usable energy. The South African government, Eskom and National Energy Regulator of South Africa (NERSA) are encouraging sustainable development through the use of renewable energy as it expands the electricity generation capacity of the country in terms of research and implementation [CSIR, 2013].

### **1.3 PROBLEM STATEMENT**

Biomass gasification is an old technology that is rapidly growing in terms of research and development of projects. The technology produces a clean fuel used for electricity production and fine chemical production. However, not much attention has been given to the by-products of the process such as resultant charcoal, liquids and tarry substances that are normally regarded as waste. These by-products pose a challenge to the future of the technology, hence there is a need to consider their further utilization in other areas so as to add value to them and render the technology free of waste.

## **1.4 RESEARCH OBJECTIVES**

The research project was aimed at investigating the characteristics of biomass gasification by-products. In order to achieve this, the following aspects were studied.

- i. Investigation of the chemical and structural properties of biomass before the process of gasification.
- ii. Identification of by-products of the gasification process, their chemical and structural composition.
- iii. Investigation of the processing and use of gasification by-products for other applications.

## **1.5 RESEARCH QUESTIONS**

- i. What is the chemical and structural composition of biomass before process of gasification?
- ii. What are the by-products of biomass gasification?
- iii. How can these by-products be utilized in other areas?

## 1.6 METHODOLOGY

### 1.6.1 EXPERIMENTAL

#### 1.6.1.1 FEED MATERIAL

In the experiment, the type of biomass that was used is pine wood. Pine wood was chosen as the test material for this study due to its freely availability and low ash content generation. Pine wood gasification was undertaken in a 150kVA biomass gasifier at Melani village, Alice, Eastern Cape, South Africa. The gasifier developed by K. G. Johansson was built and installed in 2007. This was installed to produce gas to the engine that powers the nearby bakery. The construction of the gasifier was funded by Eskom. Figure 1.1 presents a flow chart of the gasification process that resulted in the products and by-products studied.

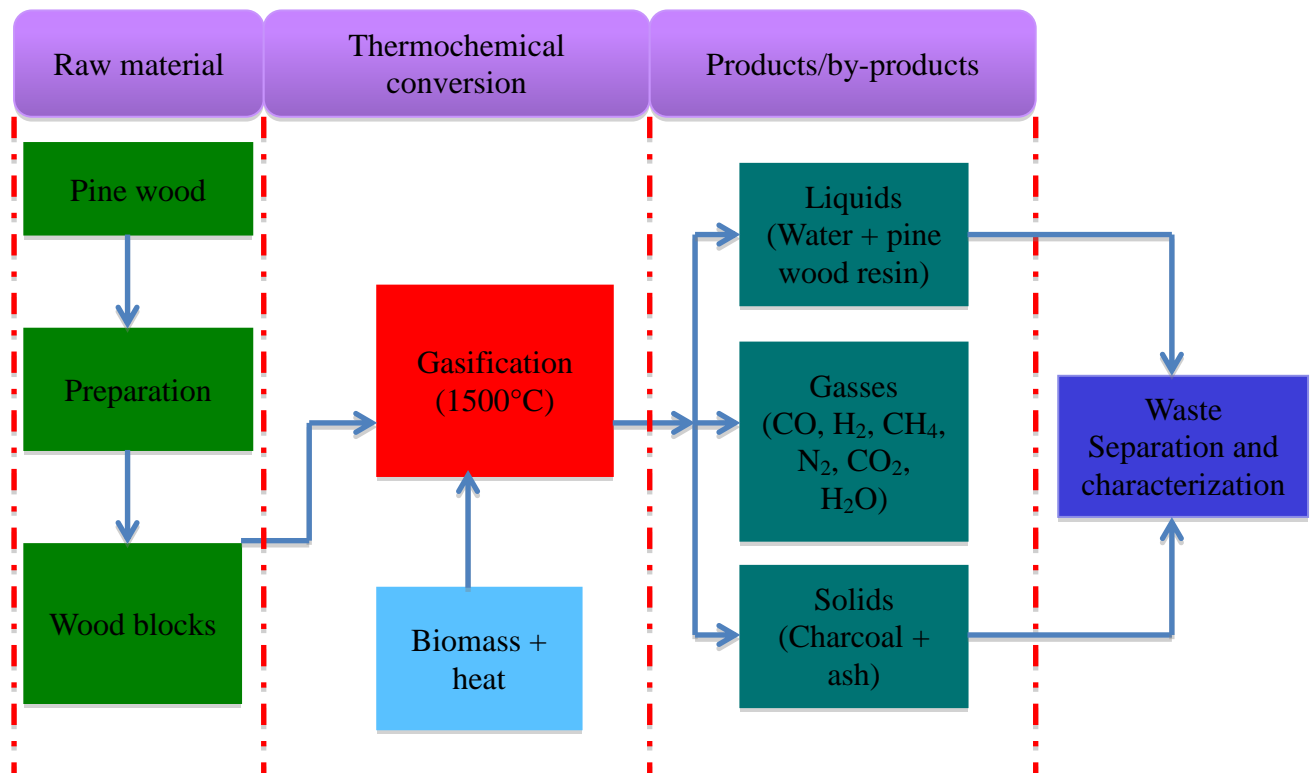


Figure 1.1: A flow chart of the gasification process for generation of the products and by-products studied

### **1.6.1.2 A DOWNDRAFT GASIFIER**

A downdraft gasifier was used to carry out the process of gasification because it produces low tar content. To commence the process of gasification, the biomass feed material is fed into the reactor through top loading zone. Biomass material should contain moisture content of less than 20% [Jared *et al.*, 2002].

The ignition of the reactor is prepared by inserting two or three sparklers. Within the reactor, biomass material is combusted with limited oxygen supply. The chemical processes that take place within the reactor are: drying, pyrolysis/carbonization, oxidation and reduction reactions. These chemical reactions are occurring simultaneously at different zones within the gasifier. Combustion occurs in the oxidation zone. Introduced air in the oxidation zone contains inert gases such as nitrogen and argon; these gases are considered to be not reactive with the constituents of the fuel [Mamphweli and Meyer, 2010].

Eventually, the unconverted char and ash pass through the bottom of the grate and are sent to disposal. The condensates are collected via condensate tank for disposal. Figure 1.2 presents the downdraft gasifier with different zones.

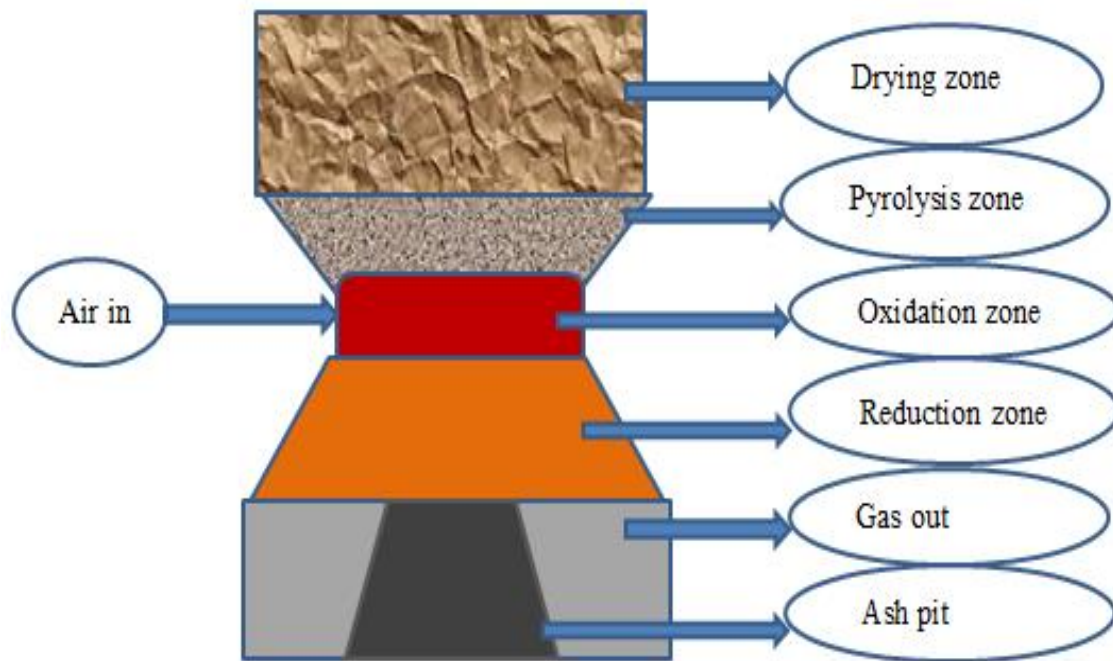


Figure 1.2: Downdraft Gasifier with different zones [adapted from Bhavanam Sastry, 2011]

## 1.6.2 MATERIAL CHARACTERIZATION

The improvement of energy conversion process for biomass requires an understanding of the chemical composition and behaviour of the biomass to be converted. The composition of pinewood was determined using ultimate and proximate analyses with a view to establish not only its composition but also its thermal parameters as well as its energy content. The by-products of pinewood gasification were also characterized to establish their potential for utilization in other areas such as polymers, chemical industries, medicines, fragrances, filtration, etc. The ultimate analysis includes elemental analysis of the dominating elements such as Carbon (C), Oxygen (O<sub>2</sub>), Nitrogen (N), Hydrogen (H<sub>2</sub>), and Sulphur (S). The proximate analysis was undertaken to determine moisture content, volatile matter, fixed carbon and ash content. The characterization also included Oxygen Bomb Calorimeter, SEM, CHNS, XRD as well as FTIR analysis.

## **1.7 DELINEATION AND LIMITATIONS**

The study investigated the characteristics and the applications of the by-products produced from a 150kVA downdraft gasifier. It involved the ultimate and proximate analysis of the by-products as well as characterization using different techniques. The possible applications of the by-products in other areas were then studied based on the obtained results. The research did not focus on the syngas produced, its purification and utilization. The mass and energy balance of the system were neglected.

## **1.8 RATIONALE/ SIGNIFICANCE OF THE STUDY**

The need for imported fossil fuels could be decreased by increasing the production of energy fuels from woody waste material [Puettmann, 2012]. Bioenergy is renewable and easily accessible. Its easy accessibility implies that it is cheap and affordable. It is one of the most widely used bio-fuel because it is a reliable, environmentally friendly renewable source than fossil fuels and it reduces carbon dioxide emission. Biomass offers great potential to decrease production of greenhouse gas [Dogru, 2002]. The gases produced from the process of biomass gasification can be converted to biofuels and chemicals such as Fischer-Tropsch fuels, green gasoline, hydrogen, dimethyl ether, ethanol, methanol, and higher alcohols [Kumar *et al.*, 2009].

It is estimated that 90% of world energy consumption comes from fossil fuels. The use of fossil fuels as an energy causes serious social and economic problems. The main environmental problem is the global warming.

The design and the operation of biomass combustion systems significantly relies on biomass characteristics such as the heating value, moisture content, elemental composition, ash properties, etc. Therefore it is of great importance to characterise physical and chemical properties of biomass and its products. Many researchers have worked on biomass gasification but did not put the focus on by-products of gasification. Hence it is important to focus on the environmental aspect. This project was aimed at bridging this information gap since not much work has been done on this perspective. The success of the study will help in keeping the expected life span of the gasifier with reduced clogging and other problems.

## **1.9 DEFINITION OF TERMS**

The following terms are frequently used throughout the dissertation and should be vividly understood as defined in this section unless the context suggests otherwise.

***Biomass*** refers to organic matter that can be used as a fuel.

***Biomass gasification*** is a thermochemical process that converts organic material to syngas under a controlled supply of air, oxygen or even steam.

***By-products*** are unwanted products of the gasification process which are normally regarded as waste.

***Cyclone carbon fine particles*** are fine particles of carbon trapped in cyclone part of the gasifier system as the gas passes for purification.

*Gasifier* is the reactor component of the gasification system.

*Gasifier tar/resin* tarry hydrocarbons released from devolatilization stage of gasification process to the condensate tank

*Pure material* refers to unblended samples

*Pyrolysis* refers to thermal destruction of organic material in the absence of oxygen.

*Scrubber carbon fine particles* are fine particles of carbon that managed to escape with scrubber water during gas purification.

*Syngas* is a mixture of gases primarily consisting of hydrogen, carbon monoxide and some carbon dioxide.

## **1.10 DISSERTATION OUTLINE**

This dissertation is divided into five chapters. A summary of the five chapters and an overview of the scope of the study is provided in this section.

Chapter one provides the background of the study. The objective of the research and research questions are presented in this chapter. The significance of the study is explained in this chapter. Limitations and delineation of the study are also presented in this chapter

Chapter two is a synthesis of the relevant literature on the composition and properties of biomass materials. The various types of gasifiers have been discussed in this chapter with their advantages and disadvantages. The biomass gasification by-products have been identified and discussed. The various uses of the by-products of the gasification process are also presented in this chapter.

Chapter three presents the methodology of the research used to collect data. These include ultimate analysis. The different instruments used to acquire various data sets to achieve the objectives of this study are presented and discussed in this chapter

Chapter four presents the results obtained for this research. These results include proximate and ultimate analysis. The spectra results obtained from XRD and FTIR are presented in this chapter. The elemental analysis and images of the analytes are presented. The calorific values of the measured samples are also presented in this chapter.

Chapter five provides summary, conclusion and recommendations of the study. This is where the major contributions of the research are presented and a conclusion drawn from the results is also presented in this chapter. The conclusion was based on the objectives of the study.

In addition to the five chapters, there is also an appendix section that presents the research outputs associated with this work.

## **CHAPTER 2**

### **REVIEW OF LITERATURE**

#### **2.1 BIOMASS FEEDSTOCK**

Biomass is the organic matter that can be used to produce fuels, chemicals, electricity and other products. Biomass resources include agricultural residues, animal manure, wood wastes from forestry and industry, residues from food and paper industries, municipal green wastes, sewage sludge [Muzee, 2012]. The chemical composition varies with the type of biomass material but the fundamental components of the plant biomass include cellulose, hemicellulose, lignin and some extractives. The preparation and properties of the biomass feedstock are key design parameters when choosing the gasifier system [McKendry, 2002 (3)]. Low moisture content biomass feedstock is used in thermo-chemical gasification process and high moisture content in the bio-chemical process.

##### **2.1.1. TYPES OF BIOMASS**

Some of the types of biomass include: woody biomass material, aquatic plants, grasses/ herbaceous plants, agricultural residues and waste from municipality. Figure 2.1 presents different sources of biomass.



Figure 2.1: Different types of biomass sources [Biomass Innovation Centre, 2013; Chhiti *et al.*, 2011]

### 2.1.2 CHEMICAL COMPOSITION OF BIOMASS

Each and every biomass type is composed of carbon, hydrogen, and oxygen as major chemical constituents and the fractions of these elements can be quantitatively measured with the ultimate analysis [Bhavanam and Sastry, 2011]. The chemical composition of biomass varies with the type of biomass. Different types of biomass are composed of different chemical structures; hence their reactivity will also not be the same. The elements commonly found in biomass include: C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, and Ti and these elements are arranged in decreasing order of their abundance [Vassilev *et al.*, 2010].

### 2.1.2.1 CELLULOSE

Cellulose is a water insoluble, fibrous, tough material that prevents damage of the cells and maintains structure of the plant cell wall [Habibi *et al.*, 2009]. It is a polysaccharide structure of  $\beta$ -D glucopyranose unit joined together with (1-4) glycosidic bonds. Glycosidic bond joins carbohydrates to another group, which may or may not be carbohydrate between hemiacetal group of a saccharide and hydroxyl group. Repeating  $\beta$ -D glucopyranose units and three hydroxyl groups per anhydroglucose unit (AGU) give the cellulose molecule a high degree of functionality [Peng *et al.*, 2011]. The cellulose structure is crystalline, which is unusual for a polysaccharide and this crystallinity of cellulose vary with respect to its source [FitzPatrick, 2011]. The chemical structure of cellulose is presented in Figure 2.2.

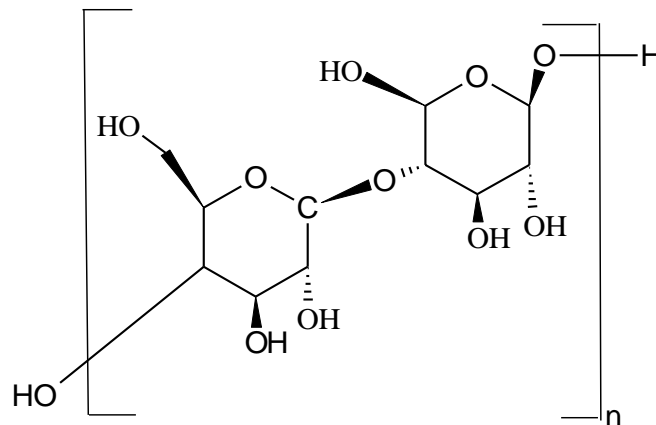


Figure 2.2: The simpler chemical structure of Cellulose [Adapted from FitzPatrick, 2011]

### 2.1.2.2 HEMICELLULOSE

Hemicellulose is a polysaccharide made up of different sugars. The hemicellulose fraction of lignocellulosic biomass is an amorphous polymer that is generally comprised of five different

sugar monomers, D-xylose, L-arabinose, D-galactose, D-glucose, and D-mannose, with xylose being the most abundant [Alonso *et al.*, 2010]. The five saccharides are grouped into hexoses (glucose, mannose and galactose) and pentoses (xylose, arabinose). The difference between cellulose and hemicellulose is that hemicellulose is a branched polysaccharide whereas cellulose is linear polysaccharide. The chains of hemicellulose are shorter when compared to simpler cellulose, they can be branched and have side attaching groups like acetyl groups and monosaccharides [FitzPatrick, 2011]. The structure of hemicellulose is presented in Figure 2.3.

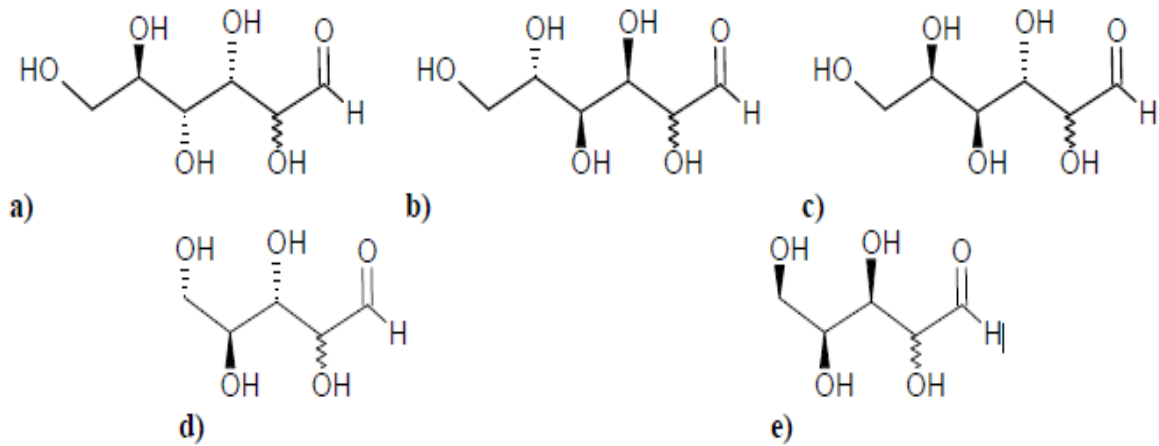


Figure 2.3(a): Structure of primary sugar groups in Hemicellulose. a) Glucose, b) Mannose, c) Galactose, d) Xylose, e) Arabinose [FitzPatrick, 2011]

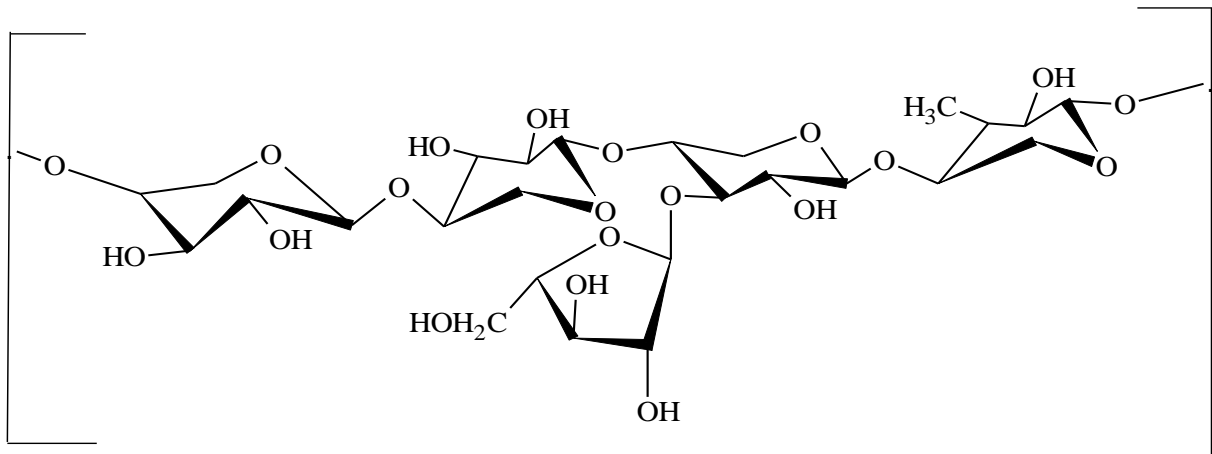


Figure 2.3(b): Represents the complete chemical structure of Hemicellulose [Adapted from Astner, 2012]

### **2.1.2.3 LIGNIN**

Lignin provides plants with rigidity structure and a hydrophobic vascular system for the transportation of water and solutes. It surrounds the hemicellulose and cellulose fractions. Lignin can be removed from biomass to isolate the carbohydrate fraction through depolymerisation/ solubilisation in alkaline-alcohol solutions. Residual lignin can be collected following pre-treatment and acid or enzymatic hydrolysis for the extraction of pentose and hexose sugars [Alonso *et al.*, 2010]. Lignin limits the degradation of structural polysaccharides by hydrolytic enzymes [Grabber, 2005]. Lignin structure depends on wood species as well as the location of the lignin within the plant; softwoods generally have higher lignin content (26–34%) than hardwood (23–30%) [Amaral *et al.*, 2014 and FitzPatrick, 2011]. The structure of the lignin is illustrated in the Figure 2.4.

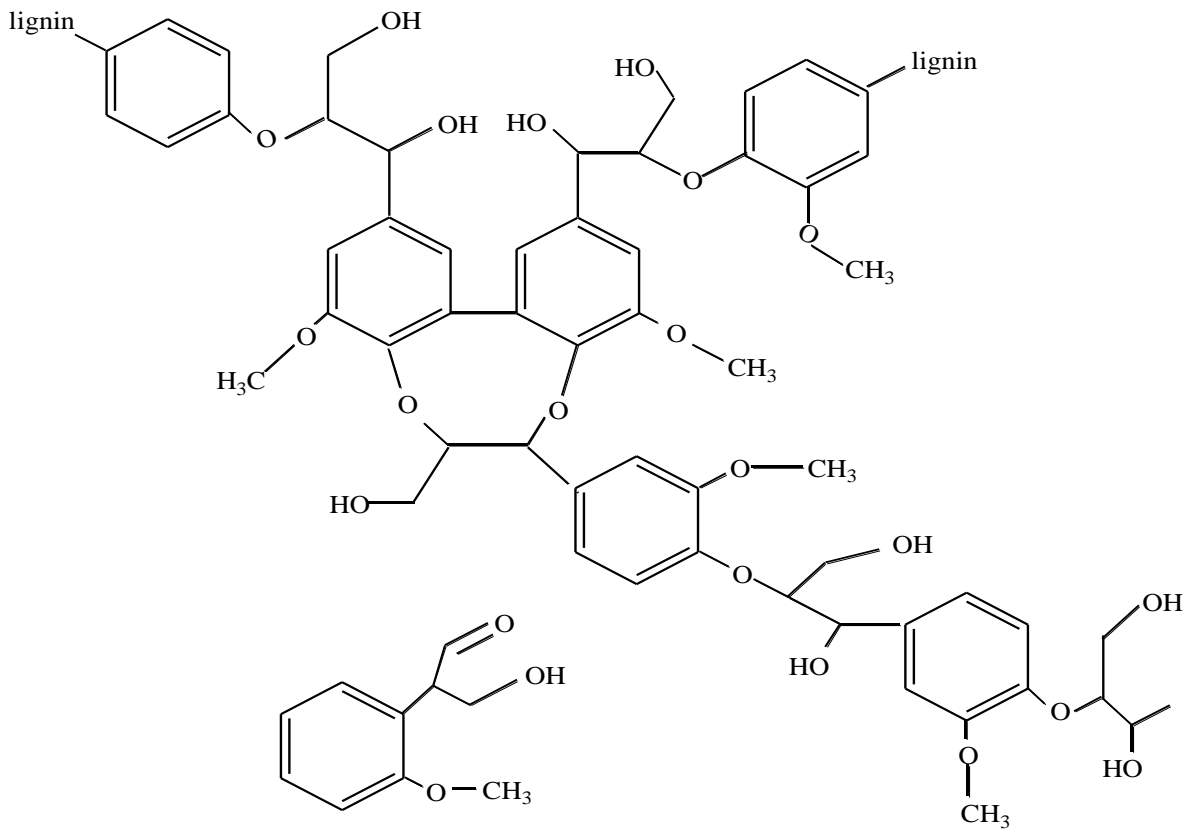


Figure 2.4: The chemical structure of lignin [SMRI, 2011]

## 2.2 PROPERTIES OF BIOMASS

### 2.2.1 PHYSICAL PROPERTIES

The physical properties of biomass include the calorific value, bulk density, alkali metal content, ash/ residue content, moisture content, proportion of fixed carbon and volatiles. An overview of these properties is as follows:

### **2.2.1.1 CALORIFIC VALUE (CV)**

Calorific value (CV) refers to the amount of heat released when the biomass material is combusted. It is one of the most important properties of biomass fuels for design calculations or numerical simulations of thermal conversion systems for biomass [Sheng and Azevedo, 2005]. Calorific value is quantified in terms of the energy content per unit mass, or volume. In gaseous phase the units of measurements are MJ/Nm<sup>3</sup>, MJ/kg for solid state and MJ/l for liquids.

The calorific value of a fuel is categorized into two forms, which are higher heating value (HHV) and lower heating value (LHV). Higher heating value (HHV) is the maximum amount of energy that can be potentially recoverable from a certain biomass material, whereas lower heat value (LHV) is the energy available for use [McKendry, 2002(1)]. The calorific value of a given biomass is greatly reduced by its high moisture content. The higher heating value includes the latent heat of vaporization for the moisture in the material, which is not available for use whereas the lower heating value excludes this energy.

### **2.2.1.2 BULK DENSITY**

Bulk density is defined as the weight of biomass material divided by volume occupied by biomass. Bulk density is one of the most significant characteristics of biomass both as produced and as-subsequently processed. The importance of the as-produced, bulk density is in relation to transport and storage costs. The density of the processed product impacts on fuel storage requirements, the sizing of the materials handling system and how the material is likely to behave during subsequent thermo-chemical/bio-chemical processing as a

fuel/feedstock. Bulk density of biomass material is increased by transportation, handling, and storage, this can be caused by compaction due to vibration, tapping, or normal load [Chevanan *et al.*, 2010].

#### **2.2.1.3 ALKALI METAL CONTENT**

Alkali metal content of biomass is significant for thermo-chemical conversion process. Alkali metals react with silica found within the ash to produce a sticky, mobile liquid state, which can lead to obstructions of air routes within the furnace and boiler plant [McKendry, 2002(1)]. Alkali compounds evaporate at high temperatures above 700°C during gasification, below 650°C when condensed and form particles (<5 µm) in downstream equipment [Kumar *et al.*, 2009]. They stick to metal surfaces, which ends up in corrosion. Alkali salts reform and converts syngas into hydrocarbons by inactivating the catalyst used in tar cracking if a catalyst is used for this purpose.

#### **2.2.1.4 ASH CONTENT**

Ash is the non-combustible content of biomass. Ash content is derived from the conversion of biomass feedstock to fuel by thermo-chemical process. Biomass ash predominantly consists of elements, such as potassium, calcium, sulphur, sodium, iron, silicon and other trace elements [Malatji, 2009]. High ash content causes pollution problems. Wood core (without bark) has less than 1% ash and its bark can have up to 3% ash [Clarke *et al.*, 2011]. In a thermo-chemical conversion process, the chemical composition of the ash can show some operational problems because during combustion the ash can react to form a stony waste

matter [McKendry, 2002(1)]. More ash content implies more equipment maintenance. The high ash content also, implies lower energy value of the biomass material.

#### **2.2.1.5 MOISTURE CONTENT**

Moisture content of biomass refers to the amount of water found in the biomass and is normally expressed as percentage of the material weight. High moisture content decreases the temperature in the oxidation zone, which then results in the incomplete combustion of the hydrocarbons released from the pyrolysis zone. The low moisture content of feedstock increases the heating value [Ghassemi and Shahsavan-Markadeh, 2014]. The upper limit of moisture content acceptable is around 40% on dry basis in downdraft reactor, while higher values of moisture content could be used in updraft reactor [Bhavanam and Sastry, 2011]. Biomass material can undergo thermochemical or biochemical conversion process. High moisture content of a feedstock favours biochemical process (fermentation), while thermochemical conversion process is favoured by low moisture content.

#### **2.2.1.6 PROPORTION OF FIXED CARBON AND VOLATILES**

Fixed carbon (FC) is defined as the remaining material after the determination of volatile matter, moisture content, and ash content. The amount of fixed carbon determines the efficiency of the biomass conversion equipment. Volatile matter (VM)/Volatile content of a solid material is the percentage released in form of a gas (including moisture content) by combustion.

Volatile matter (VM) and fixed carbon (FC) contents are significant because they provide a measure of simplicity with which the biomass can be ignited and gasified, or oxidised, depending on how the biomass is to be utilized as a source of energy [McKendry, 2002(1)].

## **2.3 CONVERSION OF BIOMASS**

When biomass material is collected, many conversion processes are allowed to take place during its conversion to energy. The biomass material can be converted through biological or thermochemical conversion processes. Thermochemical gasification process of biomass produces a useful gas (a mixture of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, small hydrocarbons) using a gasifying agent, usually air [Corella *et al.*, 2005]. In biological process biogas is produced by conversion of biomass material by bacteria. Biogas is mainly composed of carbon dioxide and methane.

### **2.3.1 THERMO-CHEMICAL CONVERSION PROCESS**

There are three main thermochemical conversion processes for biomass materials, and they are:

- I. Combustion Process
- II. Pyrolysis
- III. Gasification Process

The research is focussed on biomass gasification; therefore the two other processes will not be discussed in this research.

### **2.3.1.1 GASIFICATION PROCESS**

The generation of syngas in the presence of heat with limited oxygen supply from an organic feedstock is known as the gasification process. However, this process does not only produce syngas but by-products as well. The syngas formed is contaminated by some constituents such as particles, alkali metals, nitrogen components, tars, sulfurs and chlorides [Couto *et al.*, 2013]. Biomass gasification occurs under extremely high temperatures that can rise up to 1500°C. Inside the gasifier system the loaded feedstock gets through dehydration zone, devolatilization zone, oxidation zone and eventually reach reduction zone. During gasification process, air, pure oxygen, steam or a mixture of these gases is used as gasifying agent [Bhattacharya *et al.*, 2014 and Jared *et al.*, 2002]. The process of gasification includes both biochemical and thermochemical processes. The quantity of produced volatiles and their compositions depend mainly on the type of gasifier, temperature, as well as the characteristics of fuel material.

### **2.4.1 TYPES OF GASIFICATION PROCESSES**

Figure 2.5 presents the processes of biomass gasification.

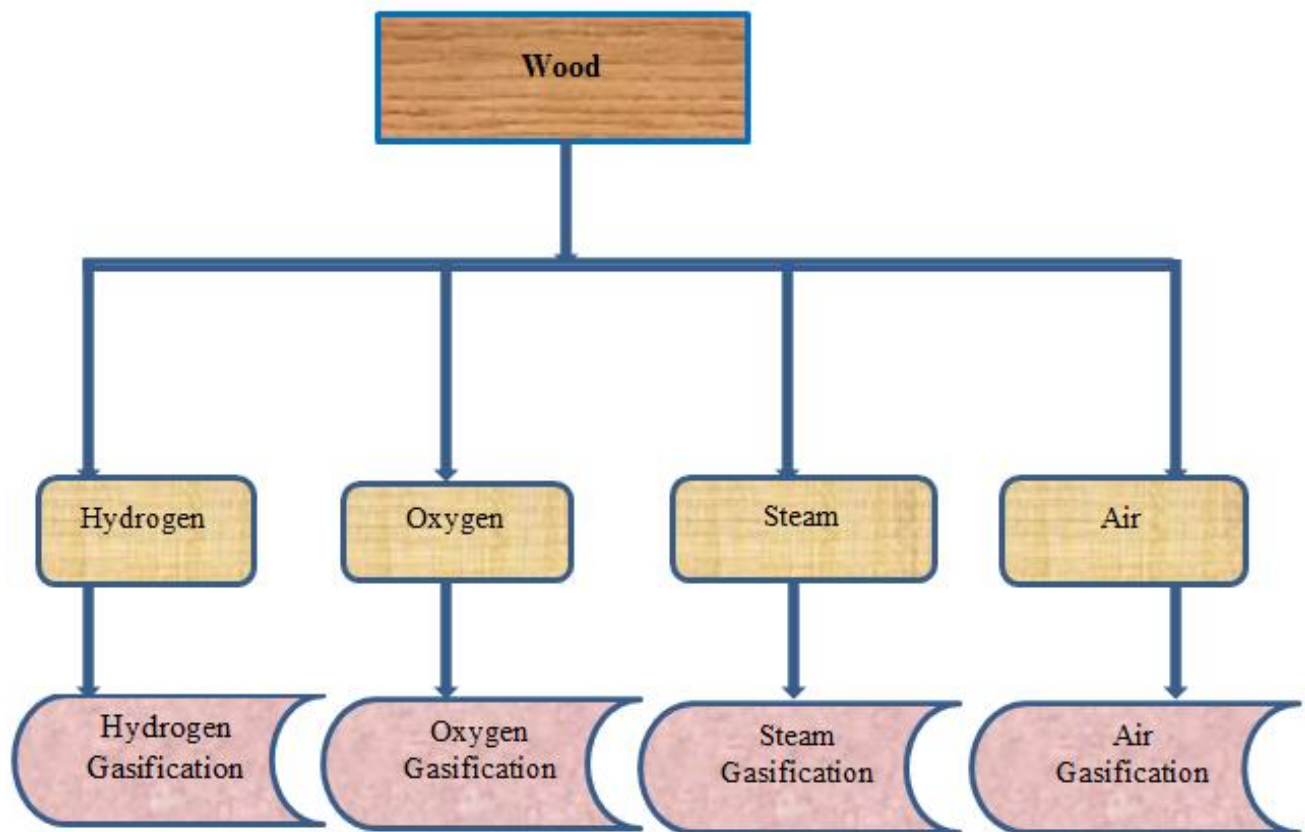


Figure 2.5: Biomass gasification process [Adapted from Sadaka *et al.*, 2002]

#### 2.4.1.1 HYDROGEN GASIFICATION

Hydrogen can be used as one of the reactive agent in gasification, but its use requires high pressure. It is of great importance to monitor the reaction conditions since the majority of the products are normally in the gaseous state. This process is unfavourable because of the degree of control necessary as well as the fact that hydrogen must be readily available [Sadaka *et al.*, 2002].

#### 2.4.1.2 OXYGEN GASIFICATION

Oxygen-based gasifiers produce a product gas containing a relatively high concentration of hydrogen and CO with a heating value between 10 and 20 MJ/m<sup>3</sup> [Jared *et al.*, 2002 and

Shrivastava, 2012]. The use of oxygen rather than air as the gasifier agent decreases the quantity of nitrogen supplied to the gasification reactions, which creates a medium energy syngas that is much lower in nitrogen and higher in methane, hydrogen and carbon monoxide [Sadaka *et al.*, 2002]. Oxygen gasification results in high content of CO, H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O with a relatively low methane and tar content [Wiinikka *et al.*, 2014]. Medium energy syngas can be used for a wide variety of applications and can be transported through a pipeline due to its relatively low tar content. A drawback to the use of oxygen as a reactive agent is the need for a nearby source of oxygen, which may increase capital and operating costs.

### 2.4.1.3 STEAM GASIFICATION

Steam-based gasifiers produce a product gas containing a relatively high concentration of hydrogen and carbon monoxide with a heating value between 10 and 20 MJ/m<sup>3</sup>. In steam gasification, steam can be added from an external source or obtained from the water vapour within the fuel. Syngas energy produced from gasification in the presence of steam is at high levels when compared to the air as a gasifying agent. Steam gasification generates more tar in the producer gas than air gasification [Hejazi *et al.*, 2014]. Steam gasification is used to recycle waste in a bubbling fluidized reactor [Slapak *et al.*, 2000]. The reaction of steam and carbon monoxide produces hydrogen and carbon dioxide. The principal gas-phase reaction in the steam gasification system is the water gas-shift reaction:



Under low temperature conditions, low heat rates and high pressure, secondary reactions involving tars occur, but these reactions are not as prevalent under conditions of low pressure, high temperature and high heat rates. Gasification in the presence of steam as a gasifying

agent produces a higher energy product gas relative to using air as the gasifying agent [Hosseini *et al.*, 2012].

#### **2.4.1.4 AIR GASIFICATION**

Air-based gasifiers normally produce a syngas containing a relatively high nitrogen concentration with a low heating value ranging between 4 and 6 MJ/m<sup>3</sup> [Bhattacharya *et al.*, 2014 and Jared *et al.*, 2002]. During air gasification, the nitrogen dilutes the produced gas and softens the increase of some parameters. Air-blown gasification process is a simpler technique in comparison to oxygen or steam-blown gasification [Kim *et al.*, 2013]. The excess char content produced from the pyrolysis process within the reactor is burned with a limited supply of air.

In air gasifiers, the temperature of the gasifier depends on biomass feed rate and the rate of air flow, if the inlet air is low, the system results in low bed temperature which produces low gas and higher levels of tar. Air gasification is a less complicated technology therefore many researchers are strongly using it for various types of biomass.

#### **2.4.2 MECHANISM OF GASIFICATION**

During gasification, as gasifying agent passes through the fuel bed a lot of processes are taking place. The processes that occur are drying, pyrolysis, oxidation and reduction. The location of the reaction zones primarily depends on the relative movement of the fuel and air. The depth and importance of each stage highly depends on the chemical composition of the feedstock, its moisture content and particle size, the mass current of the gasifying agent, and

the temperature [Sadaka *et al.*, 2002]. The temperatures of the reactions vary from zone to zone. Figure 2.6 presents the different zones within the downdraft gasifier system.

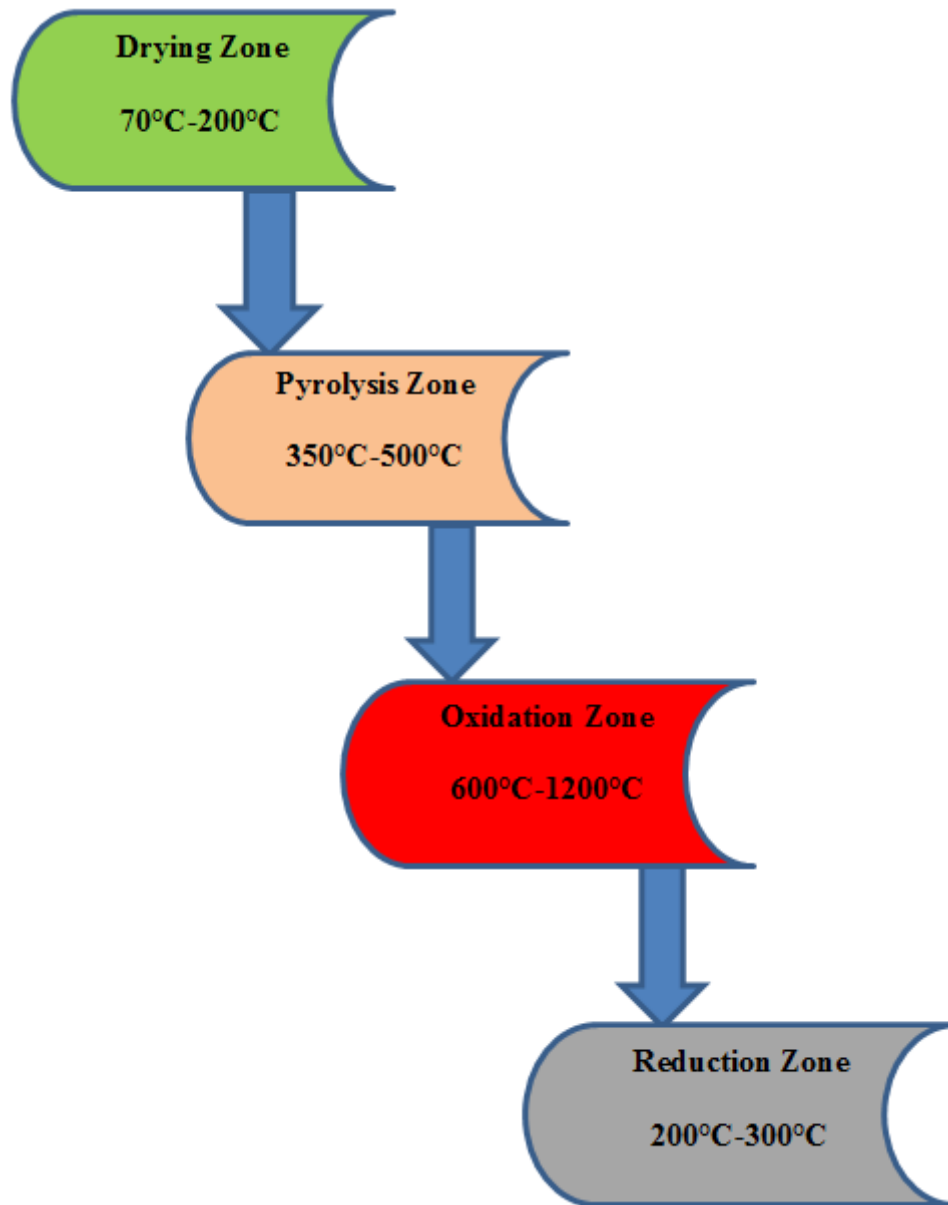


Figure 2.6: Different zones of downdraft gasifier

#### **2.4.2.1 DRYING /DEHYDRATION ZONE**

This is a zone where moisture is reduced using the heat. The rate of drying of biomass mainly depends on the surface area of the biomass material, the temperature difference between the feed and the hot gases, the re-circulation velocity and relative humidity of these gases as well as the internal diffusivity of moisture within the fuel [Dogru *et al.*, 2002]. The temperature of drying zone is about 70–200°C.

#### **2.4.2.2 PYROLYSIS ZONE**

Pyrolysis zone is where the dried biomass is thermally broken down into char, tar and gases in the absence of air. In pyrolysis zone, the irreversible thermal degradation of dried fuel descending from the drying zone takes place using the thermal energy liberated by the partial oxidation of the products of pyrolysis. The pyrolysis zone produces solid char, condensates and gas mainly composed of CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and higher hydrocarbons [Jaojaruek and Kumar, 2009]. The temperature of the pyrolysis zone is approximately 350–600°C. The pyrolysis oil produced can further be converted into chemicals and fuels [Anderson *et al.*, 2013 and Gujar *et al.*, 2014].

#### **2.4.2.3 OXIDATION ZONE**

Combustion occurs in the oxidation. This combustion is due to the introduction of air that contains inert gases such as nitrogen and argon, these gases considered to be non-reactive [Mamphweli and Meyer, 2009(a)]. In oxidation zone, the volatile products produced from pyrolysis are oxidised partially in highly exothermic reactions resulting in a speedy increase

in temperature up to 1200°C in the throat region and the heat generated is used to drive the drying and pyrolysis of the fuel and the gasification reactions. Gas is consumed before it can spread to the surface of the char; this is due to the rapid reactivity of the volatiles. When air is used as a gasifying medium its oxygen content decreases from 21% to 0%, while the carbon dioxide percentage increases proportionally [Sadaka *et al.*, 2002]. The injected gas then reacts with tar and char to yield carbon dioxide and water. The combustion is generally noted by the yellow flames [Zhang *et al.*, 2010].

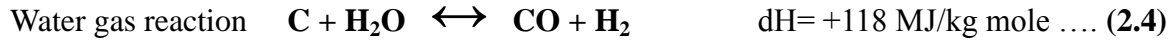
#### 2.4.2.4 REDUCTION ZONE/ GASIFICATION ZONE

Reduction zone is commonly known as gasification zone. In this zone, the char is converted to the produced gas by reaction with the hot gases from the upper zones and the gases are reduced to form a greater proportion of H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>2</sub> [Midilli *et al.*, 2001]. The combustible gases leave the gasifier at a temperature between 200 and 500°C and are loaded with dust, pyrolytic products (tar) and water vapour. The collected gas products are then cooled and cleaned to remove the unnecessary contaminants.

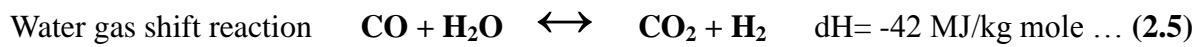
#### 2.4.3 BASIC CHEMISTRY OF BIOMASS GASIFICATION

During the process of gasification, many chemical reactions are taking place within the reactor. The occurring reactions are summarised as follows :





For the latter three processes, the heats of reaction divulge that the largest energy release is coming from the complete oxidation of carbon to carbon dioxide (combustion), while the partial oxidation of carbon to carbon monoxide (CO) accounts for only about 65% of the energy released during complete oxidation. Carbon monoxide (CO), hydrogen (H<sub>2</sub>) and steam (H<sub>2</sub>O) can undergo further reactions during gasification as follows:



The negative heats of reaction imply that the reactions are exothermic while endothermic reactions have positive heat of reaction. The reactions are in equilibrium and they can yield more of the reactants or more of the products depending on the temperature, pressure and concentration of the reacting species [McKendry, 2002(3)].

## 2.5 TYPES OF GASIFIERS

Gasifiers are classified according to the way air or oxygen is introduced in it, the air introduced then interacts with biomass within the gasifier. The gasifiers can be classified as fixed bed gasifier and fluidised bed gasifier. Fluidised bed gasifiers are divided into bubbling fluidized gasifier and circulating fluidized gasifier, while fixed bed gasifiers consist of downdraft, updraft and cross-draft gasifiers. Classification of the gasifiers is based on the means of supporting the feedstock material in the gasifier, the direction of the flow of both the feedstock and gasifying agent, as well as the way heat is supplied to the reactor.

### **2.5.1 FIXED BED GASIFIER**

The fixed bed reactors have been the traditional process used for gasification, being operated at temperatures around 1000°C. Fixed bed gasifier can be countercurrent, co-current or crosscurrent flow of mass [Warnecke *et al.*, 2000]. Each gasifier is named by the direction of the reactive material which can be air or steam. Fixed bed gasifier has a grate at the lower section of the reactor which supports the fuel. Fuel is loaded from the top of the gasifier and will be stationary on the grate. The grate is then moved by the external handle to ensure that the fuel bed is properly reacted.

#### **2.5.1.1 DOWNDRAFT GASIFIER**

Downdraft gasifier is also known as co-current flow gasifier. The mechanical configuration is the same as the updraft reactor except that the air and producer gases flow down the gasifier, in the same direction as the biomass. The downdraft gasifier is cheaper and produces low tar (~0.1%) during gasification [Singh *et al.*, 2014]. Downdraft gasifier uses feedstock with moisture content of less than 25% [Prokkola *et al.*, 2014]. The moisture content vaporized from the biomass material enters the gasification zone and serves as a gasifying agent.

The biomass material is introduced at the top of the gasifier, and the reactive agent is introduced through a set of outlets on the side of the gasifier. The introduced biomass goes through the drying zone, pyrolysis zone, oxidation and reduction zone. Air and biomass are ignited in the reaction zone at the top of the gasifier. The syngas with less tar content leaves the gasifier from the bottom. The final product gases, which leave the reactor from the bottom at a fairly high temperature (700°C) containing less tar content than the updraft

gasifiers. This type of a gasifier produces the cleanest syngas containing less than  $1\text{g}/\text{Nm}^3$  tar content [Menya, 2012].

The less tar content decreases the need for syngas cleaning. The solid unconverted residue forms an ash pit at the bottom of the gasifier, the ash pit then gets discarded. Figure 2.7 illustrates a downdraft gasifier system with different processes.

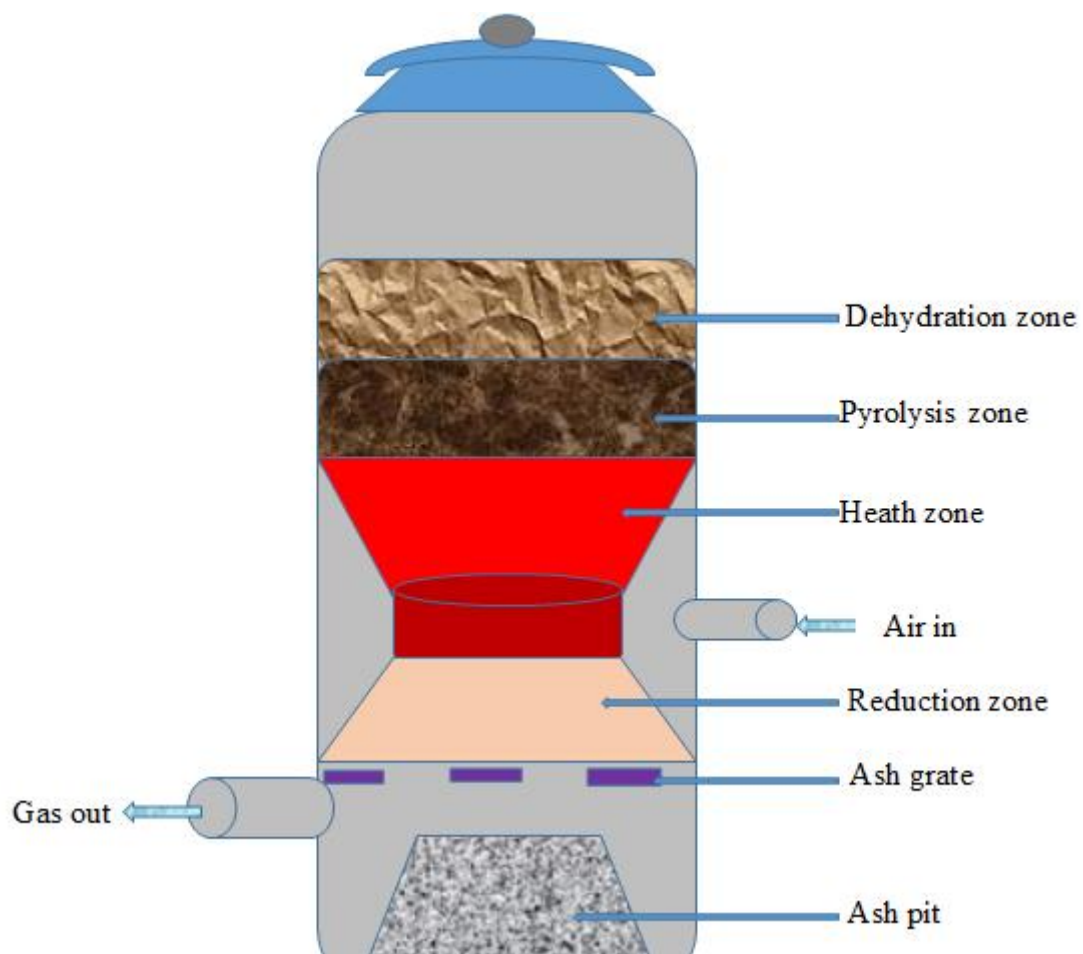


Figure 2.7: Downdraft gasifier [Adapted from Mamphweli and Meyer, 2009]

**a) Advantages of Downdraft gasifier** [Guo *et al.*, 2014; Jared *et al.*, 2002 Rajvanshi, 1983]

- i. Flexible adaptation of gas production to load
- ii. Low sensitivity to charcoal dust and tar content of fuel
- iii. Up to 99.9% of the tar formed is consumed, requiring minimal or no tar clean-up in the gas
- iv. Minerals remain with the char/ash, reducing the need for a cyclone
- v. Proven, simple and low cost process

**b) Disadvantages of Downdraft gasifier** [Jared *et al.*, 2002; Rajvanshi, 1983; Reed and Das, 1988 and Shrivastava, 2012]

- i. Design tends to be tall
- ii. Not feasible for very small particle size of fuel
- iii. Requires feed drying to a low moisture content (<20%)
- iv. Syngas exiting the reactor is at high temperature, requiring a secondary heat recovery system
- v. About 4-7% of the carbon remains unconverted

#### **2.5.1.2 CROSS-DRAFT GASIFIER**

In cross-draft gasifier, the operations are the same as downdraft except that the syngas is produced on the opposite side. The air is introduced near the bottom of the gasifier and product gas is given off on the opposite side. The oxidation and drying zones are

concentrated on the sides of the gasifier [Sadaka *et al.*, 2002]. Ash is removed at the bottom and the temperature of the gas leaving the unit is about 800–900 °C, as a consequence this gives a low overall energy efficiency of the process and a gas with high tar content [McKendry, 2002(3)]. The diagram in Figure 2.8 shows different processes occurring in the cross-draft gasifier.

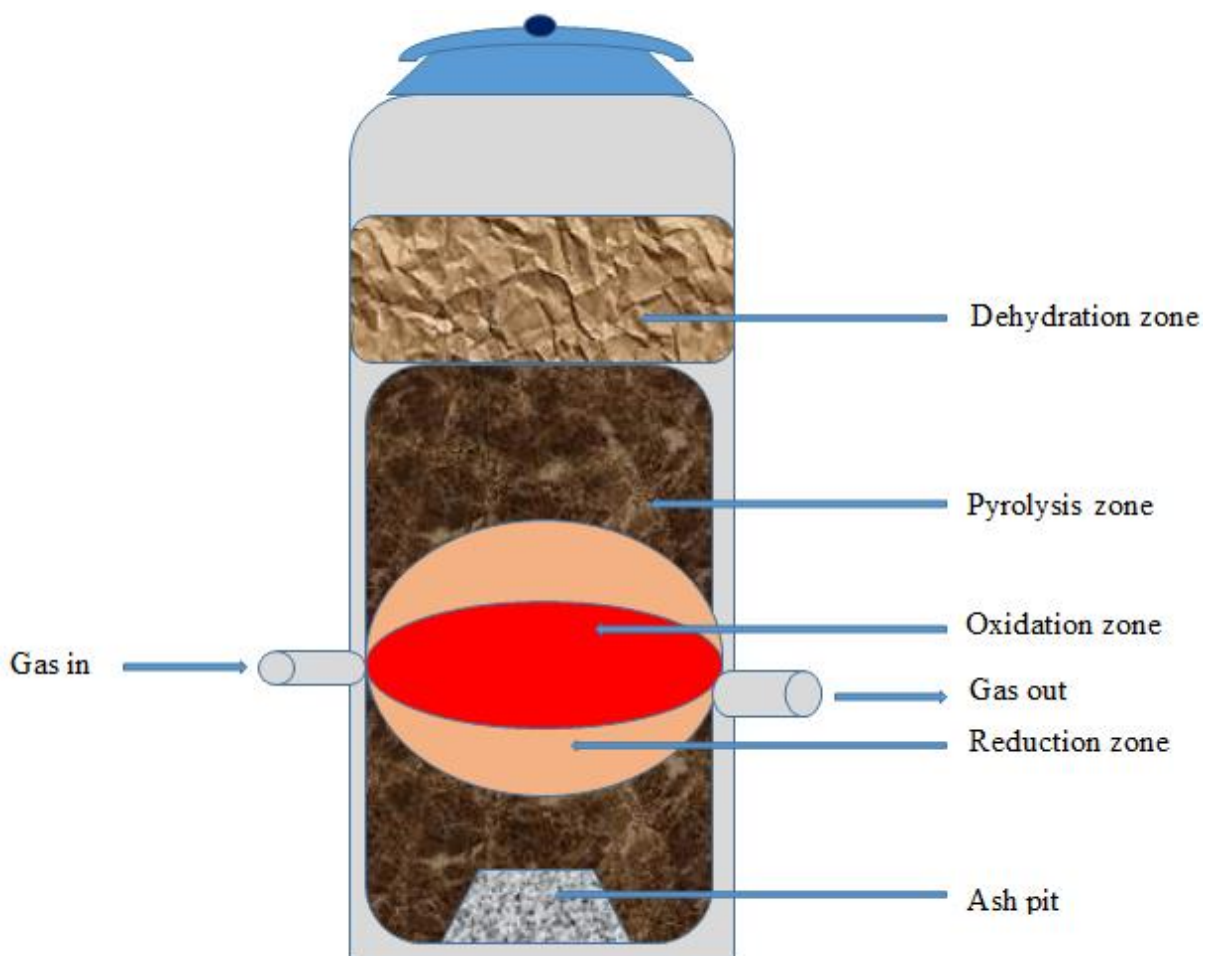


Figure 2.8: Cross-draft gasifier [Adapted from Mamphweli and Meyer, 2009]

**a) Advantages of cross-draft gasifier** [Rajvanshi, 1983 and Shrivastava, 2012]

- i. Short design height
- ii. Very fast response time to load

iii. Flexible gas production

**b) Disadvantages of cross-draft gasifier** [Rajvanshi, 1983 Shrivastava, 2012]

i. Very high sensitivity to slag formation

ii. High pressure drop

**2.5.1.3 UPDRAFT GASIFIER**

The updraft is also known as a countercurrent flow gasifier where the air and other gasifying agents are loaded from the bottom, while the biomass is fed from the top and moves downward under the force of gravity [Asadullah, 2014]. It is the oldest and simplest form of a gasifier. The biomass material is loaded on top of the gasifier, and a grate at the bottom of the gasifier is supporting the reacting bed. The highest concentration of gasifying agent is introduced below the grate and moves up the bed of biomass and char. Liberation of water and carbon dioxide is due to the complete combustion of char occurring at the bottom of the bed. The gas produced by an updraft gasifier usually leaves at low temperatures (approximately 400°C), contains hydrocarbons and has high tar content [Pedroso *et al.*, 2013 and Sadaka *et al.*, 2002]. A diagram of updraft gasifier showing different zones is shown in Figure 2.9

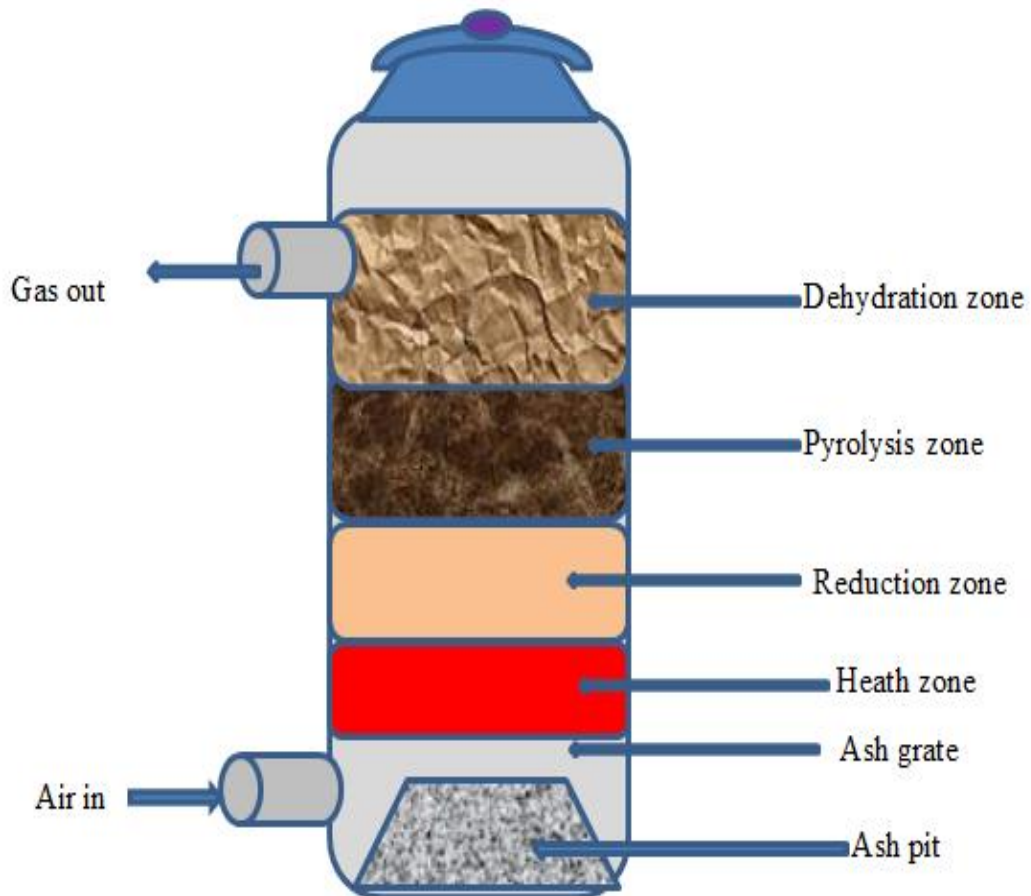


Figure 2.9: Updraft gasifier [Adapted from Mamphweli and Meyer, 2009]

**a) Advantages of updraft gasifier** [Held, 2012; Jared *et al.*, 2002 and Rajvanshi, 1983]

- i. Simple, low cost process
- ii. Able to handle biomass with a high moisture and high inorganic content (e.g., municipal solid waste)
- iii. Proven technology
- iv. Small pressure drop
- v. Good thermal efficiency
- vi. Little tendency towards slag formation

**b) Disadvantages of updraft gasifier** [Li *et al.*, 2004; Rajvanshi, 1983 and Jared *et al.*, 2002]

- i. Syngas contains 10-20% tar by weight, requiring extensive syngas clean-up before engine, turbine or synthesis applications
- ii. Great sensitivity to tar and moisture content of fuel
- iii. Relatively long time required for start-up of IC engine
- iv. Poor reaction capability with heavy gas load

## **2.5.2 FLUIDISED BED GASIFIER**

A fluidized bed reactor consists of a bed made of an inert material (such as sand, ash or char) that acts as a heat transfer medium [Sadaka *et al.*, 2002]. In fluidized bed gasifiers, the zones of reaction are clearly separated because the drying, pyrolysis and gasification reactions are all occurring at one stage. Fluidized bed gasifiers are categorized by configuration and the velocity of the gasifying agent. This gasifier type can be classified into bubbling fluidized bed and circulating fluidized bed.

### **2.5.2.1 BUBBLING FLUIDIZED GASIFIER**

A bubbling fluidized bed reactor consists of tiny, inert particles of alumina or sand, which have been selected for density, size, and thermal characteristics [Jared *et al.*, 2002]. Ash and some of the fine bed material contained in the syngas are separated out in a cyclone [Brown, 2006]. This type of gasifier is more expensive, complicated and produces a gas that has a high heating value [Salam *et al.*, 2002]. The biomass is fed on top of the gasifier to increase

the pyrolysis process at the freeboard zone [Surjosatyo *et al.*, 2010]. As the gasifying agents are injected as non-reactive particles, a point is reached when the frictional force between the particles and the gas counterbalances the weight of the solids.

**a) Advantages of bubbling fluidized-bed gasifiers** [Cruz-Ceballos, 2013 and Jared *et al.*, 2002]:

- i. Yields a uniform product gas
- ii. Exhibits a nearly uniform temperature distribution throughout the reactor
- iii. Provides high rates of heat transfer between inert material, fuel and gas
- iv. High conversion possible with low tar and unconverted carbon
- v. Able to accept a wide range of fuel particle sizes, including fines

**b) Disadvantages of bubbling fluidized-bed gasifiers** [Jared *et al.*, 2002]:

- i. Large bubble size may result in gas bypass through the bed

#### **2.5.2.2 CIRCULATING FLUIDIZED GASIFIER**

Circulating fluidized reactor is similar to the bubbling fluidized reactor but circulating reactor has the ability of re-circulating the sand particles involved in the process [Ravindran, 2011].

Circulating fluidized bed gasifier operates at gas velocities higher than the maximum fluidization point, resulting in the entrainment of the particles in the gas stream. In circulating fluidized reactor the velocity of the upward flowing gasification agent is around 5–10 m/s [Belgiorno *et al.*, 2003]. The entrained particles in the gas exit the top of the reactor, are

separated in a cyclone and returned to the gasifier [Jared *et al.*, 2002]. Circulating gasifiers are able to withstand high capacity throughputs and are mainly used in the paper industry for the gasification of bark and other forestry residues [McKendry *et al.*, 2002(3)]. Circulating fluidized bed gasifier are more flexible but are still limited by the fine feedstock quantity that they can process [Worley and Yale, 2012].

**a) Advantages of circulating fluidized-bed gasifiers** [Ahrenfeldt *et al.*, 2011; Jared *et al.*, 2002 and Siedlecki *et al.*, 2011]:

- ii. Suitable for rapid reactions
- iii. High heat transport rates possible due to high heat capacity of bed material
- iv. High conversion rates possible with low tar and unconverted carbon

**b) Disadvantages of circulating fluidized-bed gasifiers** [Jared *et al.*, 2002]:

- i. Temperature gradients occur in direction of solid flow
- ii. Size of fuel particles determine minimum transport velocity; high velocities may result in equipment erosion
- iii. Heat exchange less efficient than bubbling fluidized-bed

## **2.6 PRODUCTS AND BY-PRODUCTS OF BIOMASS GASIFICATION**

Biomass gasification converts carbonaceous materials into charcoal giving gas as a by-product, however the gas is largely regarded as the main product it is the useful part of the by-products. The process also produces a number of other by-products that are considered as

waste, these include char, tar, fine carbon particles, condensates (water and tar) and other hydrocarbons.

The by-products of gasification process are released as waste products from the gasifier system. These by-products can be collected, processed and used in different applications. The basic types of biomass gasification by-products to be considered include char, tar and soot. These by-products can be blended to generate stronger materials which can then be employed in different areas.

### **2.6.1 CHAR**

Char phase is an unconverted material mainly composed of carbon, minerals, and metals that are present in the raw substrate; this is pyrolysed in a zero or low oxygen environment [Verheijen *et al.*, 2009]. Some of the metals that are found in biomass char include copper, iron, manganese, or magnesium as well as minerals such as calcium, potassium, or phosphorus which will not enter the gas phase at characteristic gasification temperatures of 500-900°C [Klinghoffer *et al.*, 2011]. If there is higher carbon content within the unconverted matter, then it is called char and ash when it has lower carbon content. Char can easily be gasified to recover its energy without the need of regeneration [Song *et al.*, 2014]. Char can be further burnt to produce heat and ash. Char has a porous structural morphology.

This char is detrimental to the future of the gasifier because it may cause clogging which will require often maintenance of the system; char content is directly proportional to the maintenance of the gasifier system. Although char is regarded as a waste within the life of a gasifier system, it has positive applications in other areas.

### **2.6.1.1 APPLICATION OF CHAR IN OTHER AREAS**

It has been reported that when char is used as a soil amendment, it boosts soil fertility and improve the quality of soil by raising soil power of hydrogen, increasing moisture holding capacity, attracting more beneficial fungi and microbes ,improving cation exchange capacity (CEC) and retaining nutrients in soil [Zheng *et al.*, 2010]. Char from biomass gasification plays a catalytic role in tar removal. This is made possible by metals that are used as catalysts (Iron, Copper) in char [Klinghoffer *et al.*, 2011].

Char can also be used in filtering gasification waste water before it is released to the environment [Tripathi *et al.*, 2013]. Char is used in chemical industries for manufacturing of carbon disulphide, sodium cyanide and carbides. In tyre industries it is used as additive in rubber tyres. The activated carbon from charcoal is used in dechlorination, solvent recovery and gas purification. Using char to manufacture carbon nanoparticle materials will add value to the by-product [Yan *et al.*, 2014].

### **2.6.1.2 CHAR ELEMENTS AND THEIR ENVIRONMENTAL IMPACTS**

#### **i. Potassium**

Potassium with symbol K is an alkaline metal (Group 1) element. It is found within the char resulting from the biomass gasification process. When highly inhaled it can lead to build up of fluids within the lungs which can consequently result in death. The higher levels of potassium in blood can cause fatigue or weakness and vomiting [Wint, 2012].

## **ii. Iron**

Iron is a transition metal with a chemical symbol Fe. Chronic inhalation of huge concentrations of iron-oxide from fumes or dust may result in the development of benign pneumoconiosis called siderosis [Lenntech, 2014].

## **iii. Manganese**

Manganese with symbol Mn falls under the category of transition metals. Inhalation of its fumes in large quantities leads to diseases that may result in permanent disability since it targets the central nervous system of the human body [CDC, 2014 and Santamaria, 2008].

## **iv. Copper**

Copper is a transition metal symbolised by Cu. Exposure to fumes, mists or dusts containing large amounts of copper can result in metal fever with atrophic changes in the nasal mucous membrane. Its long-term exposure results in irritation of mouth, eyes, and may also cause headaches dizziness and vomiting [DTMSRP, 2010 and Materion, 2014].

## **v. Phosphorus**

Phosphorus is a chemical element that exists commonly in the environment as phosphates because it reacts fairly quickly with oxygen producing toxic fumes of phosphorus oxides [CDC, 2013]. Inhalation of excess amount of white phosphorous leads to health

complications such as kidney damage and osteoporosis (bones become fragile and likely to crack) [Phosphorous, 2003].

## **vi. Magnesium**

Magnesium is an alkali earth metal (Group 2) element with Mg symbol. Its high exposure by breathing contaminated fumes or dust may cause irritation and metal fume fever which is characterised by sore throat, cough, headache and fever. Drinking water with high levels of magnesium can lead to diarrhoea and vomiting [Kožíšek, 2003].

### **2.6.2 GASIFIER TAR/RESIN**

Tertiary tar is the type of tar mostly found in a downdraft gasifier; therefore the study focuses largely on it. The PAHs contained in tar can be used to preserve wood, conduct research, produce dyes, plastics and pesticides; some are even used in medicines [Polycyclic Aromatic Hydrocarbons, 2013]. The biomass tar can be further applied in furnaces, metallurgy, fire brick making, electrodes and can also be applied as a raw material for chemical industries.

In gasification tar is defined as the material in the product stream that is condensable within the gasifier and these tars are generally assumed to be largely aromatics [Milne and Evans, 1998]. Other authors define tar as a name given to collection of higher molecular weight hydrocarbons [Dayton *et al.*, 2002]

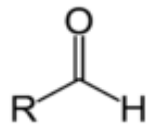
The gasification condensates consist of tar, water and some other particles. Tar is composed of a complex mixture of organic compounds (including aromatic and hetero-aromatic species

as well as polycyclic aromatic compounds, PAHs) with high boiling points [Hernández *et al.*, 2013]. Tar which is produced from a downdraft gasifier system can reach levels of 50 mg/Nm<sup>3</sup> to 2 g/Nm<sup>3</sup> [Surjosatyo *et al.*, 2012]. In downdraft gasifiers, tertiary tars are largely produced [Menya, 2012]. Tar is classified in to three categories, which are:

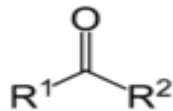
### 2.6.2.1 PRIMARY TAR

This is the first type of tar coming from the pyrolysis zone of a gasifier system. It is basically derived from lignocellulose (cellulose, hemicellulose and lignin) of a woody material [Romar *et al.*, 2013]. The resultant primary tar is oxygen rich because cellulose and hemicellulose contain a lot of oxygen. Examples of primary tar products formed at temperatures of 200°C-500°C are: alcohols, aldehydes, ketones or carbon acids [Wolfesberger *et al.*, 2009].

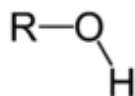
#### i. Functional groups of primary tar



Aldehyde (RCHO)



Ketone (RCOR)

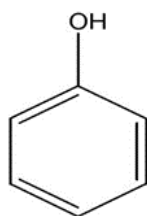


Alcohol (OH)

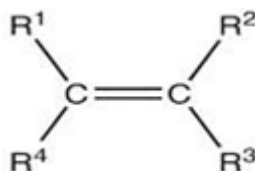
### 2.6.2.2 SECONDARY TAR

This type of tar is generally composed of phenolics (phenols) and olefins (alkenes) which are produced from the conversion of primary tars. These secondary tar products are produced in temperatures ranges of 500-800°C [Menya, 2012]. Conversion of primary tars to secondary tars is made possible by the elimination of gaseous particles [Wolfesberger *et al.*, 2009].

#### i. Structural and chemical composition of secondary tar



Phenols ( $C_6H_5OH$ )

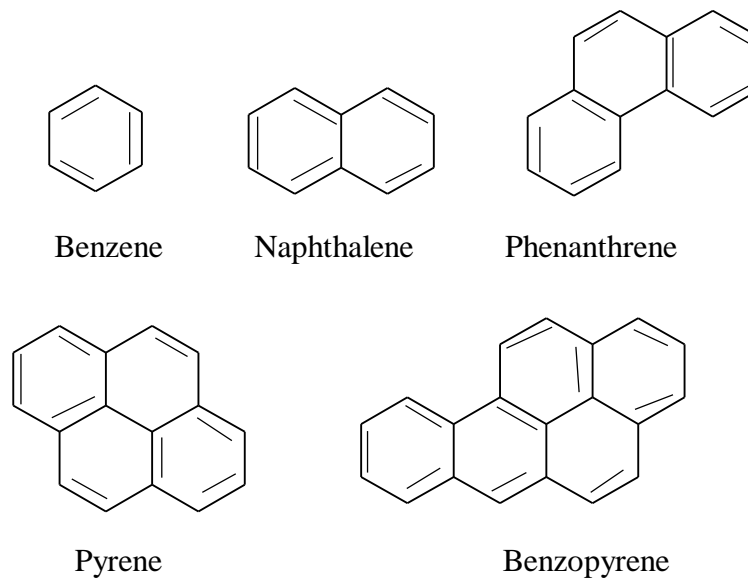


Alkenes ( $C_nH_{2n}$ )

### 2.6.2.3 TERTIARY TAR

Tertiary tars are sometimes called recombination or high temperature tars. They can be found at temperatures above 800° C. Examples of tertiary tars include benzene, naphthalene, phenanthrene, pyrene, and benzopyrene. [Wolfesberger *et al.*, 2009]. Poly-Aromatic Hydrocarbons (PAH) are fused aromatic rings without substituents and naphthalene is the simplest PAH with only two rings.

**i. Structural composition of tertiary tar**



The tar condensation causes huge technical problems in biomass gasifier system and some of them include: plugging and fouling problems, polymerisation of tar at high temperatures, the need for managing hazardous residual effluents derived from wet cleaning systems, and catalyst deactivation due to tar deposition. The added gasifying agents (oxygen or air), in combination with steam, help to produce less reactive (not easily destroyable) tars at lower levels and increases conversion of primary tars [Srinivas *et al.*, 2013].

**2.6.2.3.1 BENZENE AND ITS ENVIRONMENTAL EFFECT**

Benzene is an organic compound with chemical formula  $C_6H_6$ . The presence of oxygen in soil and water decomposes benzene. It has a highly toxic effect on aquatic life. Benzene exposure can cause short and long term effects. The long term exposure can harm bone marrow, whereas the short term exposure can cause vomiting, stomach irritation and dizziness [American Cancer Society, 2013].

#### **2.6.2.3.2 NAPHTHALENE AND ITS ENVIRONMENTAL EFFECT**

Naphthalene is an organic compound composed of two benzene rings with a chemical formula  $C_{10}H_8$ . Its characteristic odour is detectable at low concentrations around 0.08ppm. It is very toxic to aquatic organisms and can result to long-term effects within the aquatic environment. It can deplete pulmonary glutathione and dose-dependent bronchiolar epithelial cell necrosis [Menya, 2012]. Exposure to naphthalene can result to chromosomal translocations [CUMSPH, 2012]

#### **2.6.2.3.3 PHENANTHRENE AND ITS ENVIRONMENTAL EFFECT**

Phenanthrene has a chemical formula  $C_{14}H_{10}$  with a chemical structure of three benzene rings fused together. Phenanthrene occurs as a greater component of the total PAH compounds in the environment [Irwin *et al.*, 1997]. Phenanthrene can be absorbed via inhalation of ambient air, food ingestion, drinking water, and skin contact with phenanthrene or other products containing phenanthrene. Some of its effects include damage of skin, body fluids and the immune system that help the body against diseases [Phenanthrene, 2013].

#### **2.6.2.3.4 PYRENE AND ITS ENVIRONMENTAL EFFECT**

Pyrene is an organic compound composed of four benzene rings with a chemical formula  $C_{16}H_{10}$ . Pyrene is one of the major pollutants in the environment. In humans, pyrene exposure occurs predominantly through the smoking of tobacco, inhalation of polluted air and by ingestion of food and water contaminated by combustion effluents [Irwin *et al.*, 1997]. It increases weight of the liver and decrease the weight of the kidney [Pyrene, 2013]

#### **2.6.2.3.5 BENZOPYRENE AND ITS ENVIRONMENTAL EFFECT**

Benzopyrene is a five-ring polycyclic aromatic hydrocarbon (PAH) with chemical formula  $C_{20}H_{12}$ . Benzopyrene has also been reported to have phototoxic effects with exposure to ultraviolet light following benzopyrene exposure. Observed effects of benzopyrene included: haemolysis of red blood cells (erythrocytes) in humans. Benzopyrene is not commercially produced or used, it simply occurs in the environment universally as the result of incomplete combustion of fuels and other organic materials. The inhalation of the PAH mixtures has been reported to increase the respiratory irritations to lung cancer risks [Jung *et al.*, 2010 and MFE, 2014].

#### **2.6.3 GASIFICATION WASTE WATER**

Pure water is composed of hydrogen and oxygen elements only. Water produced from the gasification process contains more than two elements. The wastewater generated as a by-product of biomass gasification is contaminated with inorganic and organic substances. The contaminants of this wastewater include dissolved organics, inorganic acids, metals and ammonia ( $NH_3$ ).

The excess water content of the biomass leaves the gasifier together with the product gas. Hence water is also a component of producer gas, although it is usually cooled and cleaned [Menya, 2012]. Recycling of this wastewater can lead to higher contaminant concentrations [Milne and Evans, 1998].

The water should be treated before it is disposed to natural streams to make its pH neutral and to remove suspended solids, total dissolved solids, alkalinity, ammonia, and phenol. Char treated water is safer to discard to natural streams [Tripathi *et al.*, 2013].

#### **2.6.4 COMMERCIAL RESIN**

Resin is a sticky substance released during the carbonization stage of the biomass gasification process. It is formed as condensates during devolatilization. Mechanical company uses resin in manufacturing of advanced carbon composite fans. The resin is largely showing the lignocellulosic characteristics as they are produced from biomass material. Resin is a tough, flexible and resistant to thermal changes. Resin produced must have sufficiently low viscosity to allow processing by resin transfer molding [Orozco, 1999].

##### **2.6.4.1 APPLICATIONS OF COMMERCIAL RESIN**

These resins are used in manufacturing of advanced carbon composite fans. They are also used in circuit boards. In manufacturing of wind turbine blades, resin is applied as adhesive in binding the fibrous material of the turbine blade.

#### **2.6.5 GASIFIER SOOT**

During biomass gasification soot is produced as by-product from both the cyclone as well as from the pond. The raw gas produced from the gasifier passes through the cyclone, and this is where the coarse carbon particles are removed. The carbon particles that managed to escape with the gas will then get removed during gas cleaning through the scrubber water. Scrubber

water circulates back to the pond with these fine particles. The fine particles will then form a black layer on top the pond water.

Chemically, soot is mainly composed of carbon although it also contains hydrogen and some other elements [Ma, 1996]. Soot emission from combustion system reflects poor conditions of combustion and a loss of efficiency [Haynes and Wagner, 1981]. The formation of soot implies a number of complex physical and chemical processes that control the conversion of gaseous fuel into solid particles that are not well understood [Chen *et al.*, 2011]. Once the soot particles are generated they collide with each other creating larger particles. The soot particles look spherical and later get a fractal shape [Frenklach, 2002]. Soot can react with several gases such as O<sub>2</sub>, CO<sub>2</sub> or H<sub>2</sub>O and can be gasified; its reactivity to these gases is directly related to its structure and composition [Chhiti, 2011]. De Soete, 1988 conducted a study and used soot as gasification feedstock, it was established that there was an insignificant reaction with H<sub>2</sub>O below 527°C and that the major product obtained at higher temperature was CO.

#### **2.6.5.1 APPLICATIONS OF SOOT**

This soot can be applied in production of briquettes, cementation granulate and batteries. It is also used as active filler in rubber products and is a component of printing paints [Mansurov, 2005]

## **CHAPTER 3**

### **RESEARCH METHODOLOGY**

#### **3.1 INTRODUCTION**

This chapter describes the methods employed to collect the required data for this research. Gasification of pine wood was undertaken in the 150 kVA biomass gasifier at Melani village, Alice, Eastern Cape, South Africa. The main characteristics of pine wood, its gasification by-products and blends of the by-products were determined using ultimate and proximate analysis. The ultimate analysis included an elemental analysis of the dominating elements such as Carbon (C), Oxygen (O<sub>2</sub>), Nitrogen (N<sub>2</sub>), Hydrogen (H<sub>2</sub>), and Sulphur (S). The analytical techniques used for this study included: Elemental Analyser (CHNS), Calorimeter, FTIR, SEM, and XRD. For each sample measured three times, values were recorded and calculated average value was used. The results were presented in two parts i.e. before and after blending. The techniques used for sample collection/preparation are also presented in this chapter.

#### **3.2 THE BIOMASS GASIFIER**

The 150kVA Melani biomass gasifier used for this study is a 300m<sup>3</sup>/h fixed bed downdraft gasifier powering a 45KW container bakery. Figure 3.1 shows the gasifier flow diagram and photos of the reactor and other components:

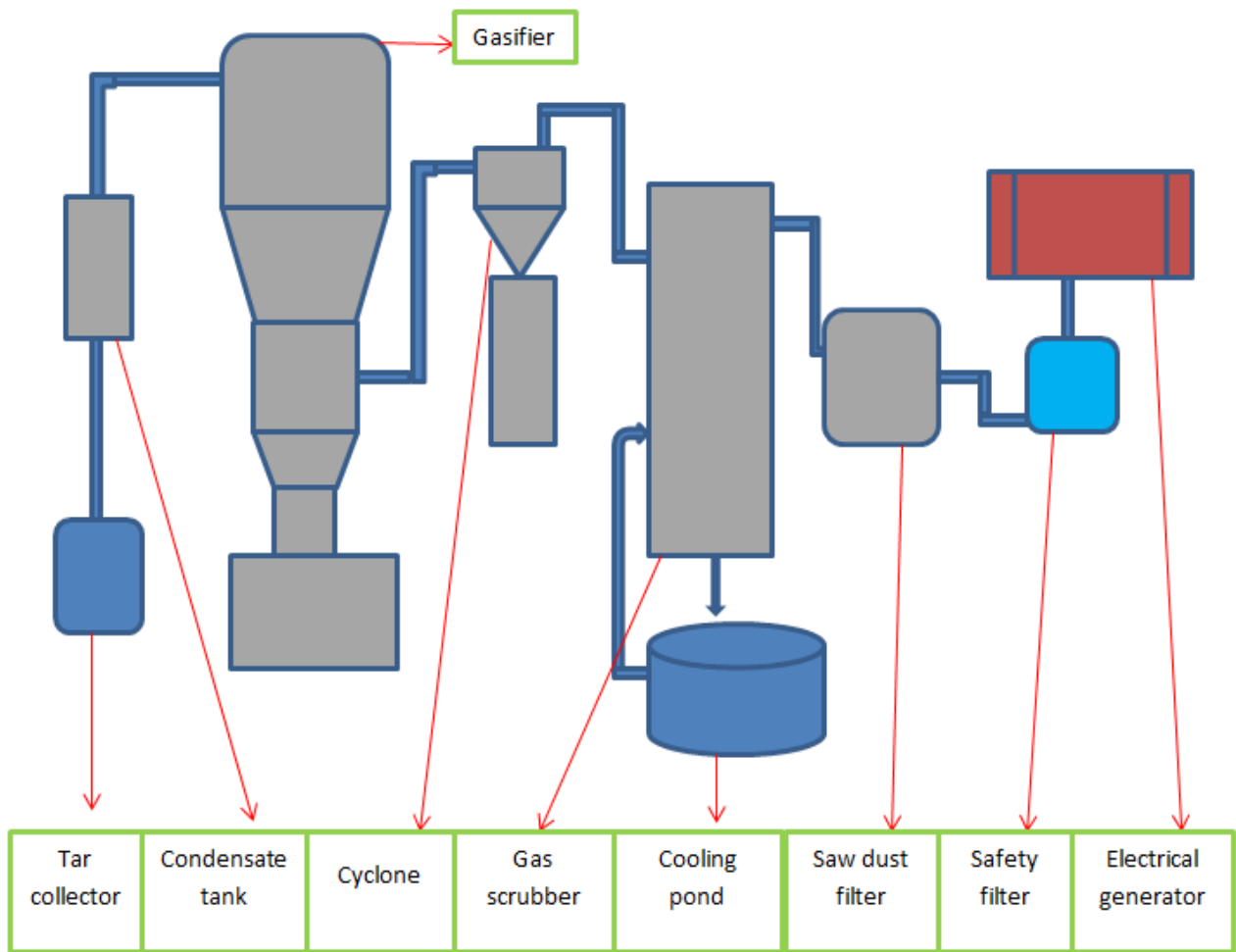


Figure 3.1(a) Flow diagram of Johansson biomass gasifier



Figure 3.1(b) Reactor and other components of Johansson gasifier system

The operating principles of the downdraft gasifier are explained in section 2.5 of chapter 2 in this dissertation.

### **3.3 DATA COLLECTION METHOD**

Figure 3.2 shows a flow diagram of the various methods/ instruments employed in data collection.

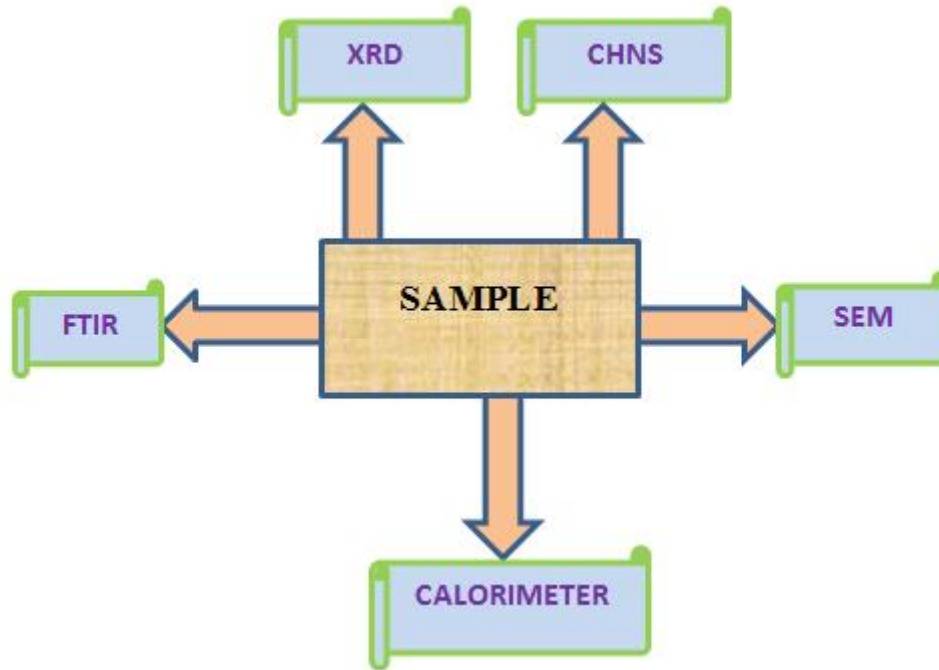


Figure 3.2: Flow diagram for material characterization

### 3.4 SAMPLE COLLECTION/PREPARATION

The pine wood material was collected at Melani village in the Eastern Cape Province of South Africa. Pieces of wood collected were then cut into small blocks as required by the downdraft gasifier. Wood blocks were dried and used as a feed material in the reactor. The feed material contained an average of 18% moisture content. The gasification by-products (scrubber carbon fine particles, char, gasifier tar/resin and cyclone carbon fine particles) were then collected using 100ml beakers to the laboratory for further analysis. These by-products were also blended at 50% ratio and characterized. Pine wood biomass feedstock was used because it's freely available at Melani village from a local sawmill as waste. It also has a low ash yield; hence it is good for the gasification process. Commercial resin was supplied by MechCal company, they use it in manufacturing of advanced carbon composite fans. Figure 3.3 presents pinewood at Melani village near the gasifier site.



Figure 3.3: Pine wood waste at Melani village near the biomass gasifier site.

### **3.5 MATERIAL CHARACTERIZATION**

To determine the usefulness of a material requires an understanding of its properties and composition, and the steps taken to establish their potential use in other areas begins with characterization of such material using different analytical techniques to quantify their components. The samples used for this study were characterized using, CHNS Analyser, Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) and Oxygen Calorimeter. These are the most important analytical techniques when attempting to predict or describe the application of gasification by-products based n their composition and properties. A brief discussion of each instrument used is given below.

### 3.5.1 ULTIMATE ANALYSIS

A Perkin Elmer elemental analyser was the type of organic elemental analyser used for the simultaneous determination of the amount (%) of Hydrogen, Carbon, Sulphur, Nitrogen and Oxygen contained in pine wood and gasification by-products as well as blended by-products. Oxygen was then obtained by difference. Helium was used as a carrier gas. Elements analysed from the samples were in solid state, although it was also possible to analyse them in liquid and gaseous states. The CHNS analyzer had been used by Sugumaran and Seshadri when they were evaluating selected biomass for charcoal production in 2009. Figure 3.4 shows the CHNS analyser.



Figure 3.4: CHNS analyser

### 3.5.2 FOURIER TRANSFORM INFRARED (FTIR)

All organic species show specific absorption bands in the ( $100$  to  $12500\text{ cm}^{-1}$ ) spectral region originating from vibrational transitions in the molecules and the absorption bands are characteristic of the chemical compound [Kalisz *et al.*, 2008]. Because of this, FTIR

spectroscopy was used for the determination of functional groups composing the samples and this was helpful in the determination of areas at which they could possibly be applied. With respect to solid samples, a common technique was to ground the sample and mix it with potassium bromide (KBr) powder in order to form samples that were transparent to FTIR beam. The mixture of sample and KBr powder was then dried in the oven at 105 °C overnight [Yang *et al.*, 2006]. The dried samples were then inserted into the FTIR for characterization.

### **3.5.3 CALORIFIC VALUE DETERMINATION**

An oxygen calorimeter (Eco Cal2K) was used to measure the heating value of the pine wood biomass, gasification by-products and blended by-products. The calorimeter was first calibrated with a 0.5g of benzoic acid ( $C_7H_6O_2$ ) before measurements were taken. About 1g of each sample was weighed using a watch-glass. The weighed samples were then transferred into a crucible in the outer electrode connected to the lid of the vessel. The vessel was then pressurized up to 3000kpa using oxygen gas. The vessel was then taken into the calorimeter for firing to take place. For each mass of the sample input in the calorimeter, the heating value returned was in units of MJ/kg. Figure 3.5 shows the oxygen calorimeter setup.

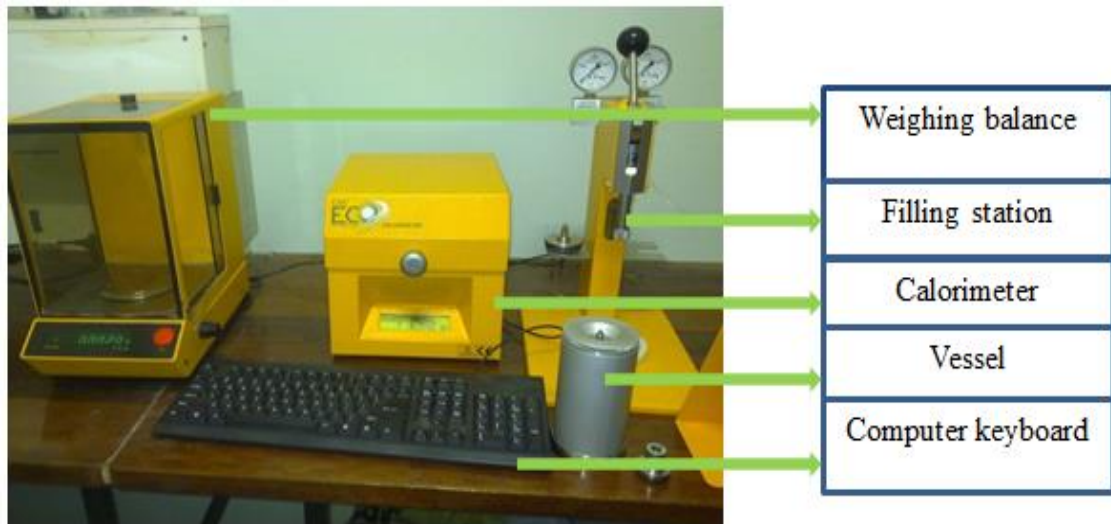


Figure 3.5: Oxygen calorimeter setup

#### 3.5.4 SCANNING ELECTRON MICROSCOPE (SEM)

SEM has been proven to be a good technique for the determination of sample size and morphology [Laskin and Cowin, 2001]. The samples analysed under SEM were pine wood, gasification by-products as well as blended by-products. Microphotographs of these samples were taken at the magnification of X200, X650, X2000 as well as X4000 at 15kV accelerating voltage.

Samples were mounted on a stub using a carbon double-sided tape. Following this, they were coated with gold-palladium using EIKO IB3 Ion Coater. The samples were then viewed with JEOL JSM6390LV Scanning Electron Microscope using the secondary electron detector operated at 15kV. Images were captured at different magnifications.

### 3.5.5 X-RAY DIFFRACTION (XRD)

XRD is a powerful technique for characterizing crystalline materials [Nyamukamba, 2011]. This technique was used to characterize the crystalline structure of carbon material present in the pine wood, gasification by-products and blended by-products. The structural determination of wood and grass chars had been performed by [Keiluweit, 2010] using XRD. The XRD technique was also employed in the characterization of charcoals by [Tchomgui-Kamga *et al.*, 2010].

The solid sample was ground into fine powder with mortar and pestle. Bruker XRD D8 ADVANCE was then used to generate the required data. XRD used in analysis is shown in Figure 3.6



Figure 3.6: Bruker XRD D8 ADVANCE

## **CHAPTER 4**

### **RESULTS AND DISCUSSION**

#### **4.0 INTRODUCTION**

This chapter focuses on the data obtained using methods explained in chapter 3. The results are presented and discussed in two parts i.e. before blending and after blending. For simplicity reasons, soot collected from the cyclone is referred to as cyclone carbon fine particles (CCFP) and soot from scrubber water is referred to as scrubber carbon fine particles (SCFP).

#### **4.1 ULTIMATE ANALYSIS FOR PURE MATERIALS**

The elemental analysis of the samples analysed in Table 4.1 show higher quantities of carbon, oxygen and hydrogen respectively. The higher level of these elements is due to the carbohydrate structure which is majorly composed of carbon, hydrogen and oxygen elements. The results display the inverse proportion relationship between carbon and oxygen. A biomass sample may or may not contain nitrogen or sulphur; hence some of the samples in Table 4.1 do not show traces of nitrogen or sulphur. The lower quantities of nitrogen and sulphur in the biomass are considered as important for selection of biomass as feed stock for bio-oil production [Rout *et al.*, 2009].

The elemental analysis of pine wood used as a feedstock material in generation of gasification by-products was found to be in agreement with the range of results obtained by

[Neves *et al.*, 2011]. The elemental analysis of char obtained by CHNS analyser was also in agreement with existing literature [Wang *et al.*, 2008]. The higher carbon content in the char would ensure an enhancement of the carbon content of the char/resin blends as the resin contains lower carbon quantity than char. The strong but light material is ideal for wind turbine blades. Table 4.1 presents weight percentage of carbon, hydrogen, oxygen, nitrogen and sulphur obtained by CHNS analyser.

Table 4.1: Ultimate analysis of the samples

<b>Sample</b>	<b>C</b>	<b>H</b>	<b>N</b>	<b>S</b>	<b>O</b>
Pine wood	46.1	6.3	0.3	–	47.3
Gasifier Tar/resin	76.3	7.4	0.2	–	14.9
SCFP	78.9	2.0	0.8	1.1	17.3
Char	89.4	1.2	–	–	9.4
Commercial Resin	77.6	5.1	0.5	–	18.2
CCFP	36.2	1.2	0.2	1.4	61.0

The chemical elements of interest are the carbon and oxygen contents. The quantity of carbon in the resin determines its quality in terms of purity while the oxygen content determines its stability. Higher carbon contents are desirable for stable resin. It is clear from Figure 4.1 that there is no significant difference between the carbon content of gasifier resin and that of commercial resin, with a 0.16% difference. This implies that gasifier resin can be used for similar applications to those of commercial resin such as strong materials like propellers etc. Figure 4.1 shows the comparison between the elemental analysis of a gasifier tar/ resin and commercial resin.

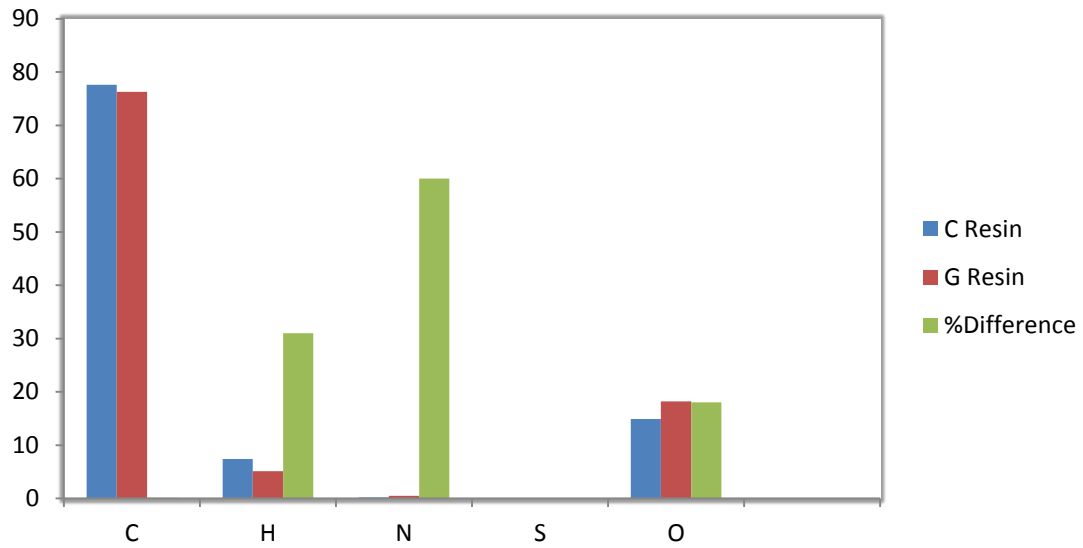


Figure 4.1: Elemental analysis of a gasifier tar/ resin and commercial resin.

It can be observed from Figure 4.2 that the carbon content of SCFP is higher (78.9%) than that of CCFP (36.2%) with a significant difference of 54%. This was attributed to the fact that SCFP were collected from the cooling pond where they settle on the surface after being washed from the scrubber. The washing removes other impurities such as the ash resulting in the purification of the scrubber carbon fine particles. The CCFP however, were collected at the bottom of the cyclone before reaching the water and was assumed to be contaminated with impurities like ash. Figure 4.2 shows the comparison between the elemental analysis of SCFP and CCFP

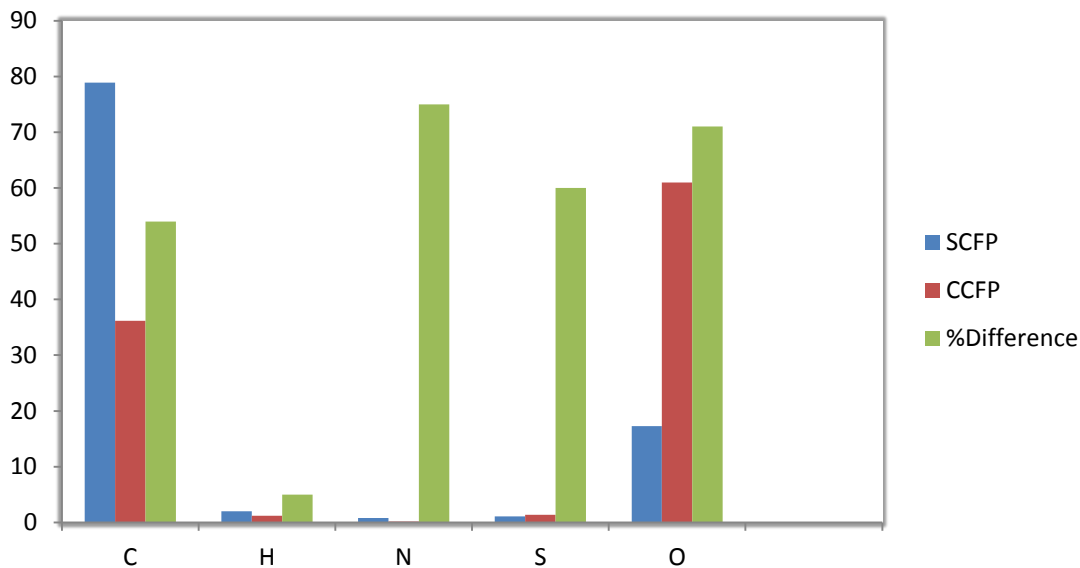


Figure 4.2 Comparison between the SCFP and CCFP

#### 4.1.1 ULTIMATE ANALYSIS FOR BLENDS

From the results presented in Table 4.2, the increased carbon content was observed in both mixtures that contain char. The char was significant in the blending as it largely contributed to the mixtures by its highest quantity of carbon (89.4%). The CCFP blended products gave the lowest carbon content (54%) and this was due to the lower carbon content in the CCFP.

After blending char with the gasifier resin and commercial resin, the nitrogen was detected, this was due to the contribution of gasifier resin and commercial resin used in blending. SCFP and CCFP increased the sulphur content of the blends when they were mixed with gasifier resin which previously did not show any traces of sulphur. It was further observed that after blending commercial resin and SCFP, the sulphur element appeared and this was due to SCFP. Sulphur was not detected in commercial resin-char, commercial resin-CCFP and gasifier resin-char blends; this was probably because sulphur level was too low to be detected

or was totally absent in the blends. Char blends contained the highest carbon when compared to CCFP and SCFP blends. Table 4.2 presents ultimate analysis of the 50%-50% blends

Table 4.2: Ultimate analysis of the 50%-50% blends

<b>Sample</b>	<b>C</b>	<b>H</b>	<b>N</b>	<b>S</b>	<b>O</b>
Commercial Resin- CCFP	75.0	5.3	0.4	–	19.3
Commercial Resin- SCFP	82.3	3.0	0.7	1.3	12.7
Commercial Resin- Char	82.7	3.6	0.3	–	13.4
Gasifier Resin-CCFP	54.0	3.1	0.2	1.0	41.7
Gasifier Resin - SCFP	81.6	4.2	0.4	1.3	12.4
Gasifier Resin - Char	89.4	3.1	0.2	–	7.3

## 4.2 SURFACE STRUCTURAL ANALYSIS FOR PURE MATERIALS

The surface structure of the pure and blended by-products was studied by JEOL JSM6390LV Scanning Electron Microscope. The essence of this analysis was to understand the structural properties of the samples and how these change with blending so as to lead in the prediction of their potential application in other process steps. The letters A, B, C and D represent resolutions at X200, X650, X1,400 and X4,000 consecutively.

The SEM image in Figure 4.3 shows a tracheid morphology of a pinewood sample. The slit-like pores are an indication of the carbon rings contained in the lignocellulose structure of the sample. The porosity is caused by fibres that make up the woody material. Figure 4.3 presents the images of Pinewood collected from SEM

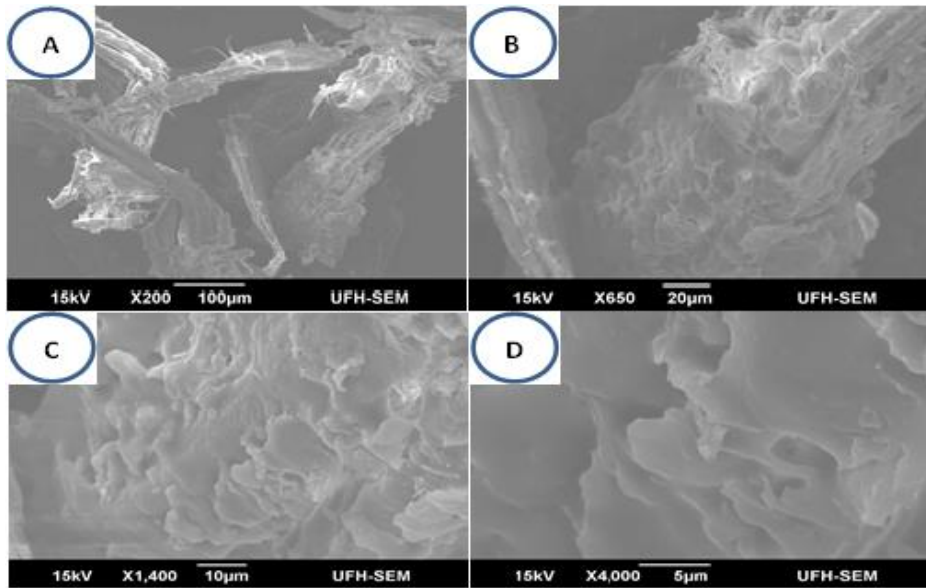


Figure 4.3: SEM images of pinewood

The SEM microphotograph of the commercial resin in Figure 4.4 shows a shiny image in this case is associated with stickiness of the resin. This sticky appearance is obviously advantageous for binding with other samples to produce a tightly bonded material. Resin is tough, flexible and viscous, hence it can be used as an adhesive and adhesives are majorly composed organic polymers which contain large quantities of carbon. Therefore, these resins have a potential for application in polymers due to high carbon component. Figure 4.4 presents SEM images of a commercial resin.

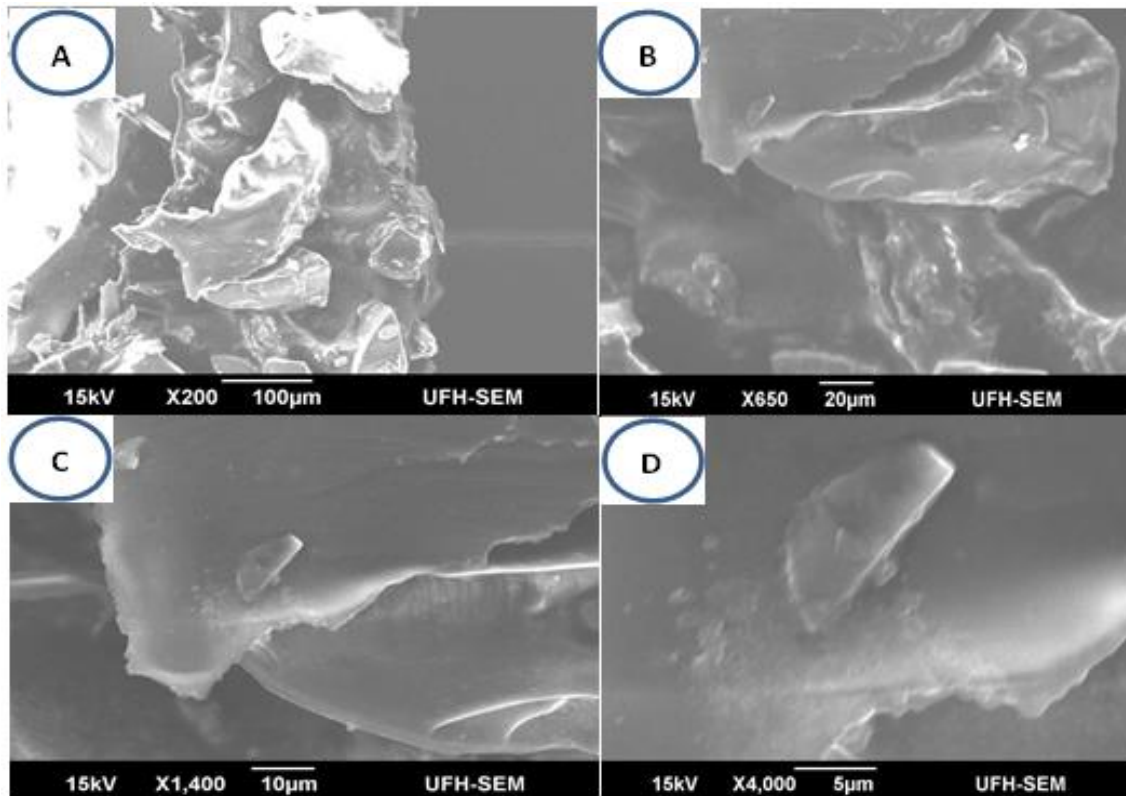


Figure 4.4: SEM image of a commercial resin

The SEM microphotographs of char in Figure 4.5 have shown the tracheid structure as expected. With reference to existing literature, pine wood biomass contains very low ash content [Amutio *et al.*, 2012]. The obtained images confirmed the amorphous and heterogeneous structure of the char. The biomass chars are highly disordered carbonaceous materials that may have structural defects [Asadullah *et al.*, 2010]. High gasification temperatures become destructive to char; hence the structure appears distorted. The tracheids of char makes it more useful in waste water filtration because it can chemically attract and trap some impurities. Figure 4.5 presents SEM micrographs of char collected from pine wood gasification.

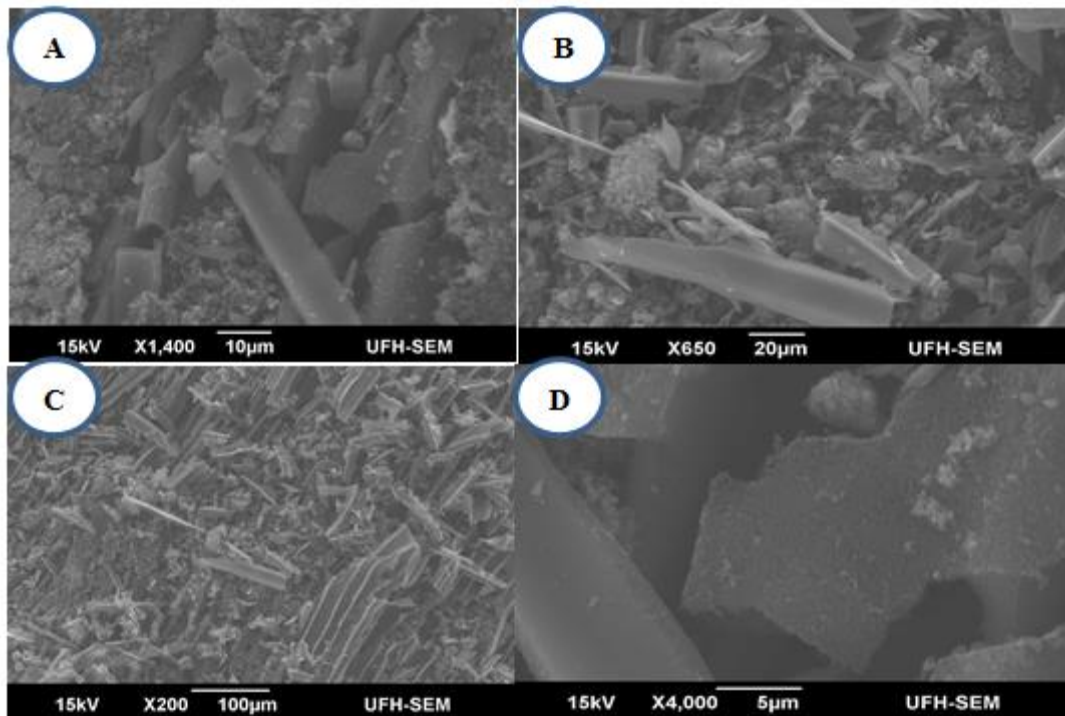


Figure 4.5: SEM micrographs of char collected from pine wood gasification

The SEM micrographs presented in Figure 4.6 are arranged in ascending order of magnification, from X200 to X4,000. The SEM structure of the cyclone carbon fine particles resembles the char structural image as it is mainly composed of similar elements but different quantities as those of char material. The cyclone carbon fine particle is just a finer carbon resulting from char production. Therefore, in the absence of contaminants they are expected to have the same quality. The lower carbon content in CCFP increases the need to blend with other materials so as to improve the elemental quantities of the material. It further shows the different pieces which may contribute to the variety of elements that are present in the sample. Figure 4.6 presents the SEM micrographs of cyclone carbon fine particles (CCFP)

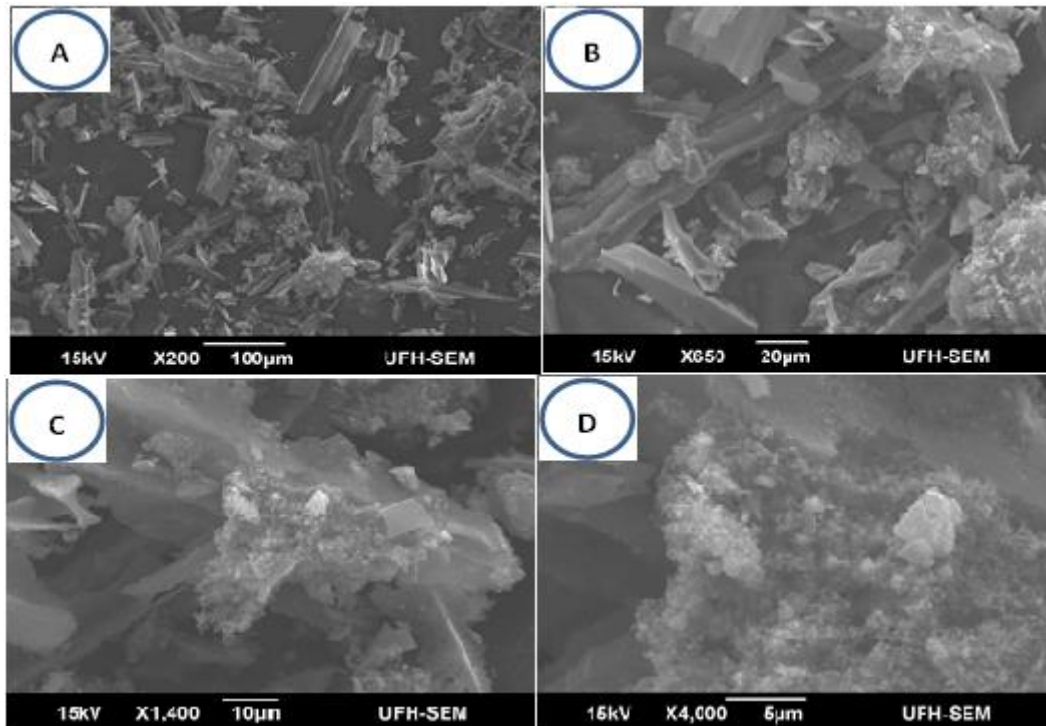


Figure 4.6: SEM micrographs of cyclone carbon fine particles (CCFP)

The SEM micrographs in Figure 4.7 present the SCFP sample taken at different magnifications and points. This was to show that the morphology of the SCFP under study was not homogenous throughout the sample. The SEM microphotograph of the material collected from the pond shows an image of a tightly bonded material. This is due to the fact that the material is made of tiny particles and secondly the water molecules act as binder of these micro-particles. SCFP finds wide application in the manufacturing of plastics due to huge components of carbon and oxygen elements consecutively. Figure 4.7 presents SEM micrographs of scrubber carbon fine particles (SCFP) collected in the cooling pond

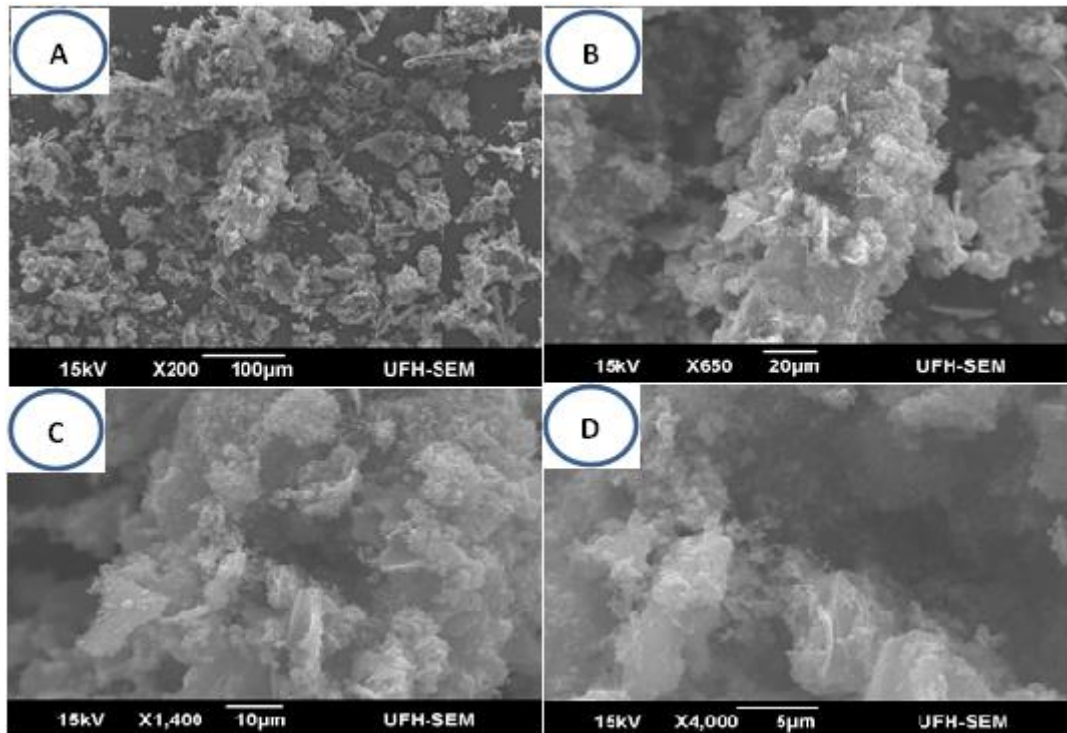


Figure 4.7: SEM micrographs of scrubber carbon fine particles (SCFP)

The images of the gasifier resin show some tightly packed surface area. The quantity of carbon content would ensure its strength. This implies that it could find a wide application as an adhesive due to its carbon content. The shiny appearance in this case is associated with the stickiness of the tar/ gasifier resin. The sticky gasifier resin is further applied in the handles of baseball bats to prevent the bat from slipping during hard swings [Pine Tar, 2009]. Figure 4.8 presents SEM images of gasifier resin.

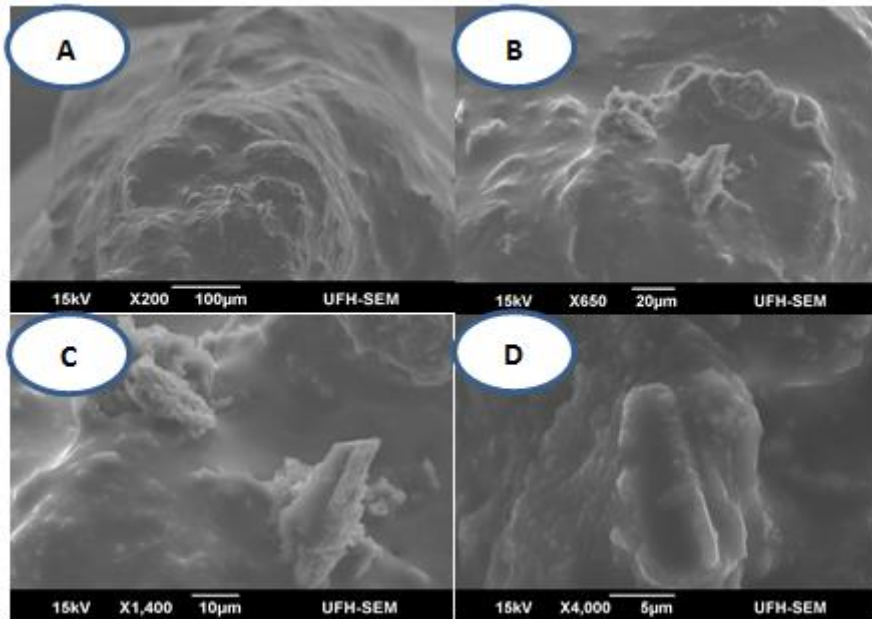


Figure 4.8: SEM images of gasifier resin

#### 4.2.1 SURFACE STRUCTURAL ANALYSIS FOR BLENDS

Figure 4.9 presents images of the mixture of commercial resin and char. The two samples in the mixture are tightly bonded because of the tracheid structure of char and high viscosity of commercial resin. The higher number of bonding sites in char were also advantageous in bonding to commercial resin. The blending of the two materials resulted to higher carbon content of 82.7% as presented in Table 4.2. This increment was due to char that had a higher carbon content of 89.4%, this is displayed in Table 4.1 of this chapter. Figure 4.9 presents SEM microphotographs of 50% commercial resin-50% Char

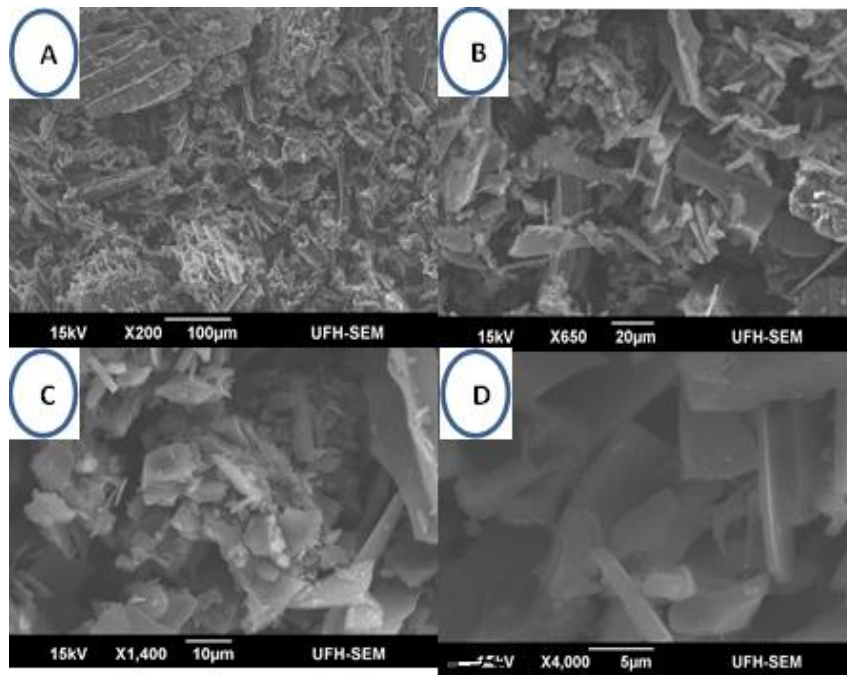


Figure 4.9: SEM microphotographs for 50% commercial resin -50% Char

Figure 4.10 presents the scattered micro carbon particles that were bound by the commercial resin. The high viscosity of the commercial resin contributed to the interaction between the cyclone carbon fine particles and the commercial resin. The interaction between the two materials i.e commercial resin and cyclone carbon fine particles led to a well mixed product of the two materials. The blending brought a slight decrease in carbon content of the mixture (75.0%) as presented in Table 4.2. This decreament was caused by the lower carbon content of cyclone carbon fine particles (36.2%), this is shown in Table 4.1. Figure 4.10 presents SEM microphotographs for 50% commercial resin - 50% CFP

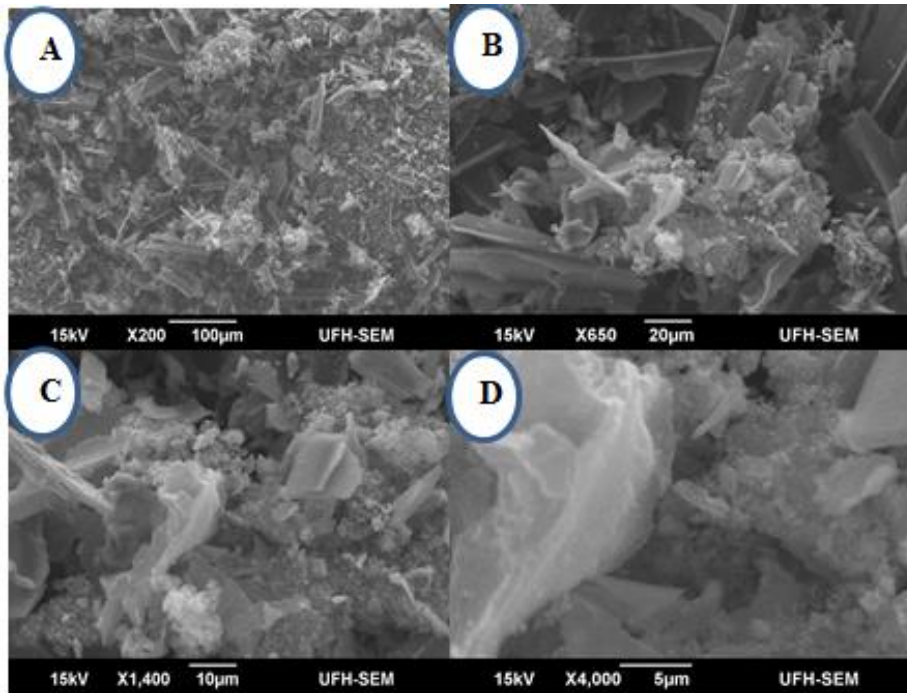


Figure 4.10: SEM microphotographs for 50% commercial resin -50% CCFP

The commercial resin was able to bind the tiny carbon fine particles, this is clearly observed in image C and D of Figure 4.11. After the blending of commercial resin and scrubber carbon fine articles, a homogenous mixture of the samples was observed as the mixture was made of equal amounts. The two different colours in the images represent the samples employed in the blending. The carbon content of the mixture enhanced to 82.3% as displayed in Table 4.2 of this chapter. Figure 4.11 present SEM microphotographs for 50% commercial resin -50% SCFP

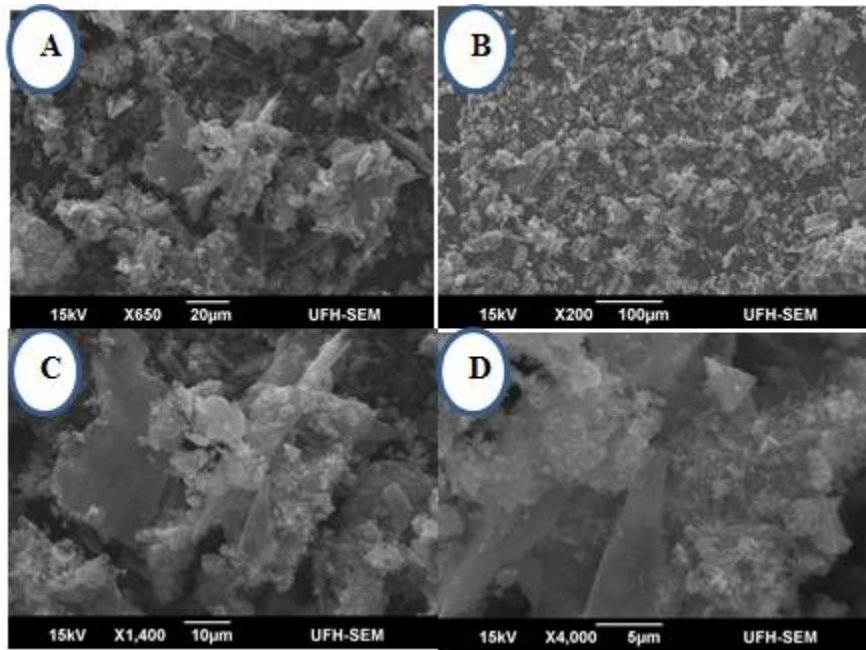


Figure 4.11: SEM microphotographs for 50% commercial resin -50% SCFP

Figure 4.12 shows the images of the mixture of gasifier resin and char. The blending of these two materials produced a mixture that has a higher carbon content (89.4%) from 76.3% gasifier resin and 89.4% char as presented in Table 2.1. This means the gasifier resin did not have much impact on the carbon content as the mixture gave the same value of carbon content as that of the char previously seen in Table 4.1. Figure 4.12 presents SEM images for 50% gasifier resin-50% Char

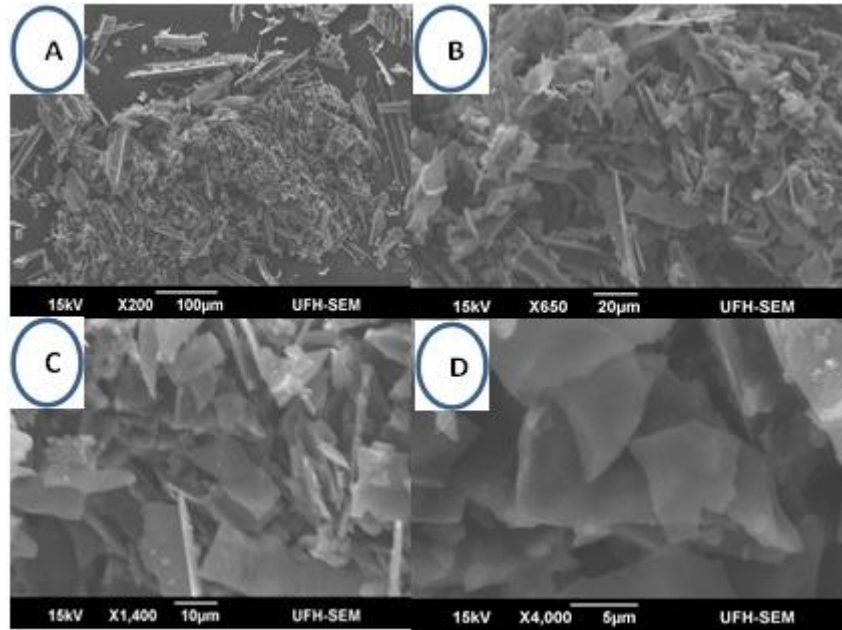


Figure 4.12: SEM images of 50% gasifier resin-50% Char

Figure 4.13 presents SEM images of gasifier resin- scrubber carbon fine particles blended product. After blending the two materials, the carbon content of the mixture increased from 76.3% gasifier resin and 78.9% scrubber carbon fine particles to 81.6%. This blending did not show any loss of carbon. The blending has generally improved the elemental quantity of both samples participated and this improvement implies that the product will be a stronger material. Figure 4.13 presents SEM images for 50% gasifier resin -50% SCFP

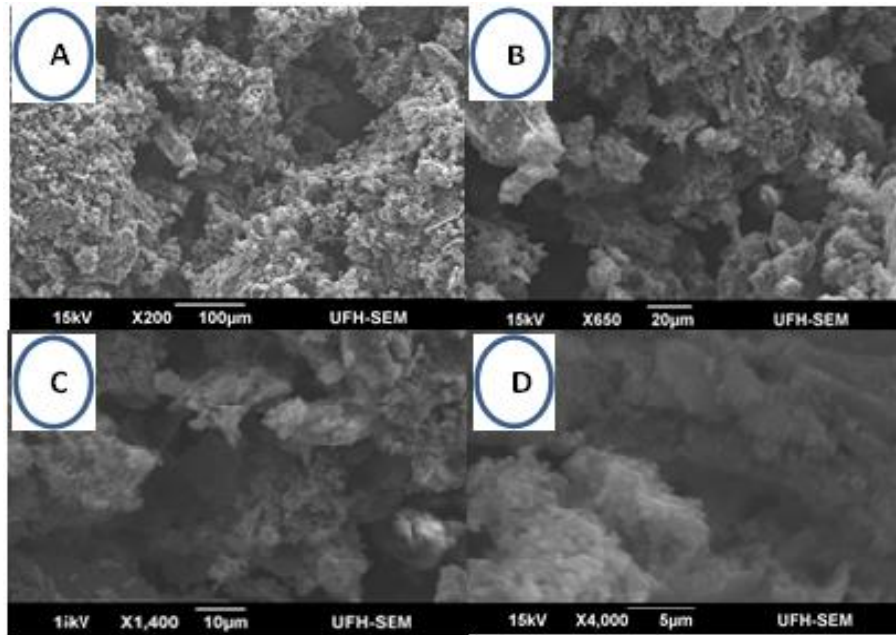


Figure 4.13: SEM images of 50% gasifier resin -50% SCFP

Figure 4.14 shows the images of cyclone carbon fine particles blended with a gasifier resin. The lowered carbon content of the mixture (54%) was caused by the lowest carbon content observed in cyclone carbon fine particles.

The homogenous character portrayed by the blends confirms the thorough blending of the materials. Blending of the materials allowed the enhancement of some major elements within the mixture. Enhancement through elemental exchange resulted to a toughened product, this was previously partially determined by CHNS analysis. The higher carbon content within the materials implies that the products could be used in many areas such as polymers. Figure 4.14 presents SEM images for 50% gasifier resin -50% CCFP

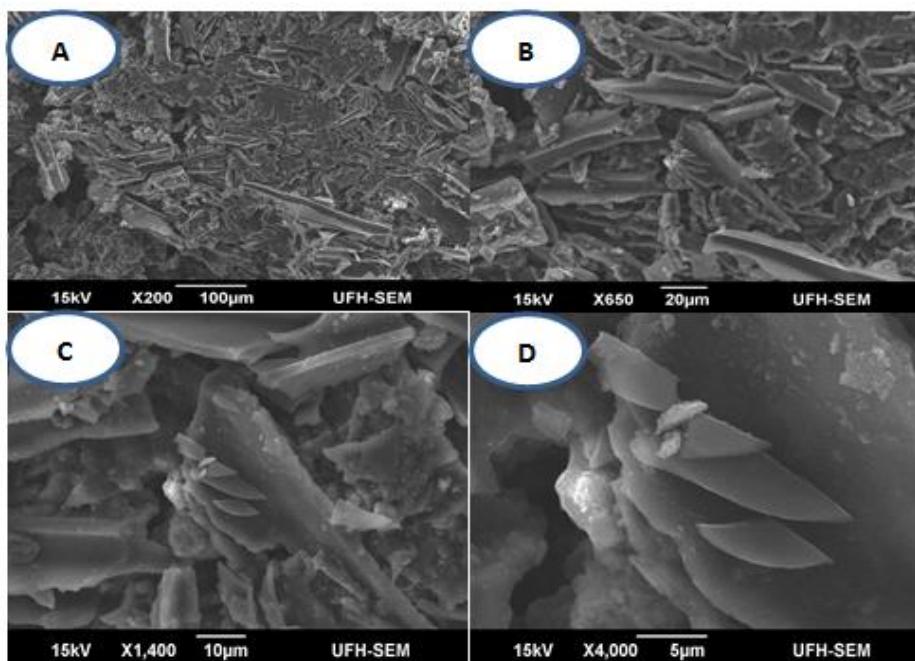


Figure 4.14: SEM images of 50% gasifier resin -50% CCFP

### 4.3 DETERMINATION OF FUNCTIONAL GROUPS FOR PURE MATERIALS

The functional groups present in the pure by-products and mixtures were determined to establish if the blending of the various by-products could have an impact in the dominant chemical bonds.

The pinewood FTIR spectrum has confirmed the expected typical lignocellulosic absorptions. The absorptions are not that far from those of the products as will be evident later in this section. Lignin and the cellulose OH groups were observed at  $3413.54\text{ cm}^{-1}$ . The C=C, C-H, C-O functional groups were some of the other absorptions observed at  $1626.05\text{ cm}^{-1}$ ,  $1399.23\text{ cm}^{-1}$ ,  $1124.49\text{ cm}^{-1}$  [Sim *et al.*, 2012]. The peak at  $2960\text{ cm}^{-1}$  was due to hydrocarbons, of which  $\text{CH}_4$  is the most abundant [Fu *et al.*, 2011].

The region below  $1500\text{ cm}^{-1}$  is the fingerprint portion of the spectra, this is where the vibrations of C-O, C-N, C-C occur [McMurry, 2008]. Figure 4.15 presents FTIR spectrum of the pinewood sample.

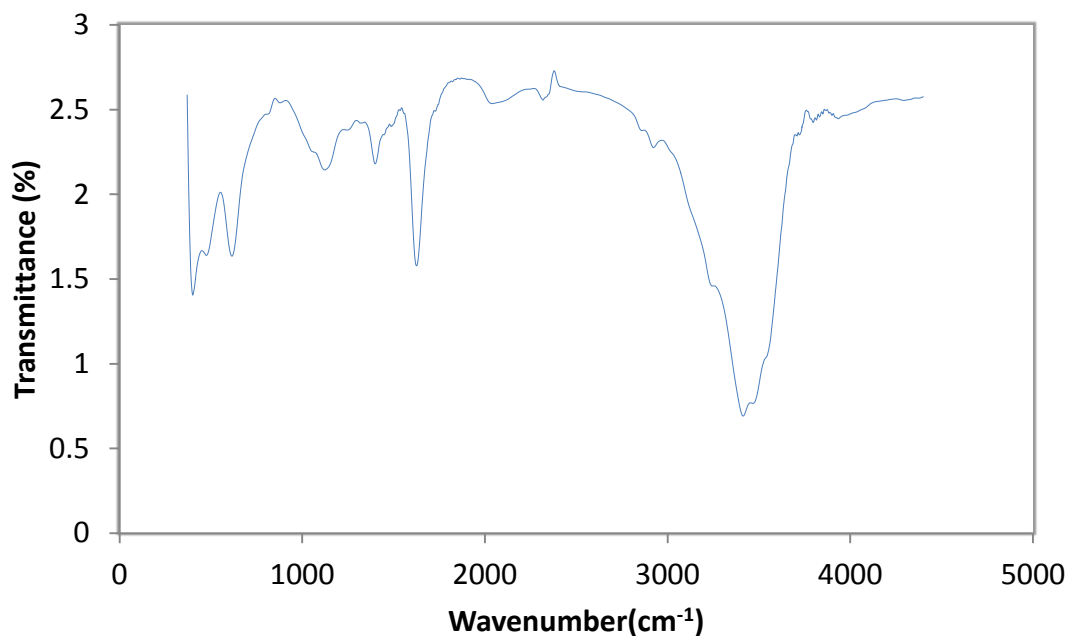


Figure 4.15: FTIR spectrum of pinewood sample

It is clear from Figure 4.16- 4.18 that the FTIR spectra of the materials under study exhibit almost the same absorption characteristics. This was due to the fact that they all emanated from the same parent material (pine wood); hence they all indicate lignocellulose characteristics. These three compounds show almost similar hydroxyl (OH) functional groups within the range of  $3400\text{-}3650\text{ cm}^{-1}$ ; the observations are due to stretching of O-H, related to water [Rajarao *et al.*, 2014]. Usually at around  $3200\text{ cm}^{-1}$ , a hydroxyl group (OH) of cellulose and hemicellulose appears, hence there are absorption peaks for all the materials at  $3239.04\text{ cm}^{-1}$ ,  $3232.54\text{ cm}^{-1}$  and  $3238.23\text{ cm}^{-1}$  respectively. Water contamination contributed to the appearance of the OH functional group.

The conjugated aromatic stretch of C=C from the lignin structure appeared at  $1621.96\text{ cm}^{-1}$ ,  $1623.39\text{ cm}^{-1}$  and  $1619.96\text{ cm}^{-1}$  for char, SCFP and CCFP respectively, this is in agreement with existing literature [Dong *et al.*, 2009]. Since all organic compounds are primarily composed of carbon and hydrogen elements, then C-H bending of alkane is evident at  $1400.70\text{ cm}^{-1}$ ,  $1400.59\text{ cm}^{-1}$  and  $1400.79\text{ cm}^{-1}$  for char, SCFP and CCFP [Silverstein *et al.*, 1981].

After thermochemical breakdown of pine wood, remains of C-O were observed within the range of  $1050\text{ cm}^{-1}$  to  $1150\text{ cm}^{-1}$ , hence for char, SCFP and CCFP there are absorption peaks at  $1127.63\text{ cm}^{-1}$ ,  $1129.36\text{ cm}^{-1}$  and  $1126.21\text{ cm}^{-1}$ . At the fingerprint region of the spectra the C-O stretch also appeared at the same point as C-C since C-C is normally found within the region of  $1100\text{ cm}^{-1}$ - $1300\text{ cm}^{-1}$ .

The observed alcohol groups imply that these materials (SCFP, char and CCFP) can be employed in pharmaceutical and cosmetic applications such as fragrances. The presence of the alkene component implies that these materials can be applied in manufacturing of plastics since alkenes are used as starting material in polymer preparation. Figure 4.16-18 presents the spectra of Char, SCFP and CCFP obtained from FTIR

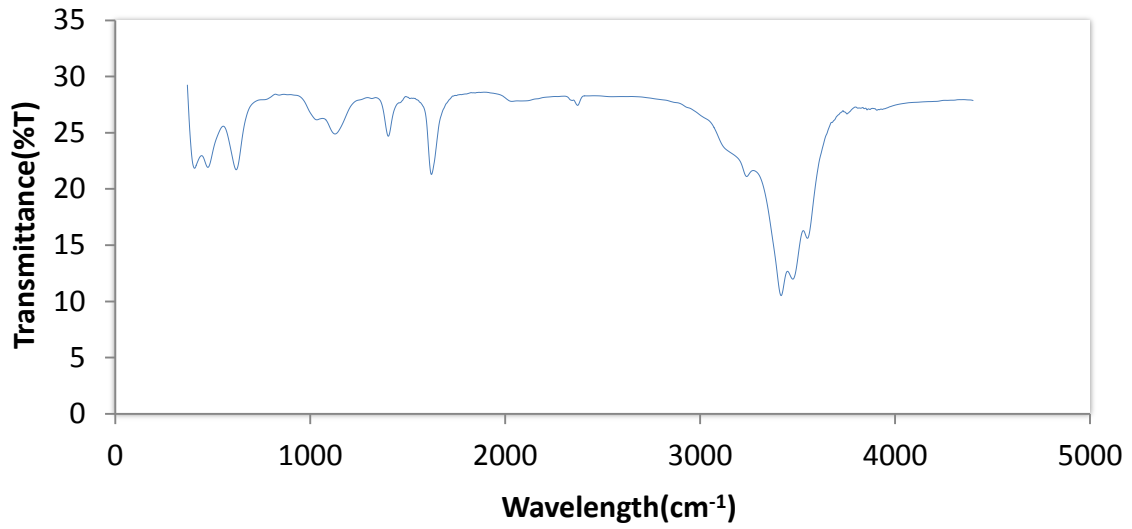


Figure 4.16: FTIR spectrum of Char

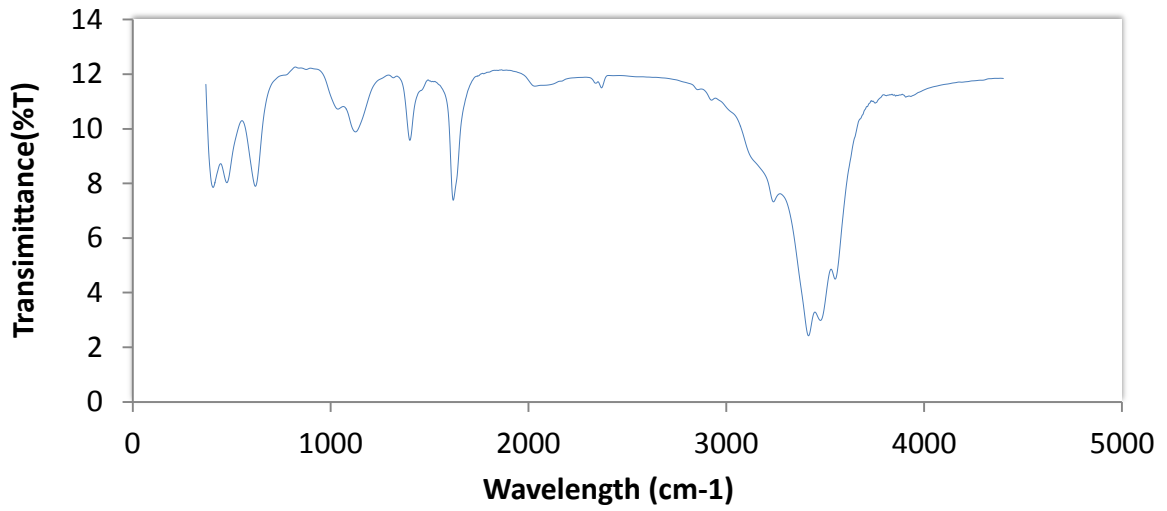


Figure 4.17: FTIR spectrum of scrubber carbon fine particles (SCFP)

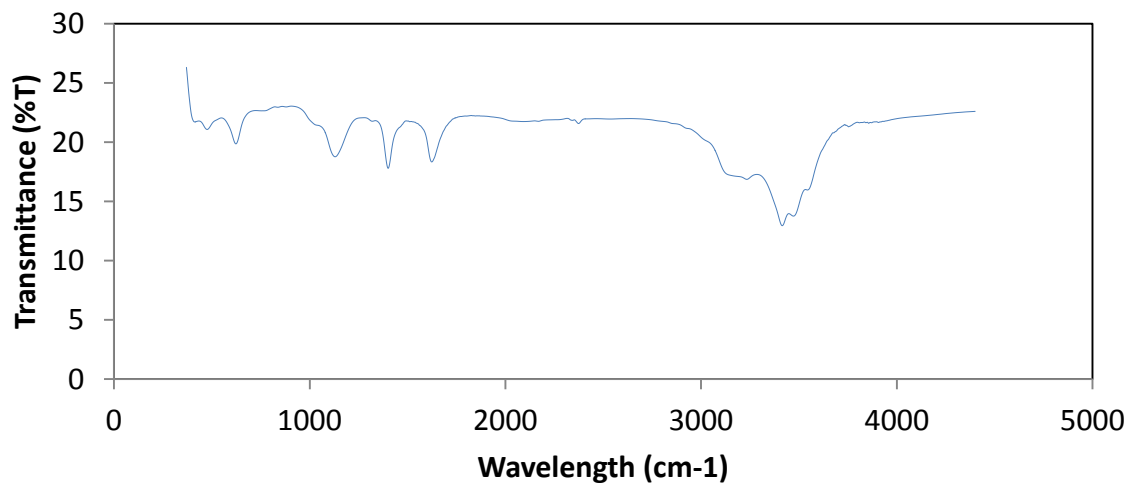


Figure 4.18: FTIR spectrum of cyclone carbon fine particles (CCFP)

The spectrum of the commercial resin shows some major absorption peaks that confirm the presence of the lignocellulosic functional groups. The functional groups obtained included stretching of OH bonds at  $3474.73\text{ cm}^{-1}$ , this was due to the moisture content of the sample. At the peak of  $2927.22\text{ cm}^{-1}$ , a C-H stretch was observed [El-Hendawy, 2006] since all organic compounds contain a carbon to hydrogen skeleton as the fundamental elements, the cracking of methoxyl group resulted to formation of methane [Fu *et al.*, 2011].

Due to aromatic skeletal vibration (C=C) in lignin, a peak arises at  $1622.86\text{ cm}^{-1}$ . Around  $1134.60\text{ cm}^{-1}$  there was an appearance of a C-O functional group of the lignocellulose. The appearance of the hydroxyl functional group (OH) implies the presence of alcohol (methanol) which is normally used in wastewater denitrification. This material can also be used in manufacturing of polymers such as polystyrene because of the unsaturated chemical compound containing at least one carbon to carbon double bond (C=C). Figure 4.19 presents FTIR spectrum of commercial resin

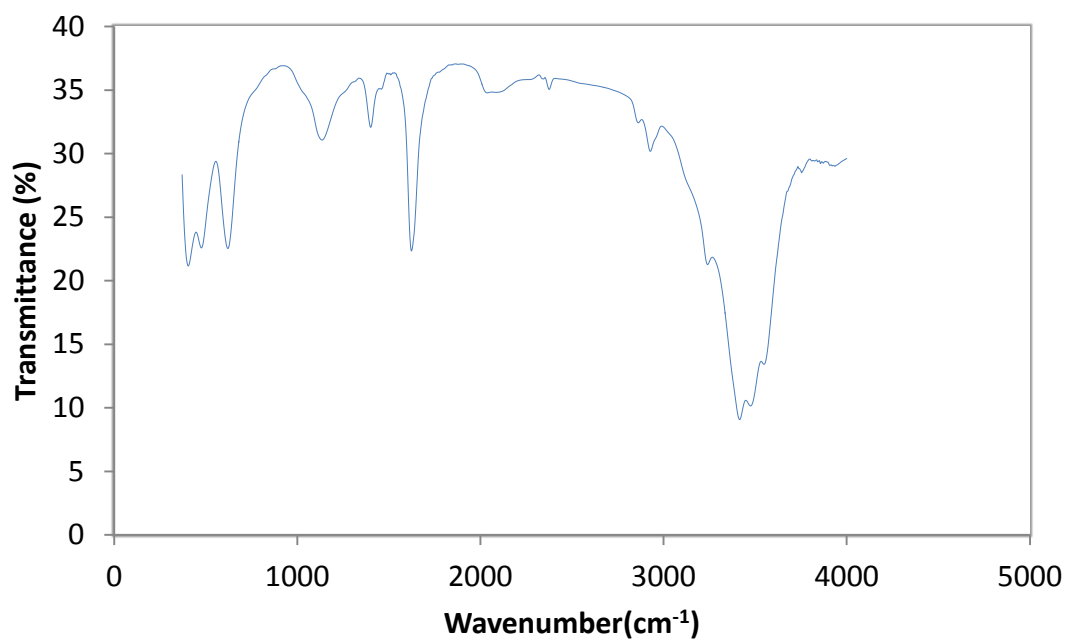


Figure 4.19: Commercial resin FTIR spectrum

The observed peak at  $3448.29\text{ cm}^{-1}$  in Figure 4.20 is contributed by the presence of the OH group that is due to water. The C=C due to aromatic ring was observed in the region of  $1509.97\text{ cm}^{-1}$ . The carbonyl functional group was observed at  $1634.32\text{ cm}^{-1}$ . The strong C-O stretch was confirmed at  $1124.12\text{ cm}^{-1}$ . Alcohol group represented by OH implies that the gasifier resin can be used in the production of medicines such as cough mixtures. The carbonyl compounds such as aldehydes and ketones allow gasifier resin to be applied as precursors for many drugs, vitamins as well as fragrances. The alkenes (C=C) are normally used as the starting material in the production of alcohols and detergents. Figure 4.20 presents the FTIR results of a gasifier resin sample

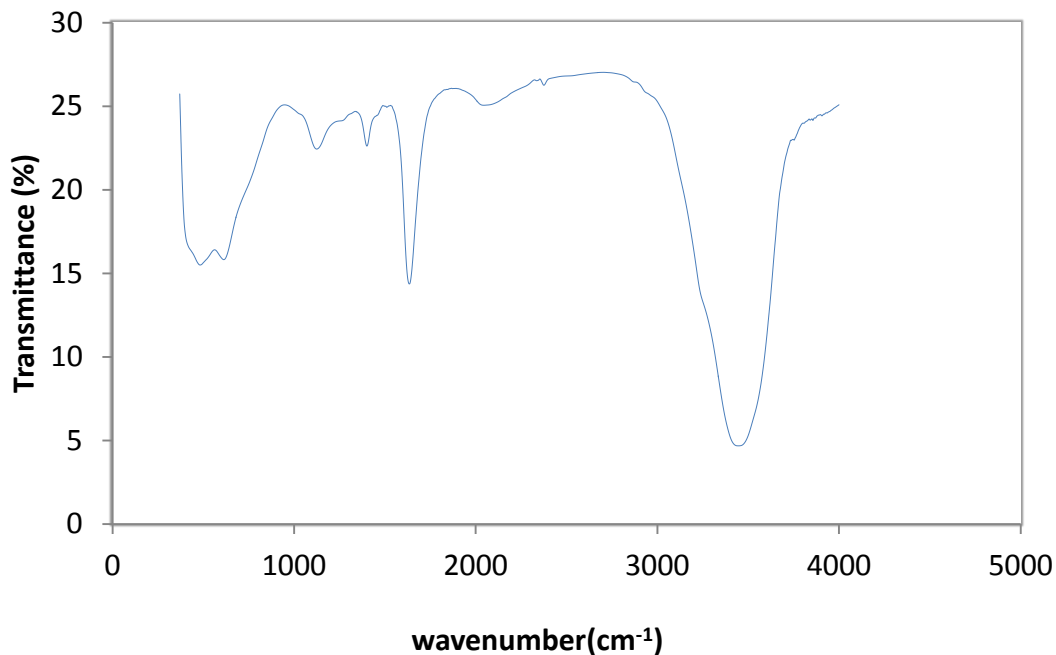


Figure 4.20: FTIR spectrum of a gasifier resin sample

#### 4.3.1 DETERMINATION OF FUNCTIONAL GROUPS FOR BLENDS

Figure 4.21 represents the FTIR spectrum of biomass gasifier resin blended with cyclone carbon fine particles in equal amounts. The SCFP sample produced a peak at  $3550.04\text{ cm}^{-1}$  which was retained again in the final product at  $3798.14\text{ cm}^{-1}$ , on the other hand the gasifier resin sample was showing none of the peak around this range of  $3550.04\text{ cm}^{-1}$  to  $3798.14\text{ cm}^{-1}$ .

The spectra of the samples and the product are all showing the presence of the moisture around  $3413.76\text{ cm}^{-1}$ ,  $3418.84\text{ cm}^{-1}$  and  $3448.29\text{ cm}^{-1}$  for the product, cyclone carbon fine particles as well as the gasifier resin. The OH group from cellulose and hemicellulose observed in the product was due to carbon fine particles spectrum as the gasifier resin spectrum confirms the absence of this functional group normally found around  $3200\text{ cm}^{-1}$ .

The gasifier resin and cyclone carbon fine particles spectra gave almost the same absorption peaks but after they were blended, many peaks were observed. The blending of the gasifier resin and cyclone carbon fine particles resulted to exchange of functional groups between the two materials.

The blended product of gasifier resin and char is illustrated in Figure 4.22 spectrum. In the spectrum of the gasifier resin-char product, it is clearly observed that the two peaks on the left hand side of the spectrum ( $3929.71\text{cm}^{-1}$  and  $3737.23\text{cm}^{-1}$ ) were absent in both samples, that is gasifier resin as well as char. The OH group in the product at  $3236.14\text{ cm}^{-1}$  was due to the char peak previously observed at  $3239.04\text{ cm}^{-1}$ , at this region gasifier resin did not show any kind of absorption.

Figure 4.23 is representing the blended equal quantities of gasifier resin and SCFP to give a homogenous product of gasifier resin-SCFP blend. The blend product came up with a peak at  $3925.57\text{ cm}^{-1}$ , this peak appeared in none of the two samples before blending. The big peak at  $3414.26\text{ cm}^{-1}$  and  $3448.29\text{cm}^{-1}$  for SCFP and gasifier resin, was also evident in the blend product at  $3413.76\text{ cm}^{-1}$ , this was confirming the OH group of the phenol. The peak around  $3200\text{ cm}^{-1}$  was due to SCFP structure while gasifier resin gave no indication of absorbance at that region.

Blending the gasifier resin with char, SCFP and CCFP added some of the functional groups which were previously not detected in latter samples. This was further proven by the introduction of the OH group (around  $3200\text{ cm}^{-1}$ ) peak which was absent in the gasifier resin sample. Figure 4.21- 4.23 shows FTIR results for 50% /50% gasifier resin- CCFP, gasifier resin- Char and gasifier resin-SCFP blends.

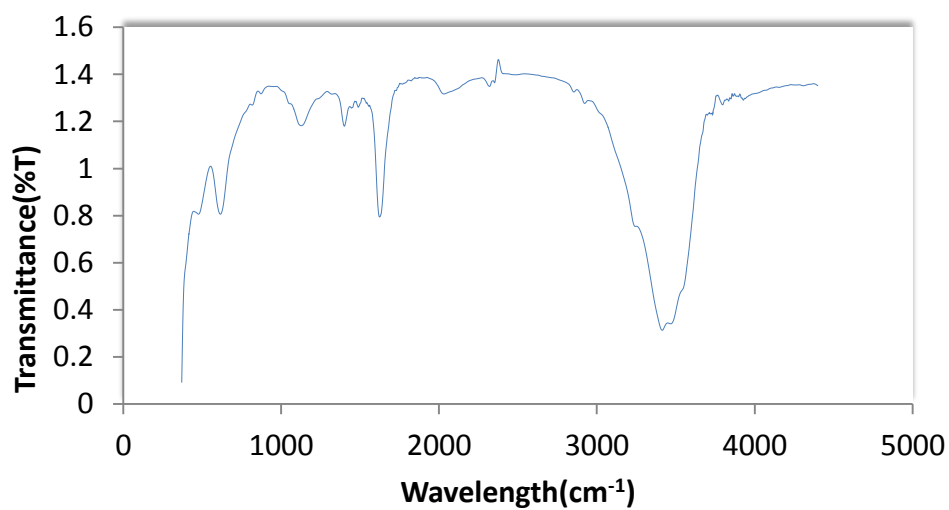


Figure 4.21: FTIR spectrum for 50% gasifier resin- 50% CCFP blend

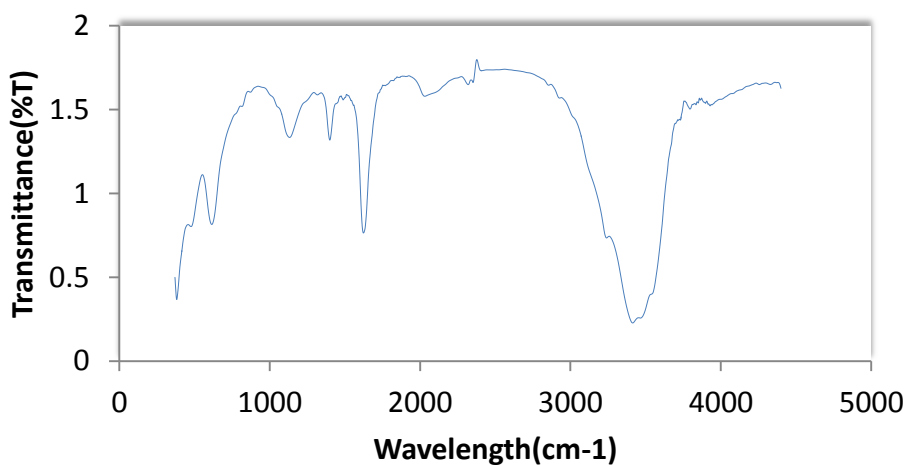


Figure 4.22: FTIR spectrum for 50% gasifier resin- 50% Char blend.

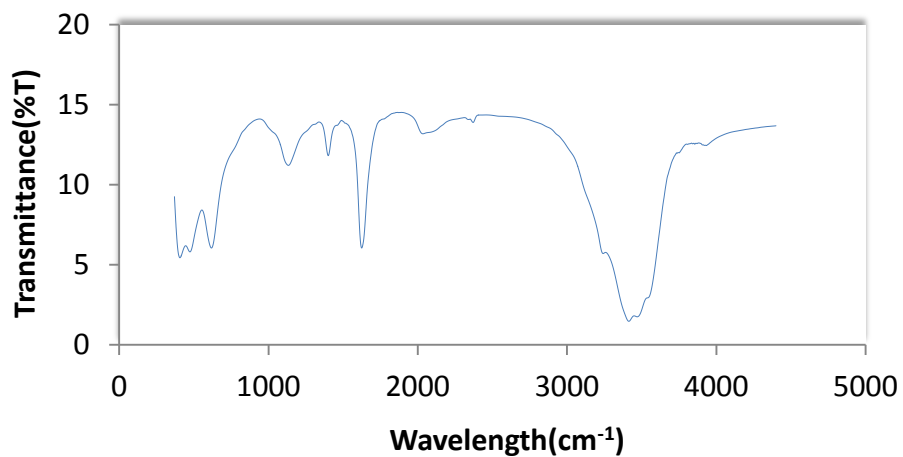


Figure 4.23: FTIR spectrum for 50% gasifier resin- 50% SCFP blend

The FTIR spectrum shown in Figure 4.24 illustrates the organic functional groups present in blended product of commercial resin and cyclone carbon fine particles (CCFP). The commercial resin- cyclone carbon fine particles blended product reveals peak at  $3931.61\text{ cm}^{-1}$ , which was not detected in cyclone carbon fine particles, this is due to the commercial resin binder which demonstrates a peak at  $3856.67\text{ cm}^{-1}$ . Commercial resin shows a peak at  $2927.22\text{ cm}^{-1}$  which does not appear in both the blended product and cyclone carbon fine particles spectra.

The FTIR spectra results obtained show mostly the same absorption wavelengths of the materials used in blending. The commercial resin-scrubber carbon fine particles blend in Figure 4.25 shows the existing functional groups after blending commercial resin with SCFP. The lignocellulose functional groups still appear in all blended products since the components are mainly lignocellulose in nature.

The commercial resin peak at  $3547.73\text{ cm}^{-1}$  contributed to the peak observed at  $3550.24\text{ cm}^{-1}$  for the blended product as for the SCFP there was no peak around that range. The other which was due to blending was the peak at  $2342.44\text{ cm}^{-1}$ , this peak is assumed to be contributed by commercial resin which shows a peak at  $2342.61\text{ cm}^{-1}$  and no peak was revealed by SCFP. The blending of commercial resin with SCFP confirms the strengthening effect to be largely contributed by the commercial resin as it shows some peaks in the product which did not previously appear in the SCFP sample. The functional groups detected increased after the blending of commercial resin and scrubber carbon fine particles.

The FTIR results spectra of commercial resin-char blended product are illustrated in Figure 4.26. The two peaks at  $3856.67\text{cm}^{-1}$  and  $3753.54\text{cm}^{-1}$  in commercial resin combined to form one peak of the blended product at  $3905.74\text{cm}^{-1}$ . The peak of the blended product at  $3905.74\text{cm}^{-1}$  and  $2345.97\text{cm}^{-1}$  were due to commercial resin peaks at  $3856.97\text{cm}^{-1}$  and  $2342.61\text{cm}^{-1}$  respectively. The char spectrum illustrates none of the latter peaks.

The results confirm the advantage of blending different samples as the products illustrate the strengthening by increasing functional groups and keeping the composition of the blended samples. Commercial resin is proven to be a good binder because of its ability of not losing the chemical composition of the samples it bonds to, this is further demonstrated in all the samples it was blended with. This blending produces tough, heat resistant, flexible material that can be used as an adhesive in wind turbine blades and other similar applications such as propellers of fans. Figure 4.24- 4.26 presents FTIR results for 50% /50% commercial resin-CCFP, commercial resin-SCFP blends and commercial resin- Char blends.

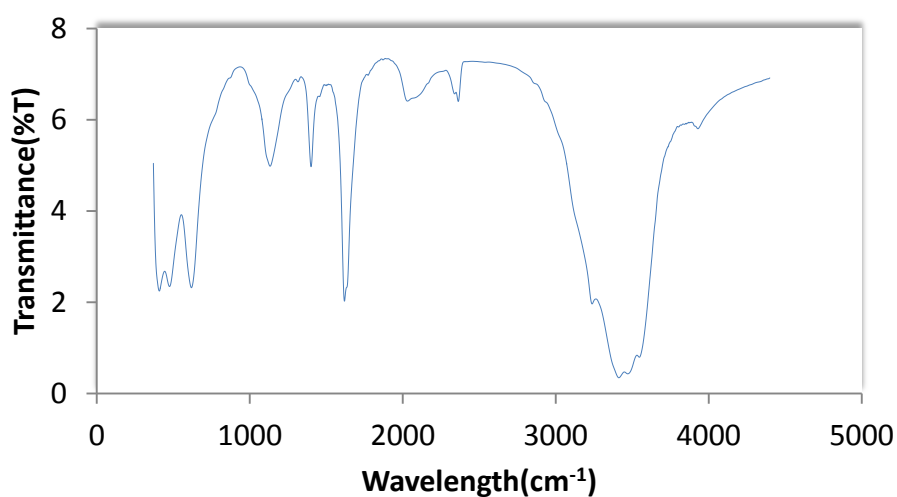


Figure 4.24: FTIR spectrum for 50%commercial resin- 50% CCFP blend

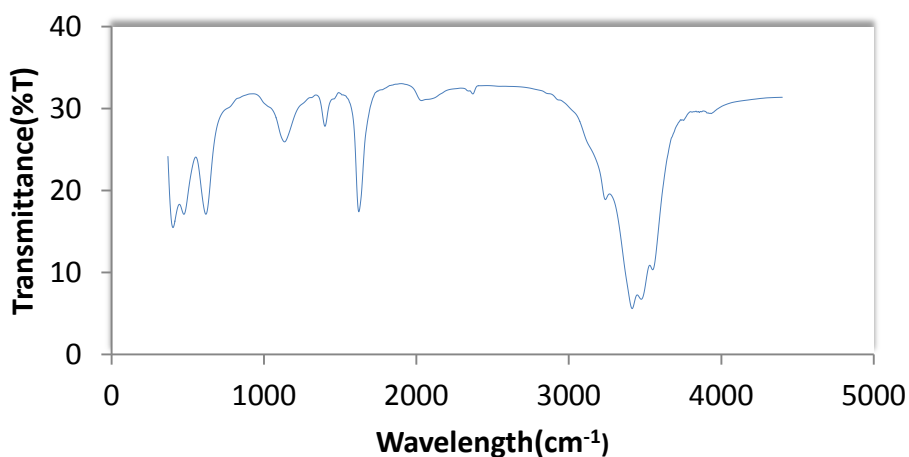


Figure 4.25: FTIR spectrum for 50%commercial resin- 50% SCFP blend

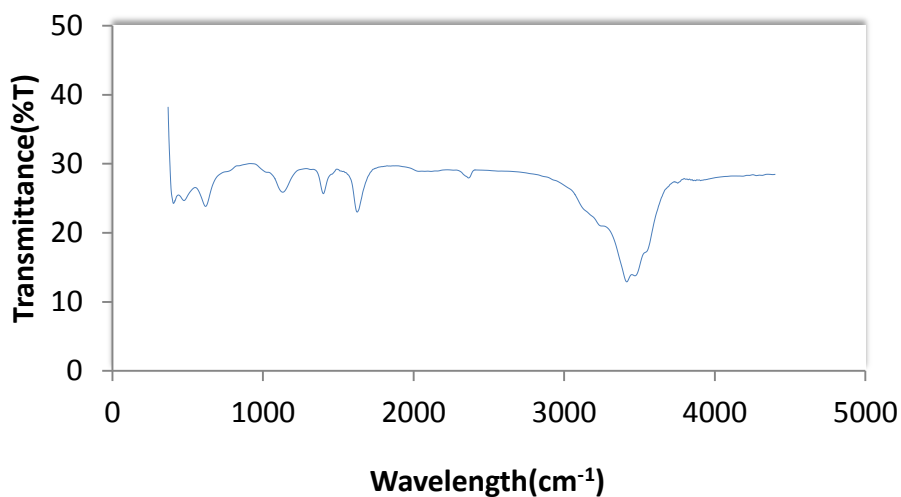


Figure 4.26: FTIR spectrum for 50%commercial resin- 50% Char blend

#### 4.4 X-RAY DIFFRACTION RESULTS FOR PURE MATERIALS

The structures of the materials were determined using D8 Bruker XRD previously described in Chapter 3. The essence of the characterization was to determine the morphology of the by-products as to predict the bonding when applied in other areas.

The pine wood structure from the XRD spectrum in Figure 4.27 confirms the amorphous nature because of the peaks observed at  $21.3587^\circ$  and  $34.8687^\circ$ . The material is indicating a highly disordered structure of the sample at  $2\theta = 23^\circ$  [Fu *et al.*, 2011]. Figure 4.27 Illustrates XRD results of pine wood.

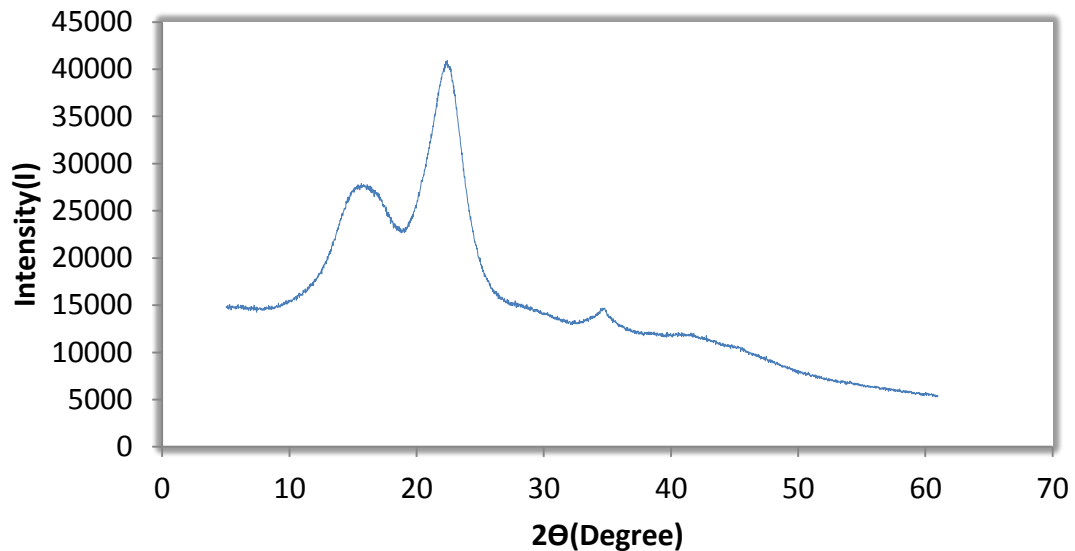


Figure 4.27: XRD spectrum of pine wood

From XRD results of commercial resin presented in Figure 4.28, an inference can easily be drawn that the commercial resin is amorphous. The range of these obtained results is in agreement for a lignocellulose amorphous compound, as amorphous structures are detected within the range of  $10^\circ$  to  $35^\circ$ . The band observed at  $44^\circ$  represents traces of ordered graphitic carbon [Klinghoffer, 2013]. Figure 4.28: presents XRD spectrum of commercial resin spectrum

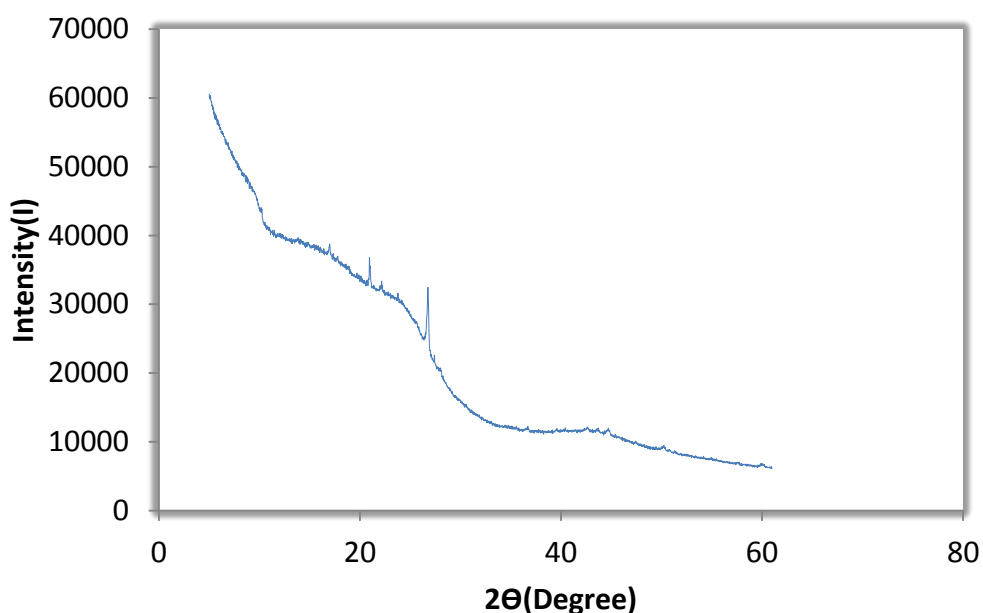


Figure 4.28: XRD spectrum of commercial resin spectrum

The XRD results presented in Figure 4.29- 4.32 indicate both broad and sharp varying intensities. The intensities within the range of  $10^{\circ}$  to  $35^{\circ}$  attributes to amorphous carbon composed of aromatic rings. The observed peaks for cyclone carbon fine particles (CCFP) were at  $21.3157^{\circ}$ ,  $26.5482^{\circ}$  and  $29.1644^{\circ}$ . For SCFP, both broad peak at  $25.0471^{\circ}$  and a sharp peak at  $26.3981^{\circ}$  appeared. The spectrum for char, gave broad peaks at  $23.7819^{\circ}$  and  $43.2963^{\circ}$ , and a sharp peak at  $29.3574^{\circ}$ . In nature Char is amorphous and contains structure of compounds that are highly conjugated [Yaghoubi, 2011; Qadeer *et al.*, 1994] The amorphous material has a great adsorbent property because of its high specific surface area and contains more active sites on the surface which makes it more advantageous for the adsorptive property [Tchomgui-Kamga *et al.*, 2010]. This therefore implies that the materials can easily form bonds with binders to produce strong materials. Figure 4.29-4.32 presents XRD spectra of gasifier resin, cyclone carbon fine particles, scrubber carbon fine particles and char

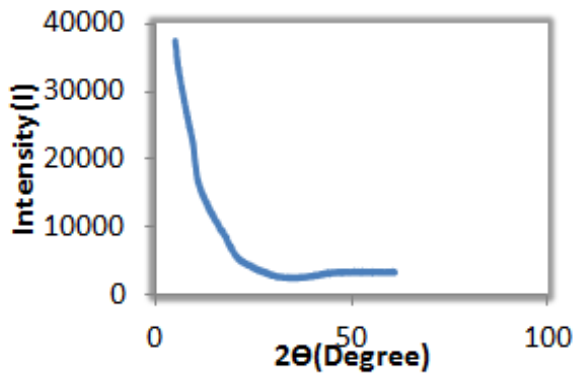


Figure 4.29: XRD spectrum of gasifier resin

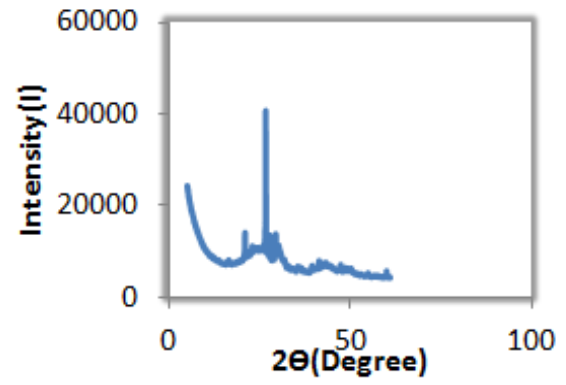


Figure 4.30: XRD spectrum of cyclone carbon fine particles

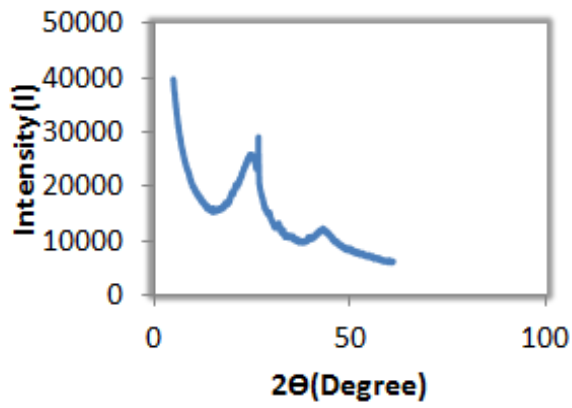


Figure 4.31: XRD spectrum of scrubber carbon fine particles

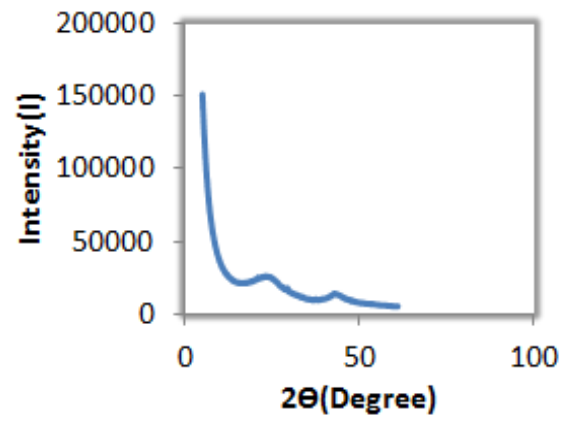


Figure 4.32: XRD spectrum of Char

#### **4.4.1 X-RAY DIFFRACTION RESULTS FOR BLENDS**

Under XRD, the blended products showed almost similar spectra to those of the pure materials presented in Figure 4.29- 4.32. The highly disordered structures were observed at  $23^\circ$  and  $25^\circ$  [Fu *et al.*, 2011 and Rajarao *et al.*, 2014]. This was due to the fact that the samples are composed of the same chemical structures. Since the products are produced from the same material, then they are expected to give similar characteristics to those of pure materials. All of those blended products show the amorphous nature, as observed in pure organic samples. This implies that blending the samples did not change the integrity of the samples. Figure 4.36- 4.38 presents XRD spectra for 50%/ 50% gasifier resin- char, gasifier resin – SCFP and gasifier resin – CCFP mixtures. Figure 4.33- 4.35 shows XRD spectra for 50% / 50% commercial resin- char, commercial resin-SCFP, commercial resin- CCFP blends

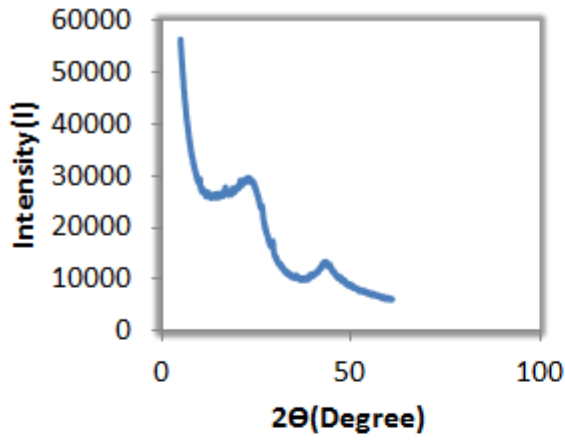


Figure 4.33: XRD results for  
50% commercial resin-50%Char

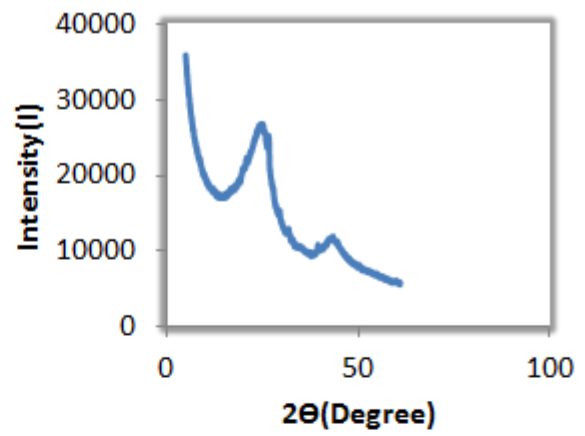


Figure 4.34: XRD results for  
50% commercial resin-50%SCFP

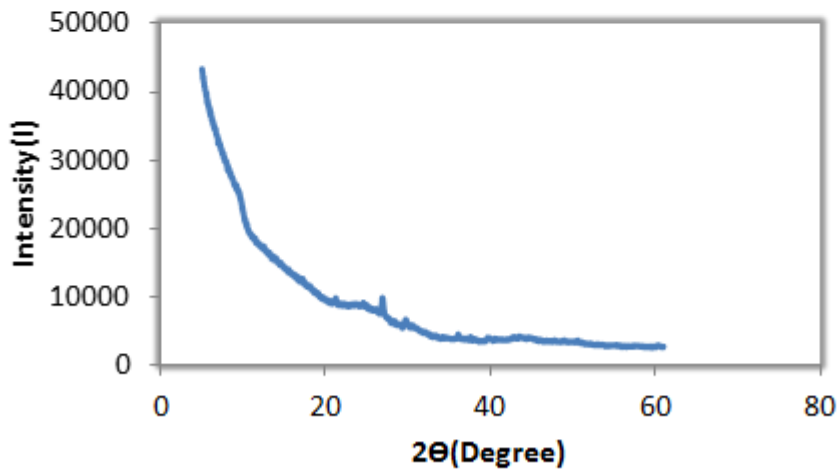


Figure 4.35: XRD results for 50% commercial resin-50%CCFP

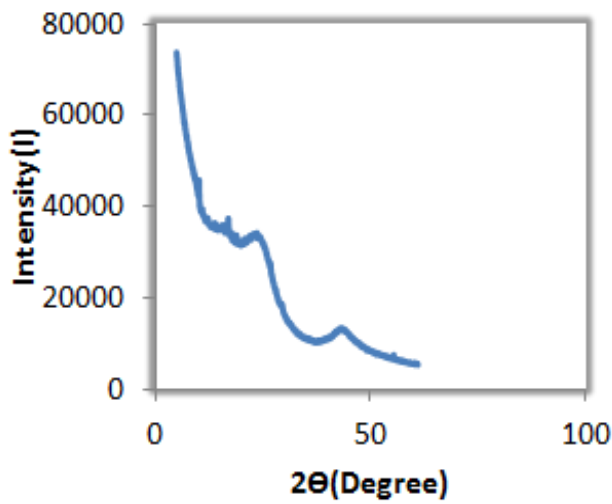


Figure 4.36: XRD results for 50% gasifier resin-50%Char

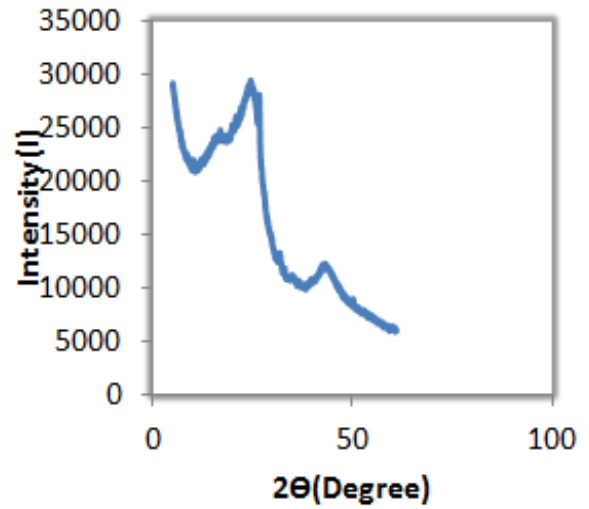


Figure 4.37: XRD results for 50% gasifier resin -50% SCFP

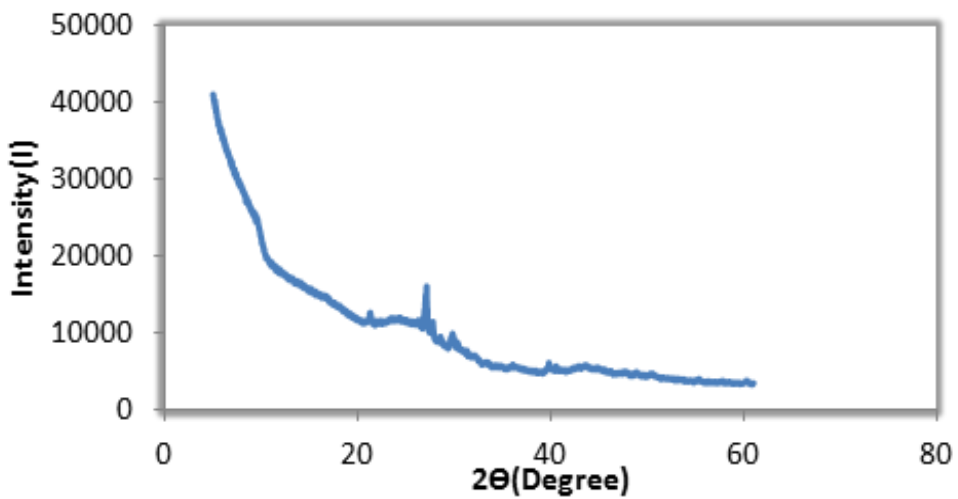


Figure 4.38: XRD results for 50% gasifier resin -50% CCFP

#### 4.5 CALORIFIC VALUES FOR PURE MATERIALS

The calorific values of the materials were determined using a CAL 2K oxygen calorimeter described in Chapter 3. This was to investigate the energy content of the samples.

The calorific value of pinewood was in agreement with those values found in literature [Naik *et al.*, 2010 and Ravindran, 2011]. The calorific values of the gasification by-products studied was found to be between 21.75MJ/Kg (lowest) and 35.37MJ/Kg (highest). The calorific value of wood is generally lower than that of char. The high calorific value of char, which is comparable with good quality coal is due to low ash yields from partially combusted pine wood material. This therefore implies that high ash yields decrease the calorific value of char and inversely low ash yields increase char calorific value. The formation of the char is largely contributed by lignin, while cellulose contributes to formation of volatile matter [López *et al.*, 2013]. The volatile matter is removed during gasification leaving the lignin behind, which then results in high calorific value of the char. The calorific value of any material in thermochemical process is hugely affected by moisture content, volatile matter as well as its ash content. A 1% increase in carbon concentration will elevate the calorific value by approximately 0.39MJ/Kg [López *et al.*, 2013]. The moisture content of the pine wood material used in gasification is revealed by the calorific values, as they confirm the dryness of the feedstock.

The downdraft gasifier used for this study works well with feedstock with moisture content below 20% but it has a tolerance of up to 25% moisture in the feedstock. Generally the gas calorific value decreases with an increase in moisture content in feedstock. The moisture in the feedstock also condenses against the walls of the condensates trap and it gets drained out with the gasifier resin thereby providing a transparent medium for the gasifier resin to the condensate tank. In the absence of the water, the viscosity of the resin could make it difficult for the resin to be drained out. The resin later settles at the bottom of the condensate container with water on top. This makes the separation of the two easy. Table 4.3 presents tabulated calorific values for various samples used in the experiment.

Table 4.3: Calorific values of various samples used in the experiment

Sample type	Calorific Values (MJ/Kg)				
	Trial 1	Trial 2	Trial 3	Mean	Standard Deviation
Pine wood	20.05	19.35	18.85	19.42	0.43
Char	35.30	36.05	34.75	35.37	0.46
CCFP	21.90	21.30	22.05	21.75	0.24
SCFP	25.54	24.80	25.20	25.18	0.26
Commercial resin	31.80	33.15	33.08	32.68	0.54
Gasifier resin	28.37	28.19	29.12	28.56	0.35

#### 4.5.1 CALORIFIC VALUES FOR BLENDS

According to the results presented in Table 4.4, it is observed that the samples blended with commercial resin have higher calorific values as compared to those blended with gasifier resin. The blends of cyclone carbon fine particles have decreased calorific values; this was due to the value of cyclone carbon fine particle as previously observed in Table 4.3 of chapter 4. The blending of the materials brought an increase in caloric values of the blended products. The caloric values of commercial resin blends imply that the gasifier resin can replace the commercial resin material as there is a small difference in their blends. These materials can also be re-gasified for the production of syngas. Table 4.4 presents calorific values of various samples blended at one ratio

Table 4.4: Calorific values of various samples blended at one ratio

Sample type	Calorific Values (MJ/Kg)				
	Trial 1	Trial 2	Trial 3	Mean	Standard Deviation
50% Gasifier Resin-50% Char	31.63	31.77	31.48	31.63	0.33
50% Commercial Resin-50% SCFP	33.82	34.25	33.95	34.01	0.25
50% Commercial Resin -50% Char	34.75	34.86	34.63	34.75	0.12
50% Commercial Resin-50% CCFP	25.10	24.89	25.18	25.06	0.11
50% Gasifier Resin - 50% SCFP	32.16	34.78	33.34	33.47	0.93
50% Gasifier Resin - 50% CCFP	26.84	27.18	27.48	27.17	0.23

## **CHAPTER 5**

### **SUMMARY, CONCLUSIONS AND RECOMMENDATIONS**

#### **5.1 SUMMARY OF FINDINGS**

The preference of biomass gasification technologies over fossil fuel technologies has increased over the years. This type of renewable energy technology is highly recommended as it provides a lot of advantages to the environment when compared to fossil fuel technology. These technologies are mainly employed for production of chemicals as well as power generation. The micro traces of tar in the producer gas make the downdraft biomass gasifier to be more preferable for the process of gasification.

This research looked at the investigation into the characteristics of biomass gasification by-products from a downdraft gasifier system. This was done because there is currently less information published on the by-products produced from the downdraft gasifier system. There is also currently no information on blending of the gasifier by-products for production of stronger materials. The research found that the by-products such as char, gasifier resin and carbon fine particles could be useful in a number of applications including wastewater filtration, adhesives, detergents, and so on. The research also established that the blending of the various by-products results in much stronger products that are suitable for various applications provided they pass certain tests required for each application.

## **5.2 SUMMARY OF CONTRIBUTIONS**

The downdraft biomass gasifier system installed at Melani village provides gas to run the engine that produces electricity to the community bakery. However, the gas production simultaneously generates the by-products. These by-products have not been well studied; hence the need to do further study towards them was necessary. The major contribution of the study was to add knowledge on the biomass gasifier by-products through characterization and an investigation into their possible applications. The study has successfully characterized the by-products and identified areas in which they could be employed. This has resulted in addition of value to the by-products that were largely regarded as waste materials that were difficult to handle.

## **5.3 CONCLUSIONS**

The elemental analysis of the char blended with gasifier resin and commercial resin was much more preferable as the mixture resulted in higher carbon content of the blends. When scrubber carbon fine particles and cyclone carbon fine particles blends were compared to those of char, the char blends were found to contain higher carbon content. It was also found that the increase in carbon content results in lower oxygen content of the blends.

The FTIR results confirmed lignocellulose structures for all the analysed samples. The investigation established C-O, C=C, C-H, O-H as the major functional groups present in the samples. After XRD confirmation, it was concluded that all the samples contained amorphous carbon. In addition, there were no traces of graphite observed in the samples.

The blends showed tightly bonded materials. The bonding resulted in the elemental exchange which gave strengthened products; this was confirmed by SEM. The blending of the materials was significant as it increased the elemental composition within the blends, this hugely contributed to the strength of the products.

The research successfully investigated the characteristics of biomass gasification by-products together with some of their applications in different areas. The study of these by-products and their utilization guarantees a technology free of waste as waste produced will be used for other applications. This will reduce the amount of hazardous materials discharged to the environment.

#### **5.4 RECOMMENDATIONS FOR FUTURE RESEARCH**

The study has successfully investigated the chemical and structural characteristics of the biomass gasifier by-products. It has further established the possible applications of the by-products in other areas. Provided that they meet certain criteria, these materials have a potential to be used for such applications as plastics, adhesives etc. However the research did not conduct any application of the by-products in the recommended areas. Therefore, there is a need for a study or studies focused on the application of the by-products in the recommended areas and beyond. These studies would include, amongst other things, the processes and processing involved up to the final products and the study of the products.

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## **APPENDIX 1**

### **Research output associated with this research**

Aviwe Melapi, Mamphweli N. Sampson, Katwire M. David, and Meyer L. Edson, (2014),  
The physical and chemical properties of fine carbon particles - pine wood resin blends and  
their possible utilization, *Journal of Chemistry*. Article under review Ref. No.: 137580