CHEMICAL AND THERMAL ANALYSIS OF EUCALYPTUS/COAL BLENDS FOR CO-GASIFICATION

University of Fort Hare
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A dissertation submitted in fulfillment of the requirements for the degree of

Master of Science (MSc)

By

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DEDICATION

This work is dedicated to my family especially my wonderful mother Mrs. Evelyn; my father Mr. Xola for all the love, encouragement and support they gave me. Not living out my special sisters, Ntombomzi and Sinazo and my one and only brother, Mongameli, and definitely not forgetting my lovely daughter, Zizipho, and everyone at home I couldn't mention. This is actually for the whole family.

Without you guys I don't know how I would have survived. May the God almighty richly bless you all.

DECLARATION

I, the undersigned, hereby declare that this dissertation entitled "Chemical and Thermogravimetric Analysis of the biomass coal blends for co-gasification" is my own work, and that all the sources I have used or quoted have been duly acknowledged. The work has not been submitted as part or in whole for a degree at this or any other University or institution of higher learning.

Signature:--

Signed on this ---------------day of-----------------year-----in------------------------------

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EXECUTIVE SUMMARY

While the industry is expected to reduce CO_2 emissions due to global warming, global electricity demand is increasing at an enormous rate. As a result, there is a need to improve the efficiency of energy use through changes in technology and to produce energy vectors that have almost zero emissions of greenhouse gases. Co-gasification of biomass and coal can be considered as a possible fuel-base for syngas production. The properties of the feedstock govern the design of the gasifier. Gasification feedstocks differ greatly in their physical and chemical properties. Each type of gasifier operates satisfactorily in terms of gas quality and efficiency within certain ranges of fuel properties. Currently there are proven coal gasifiers as well as biomass gasifiers that take the two feedstocks independently. The chemical properties of coal / biomass blends differ from those of coal or biomass alone, and that requires an entirely different gasifier type.

The coal / biomass co-gasification has the advantage of the reduction of SO_2 emissions besides the other important implications of environmental and economic concerns such as the reduction of fuel cost, and also diminishing wastes disposal problems as well as a favourable effect on the net CO_2 balance, that is the reduction of the greenhouse gases, due to the renewable characteristic of biomass materials [Cordero *et al*, 2004].

The value of a particular type of biomass depends on the chemical and physical properties of the large molecules from which it is made.

This research investigated the chemical and thermal properties of eucalyptus and coal to establish the gasification characteristics of the eucalyptus / coal blends with the aim of reducing the impact of coal combustion and utilization of large volumes of water for electricity generation. Proximate and ultimate analysis of the various coal / biomass blends was conducted to establish the optimum mixing ratios for gasification, using a muffle furnace. A bomb calorimeter was used to determine the calorific values of the various coal / biomass blends in order to establish the optimum mixing ratio that result in higher energy value and enhanced conversion efficiency. CHNS analyzer and XRF spectrometer were used for the determination of the elemental analysis of the biomass material and coal as well as the biomass / coal blends.

Thermogravimetric analysis of the various blends was undertaken to establish the thermal stability of the various blends at various temperature ranges and their possible thermal behaviour during gasification using a thermogravimetric analyzer. The results obtained suggested that there is a synergistic effect when coal and eucalyptus wood are blended before gasification. This effect was clearer with thermogravimetric analysis.

Keywords: eucalyptus, coal, co-gasification, synergy.

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EUC – eucalyptus

XRF – X-ray florescence

ODW – oven dry weight

TGA – thermogravimetric analysis

DTG – derivative thermal degradation

CHAPTER 1: INTRODUCTION

1.1. BACKGROUND

The world is facing high energy demand about three times the rate of total energy, whereas the industry is expected to reduce carbon dioxide (CO_2) emissions because of global warming. As a result, there is pressure to improve the efficiency of energy use through changes in technology and to produce energy vectors such as syngas which have almost zero emissions of greenhouse gases. The extensive increase in energy demand and consumptions of natural resources and goods, caused by the increase in world population has led to massive amounts of wastes. Biomass / coal gasification is an old technology that recently gained popularity due to the concerns of the impact of fossil fuel utilization on the environment (Collot, 2006).

A number of studies on the thermo chemical conversion of biomass or residues from wood products have been carried out. These studies revealed in principle a similar behaviour to that of coal. In general, a total gasification process can be generally separated into two main reaction stages called pyrolysis and gasification. The pyrolysis stage corresponds to reactions related to devolatilization or thermal decomposition that occur during the initial heating-up of a solid fuel, and is completed in only seconds, or less at high temperature [Pan *et al*, 1996].

Co-gasification of coal and biomass is known to offer several advantages over coal or biomass gasification. It gives the benefits of reliable supplies of abundant solid fuel such as coal and credits resulting from utilization of a renewable zero emission energy resource such as biomass.

[Howaniec *et al*, 2011]. The addition of woody biomass to coal gasification does not only reduce CO_2 emissions but also reduces the problems caused by sulfur and ash found in coal, this is because the woody biomass has almost no sulphur and has low ash content. Biomass and coal are essentially chemical opposites, coal contains larger quantities of sulfur and ash, biomass contains more oxygen and nitrogen and is more prone to producing tar. Coal contains many transition metals, while biomass contains more alkali and alkaline-earth metals, usually in the form of salts (especially sodium and potassium). Biomass is also more likely to produce ammonia, which is useful as a cleaning agent, but can be emitted as a deadly pollutant if not properly contained. Biomass also has a generally higher volatile content than coal [Kumabe *et al*, 2007, and Long III and Wang, 2011].

Biomass gasification involves an incomplete combustion of biomass that results in the production of flammable gases consisting of carbon monoxide (CO), carbon dioxide, (CO_2), hydrogen (H_2), nitrogen (N_2) and methane (CH_4), may also be present if air is used as the gasification agent. This mixture is called a producer gas or syngas. Even though biomass can be converted to syngas, the process is a bit challenging because of the formation of tar and char even if the process operated at very high temperature. One of the common ways to reduce the tar contents from the syngas is the use of catalysts such as dolomite in the process, [Shen *et al*, 2008].

Gasification of coal is a promising technology for the production of electricity. Coal that is rich in volatiles contains high-value chemical structures like aromatic rings. These chemical structures are completely converted into simple molecules of H_2O, CO_2, CO, H_2, and hydrocarbons in gasification. [Zhang *et al*, 2012]. The coal is prepared and fed to the gasifier. Inside the gasifier, the feedstock reacts with gasification agent, which could be steam or oxygen, which then result in syngas. The syngas can then undergo purification in downstream process, [Xiang *et al*, 2010].

The gasification technology is well established in heat provision and slightly established in the electricity generation industry. This is mainly due to the fact that the fixed bed downdraft gasifier that is suitable for electricity generation using gas engines cannot be practically scaled beyond 30 MWt; this is because of by the production of tar in large scale downdraft gasifier technologies which is attributed to the uneven heat distribution around the throat section of the gasifier. However, these gasifier types produce gas with [illegible] little quantities of tar at a small scale. On the other hand, the other gasifier types are easy to scale up but their problem is the production of tar laden gas, which then interferes negatively with internal combustion engines or the gas turbines as well as the downstream gas purification systems, leading to high operational costs.

1.2. PROBLEM STATEMENT

About 95% of the electricity in South Africa is generated from coal-fired power stations. The country cannot simply do away with the current practice and give way for alternative sources of energy because of the cost implications. Eskom has started co-firing of coal and biomass in their power stations to improve the carbon footprint of their coal fired power stations. However, co-firing of biomass and coal still result in high levels of greenhouse gas emissions even though biomass is carbon neutral since the carbon dioxide emitted from the coal part is not accounted for during photosynthesis, whereas the part emitted by the biomass is assumed to be used by the living plants during photosynthesis. Furthermore, co-firing also utilizes large volumes of water and results in extensive environmental impacts. This research investigated the possibility of co-gasification of coal and biomass, which is a thermochemical process that uses about a third of the water required by a coal-fired power station, and results in comparatively very less emissions. The gasification of biomass alone is not economically feasible due to its lower energy value and the coal blending solves this challenge while the biomass improves the carbon footprint of the process.

1.3. RESEARCH OBJECTIVES

The main aim of this research was to establish the possibility of gasifying eucalyptus and coal because it has the possibility of reducing the emission impact of coal combustion and utilization of large volumes of water for electricity generation. The following were investigated for fulfillment of the latter aim:

i. The impact of the blending of eucalyptus wood with coal on the energy value of coal and biomass.
ii. The chemical composition of the eucalyptus wood and coal as well as that of the various eucalyptus / coal blends, and the impact of blending coal with eucalyptus on the chemical properties of the two.
iii. The eucalyptus / coal blends that result in high gasification conversion efficiency as determined through computer simulation.

1.4. RESEARCH QUESTIONS

i. Is it possible to combine coal and biomass during gasification in a low temperature downdraft biomass gasifier and achieve the high conversion efficiency?
ii. What are the gasification characteristics and properties of coal and eucalyptus blends?
iii. What are the mass and energy balances during gasification of the various coal / biomass blends and what is the possible conversion efficiency?

1.5. RESEARCH METHODOLOGY

Proximate and ultimate analysis of eucalyptus, coal and the eucalyptus / coal blends were undertaken to establish the optimum mixing ratios for gasification, and also for simulation of the gasification process. A muffle furnace was used to determine the moisture content, volatile matter and ash contents. A bomb calorimeter was used to determine the calorific values of pure coal, pure eucalyptus wood as well as the eucalyptus / coal blends in order to establish the optimum mixing ratio that result in higher energy value and enhanced conversion efficiency. CHNS analyzer and XRF spectrometer were used for the elemental analysis of coal, eucalyptus as well as for the eucalyptus / coal blends. Thermogravimetric analysis was undertaken to establish the thermal stability of coal, eucalyptus as well as the blends at various temperature ranges.

1.6. DELINEATION AND LIMITATIONS

A number of factors affect the co-gasification of coal and biomass materials including the stoichiometric fuel/air ratio and the gasifier design in general. This project established the synergistic effect during the gasification of the eucalyptus / coal blends through thermogravimetric analysis of the eucalyptus / coal blends. The eucalyptus wood was chosen due to its availability and widespread utilization in the pulp and paper industry. This project did not undertake gasification; it only involved the proximate and ultimate analysis of coal, eucalyptus and the eucalyptus / coal blends and the thermogravimetric analysis to investigate the conversion characteristics of the blends, as well as the computer simulation of the gasification process to establish the blend that result in higher conversion efficiency.

1.7. ASSUMPTIONS

During gasification there is a synergistic effect between coal and eucalyptus, with the eucalyptus serving as a catalyst for coal gasification. This is due to the high volatile matter content in eucalyptus resulting in low activation energy and lower ignition temperature. This synergy results in eucalyptus providing energy for efficient conversion of coal.

1.8. SIGNIFICANCE/RATIONALE OF THE STUDY

The properties of the feedstock govern the design of the gasifier. Gasification feedstocks differ greatly in their physical and chemical properties. Each type of gasifier operates satisfactorily in terms of gas quality and efficiency within certain ranges of fuel properties. Currently there are proven coal gasifiers as well as biomass gasifiers that take the two feedstocks independently. The chemical properties of coal / biomass blends differ from those of coal or biomass alone, and that requires an entirely different gasifier type. This project therefore established the chemical properties of the biomass as represented by eucalyptus wood, coal and the eucalyptus / coal blends and undertook thermogravimetric analysis to establish the gasification characteristics of the blends.

1.9. DEFINITION OF TERMS

Gasification is the process that converts organic or fossil based carbonaceous materials into carbon monoxide, hydrogen, methane and carbon dioxide. This is achieved by reacting the material at relatively high temperatures, with a controlled amount of oxygen and/or steam.

Biomass is any material that is derived directly from living or previously living things. Examples include wood products, animal and plant waste, and biodegradable waste.

Coal is a delicate, carbonaceous black sedimentary rock that burns. It is made up of carbon, hydrogen, oxygen, nitrogen, and some lesser amounts sulfur and some other trace elements.

Syngas is a gas mixture that comprises of carbon monoxide, carbon dioxide and hydrogen. It is produced due to the gasification of a carbon containing fuel to a gaseous product.

1.10 DISSERTATION OUTLINE

This dissertation discusses the chemical and thermogravimetric analysis of coal, eucalyptus wood as well as the eucalyptus / coal blends for co-gasification purposes. It is divided into five chapters as follows:

Chapter 1 is the introduction part of the dissertation, it gives the background, problem statement, objectives, delineation and limitation, assumptions, research questions and rationale are presented in this chapter. The methods employed in data collection are also briefly mentioned in this chapter.

Chapter 2 presents the literature review part of the dissertation; this chapter presents a synthesis of relevant literature. The various sources of information about the chemical properties and co-gasification of biomass / coal blends are presented in this chapter. Factors governing the co-gasification of coal and biomass are also presented in this chapter. This chapter is meant to gain an understanding about the chemical properties of various materials suitable for co-gasification as available in literature.

Chapter 3 presents the various methods employed in data collection. This chapter presents the preparation of the samples as well as the details on the numerous methods employed in data collection and analysis. These methods were chosen to collect relevant data that assisted in achieving the research objectives and answering the research questions.

Chapter 4 presents the results and discussion part. This chapter presents the results obtained by using the methods presented in chapter 3. The results are presented and discussed with reference to the available literature. The implications for the results in terms of gasification are also discussed in this chapter.

Chapter 5 presents the summary, conclusion and recommendations. This is where the summary of major findings and contributions are presented. Inferences were also gathered from the results and used to draw a conclusion presented in this chapter. The recommendations for further research are also found in this chapter. The research questions asked in chapter one are also answered in detail in this chapter.

Appendix A presents the list of the research outputs associated with this research is found in this section. These are papers presented at national conferences, papers presented in conference proceedings and also papers submitted for publication in peer reviewed journals.

CHAPTER 2: LITERATURE REVIEW

2.1. INTRODUCTION

One of the most vital global issues currently is the worldwide energy crisis which is mainly attributed to earth's fast depleting fossil fuel resources. To address this issue, many countries promoted the use of alternative fuel sources such as agricultural wastes, for example biomass fuel to generate heat and electricity. The benefit of utilizing such fuel for small scale combustion or thermo–chemical conversion is clear since they are renewable resources that can provide inexpensive supplementary fuel. However, this application gives an opportunity to solve the dumping problem [Yin, 2011].

Energy plays an important role in the world's present and future. Global annual energy demand is constantly and rapidly growing. The best way of providing for this enormous increase is energy diversification, such as declining reserves and fluctuating prices of fossil fuels, national energy security, minimization of environmental impact given the increase in atmospheric carbon dioxide (CO_2), and lead to sustainable fuels. In this perspective biomass appears as an attractive resource, potentially to progressively replace fossil fuels [Garcia *et al*, 2012].

Biomass is any material that is derived directly from living or previously living organisms. Examples include wood products, animal and plant waste, and biodegradable waste. In gasification, biomass produces more highly corrosive ingredients, because it has a large amount of higher metallic ion content and it produces higher levels of acidic substances than coal. The use of biomass as an alternative energy source can be traced back to the first wood-fuelled fire. However, biomass produces cleaner syngas than coal because of its lower sulphur and ash contents and neutral traces of carbon. There is also a greater degree of complexity involved in processing biomass before gasification starts [Long III and Wang, 2011].

Biomass is a world-wide available renewable energy resource. When it is produced by sustainable means it removes just about the same amount of carbon dioxide during its energy conversion as that adsorbed by photosynthesis during plant life, as a result, the use of biomass does not contribute to the increase of CO_2 in the atmosphere, and this makes it a remarkable energy source in the present context of environmental attention towards emission levels of greenhouse gases. [Shen *et al*, 2008].

The use of biomass closes the carbon cycle, thus reducing CO_2 emissions per megawatt of power generated. Biomass are also lower in sulphur than most available coals, typical biomass contains about 0.05–0.20 wt% sulphur on a dry basis and has a heating value of about 18–20 MJ/kg. The biomass sulphur content translates to about 51–214 mg SO_2/MJ, which is less than the required standard [Chmielniak and Sciazko, 2003].

2.2. BIOMASS GASIFICATION

Biomass gasification is an incomplete combustion of biomass that result in the production of flammable gases consisting of carbon monoxide (CO), carbon dioxide, (CO_2), hydrogen (H_2) and some traces of methane (CH_4), nitrogen (N_2) may also be present if air is used as the oxidizing agent. This mixture is called a producer gas also known as syngas. The formation of tar is one of the major problems to deal with during this process [Shen *et al*, 2008 and Rajvanshi, 1986]. Especially if the gas is to be used for electricity generation or gas engines application

One of the common ways to reduce the tar contents from the syngas is the use of catalytic treatments. Catalysts can successfully eliminate tar during the biomass gasification process. The effectiveness of some catalysts have been explored, catalysts such as calcined dolomite, magnesite, and calcite for tar decomposition in a fluidized bed biomass gasifier with steam as a gasification agent. Industrial steam-reforming catalysts were also used to improve biomass gasification. Nickel-based catalysts were also developed and their effects were studied during the formation of a produced gas from biomass.

Since biomass is solid, its conversion to a gaseous energy carrier is generally favoured and has many advantages in handling and application. The gasification technology is a well-developed conversion technique for the conversion of biomass to syngas. The composition of syngas from the gasifiers strongly depends on the technology involved and also on the applied gas cleaning technologies [Toonssen *et al*, 2011]. Figure 2.1 shows the flow chat for the gasification process:

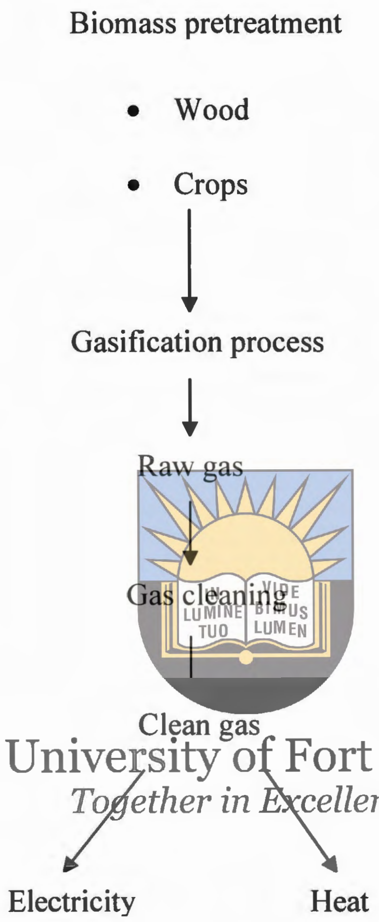

Figure 2.1: The gasification process flow chat [adapted from Kirkels and Verbong, 2011]

2.3 COAL GASIFICATION

Coal is a delicate, carbonaceous black sedimentary rock that burns. It is made up of carbon, hydrogen, oxygen, nitrogen, and some lesser amounts of sulfur and some other trace elements. There are four known types of coal, which are: lignite, subbituminous, bituminous, and anthracite. Each type is characterized by its distinctive properties. These properties are determined by some quality tests, the most used test is the proximate analysis; which determines the moisture content, volatile matter, fixed carbon and ash content. The second test that is normally used is the ultimate analysis which indicates the main elements present in the sample; elements such as carbon, hydrogen, oxygen etc. [Excerpts from RockTalk, 2005].

Unlike other usual combustion processes which fully oxidize carbonaceous fuels to generate heat, the gasification processes convert the fuels such as coal or biomass into syngas via partial oxidation reactions using oxygen and/or steam. In the coal gasification process, coal first reacts with steam and/or oxygen to generate raw syngas. The raw syngas, with pollutants such as H_2S, ammonia, and mercury, is then purified and sent to a gas turbine-steam combined cycle system used for electricity generation, and this is known as the integrated gasification combined cycle (IGCC) process [Fan *et al*, 2008].

Coal that is rich in volatiles contains high-value chemical structures like aromatic rings. These chemical structures are completely converted into simple molecules of H_2O, CO_2, CO, H_2, and hydrocarbons in gasification [Zhang *et al*, 2012]. Gasification of coal is a promising technology for the production of electricity. The coal is prepared and fed to the gasifier. Inside the gasifier, the feedstock reacts with steam and oxygen at high temperatures and pressure, which then result in syngas which is also called a producer gas. The producer gas then undergoes an additional processing to separate and purify H_2 with CO_2 capture [Xiang *et al*, 2010].

Coal is gasified to syngas and then shifted to primary H_2 and CO_2. CO_2 is then removed from the syngas, after being exposed from them solvent CO_2 is then dried and compressed for pipeline transport and underground storage. The pressure swing adsorption purge gas is compressed and burned in a conventional gas turbine combined cycle to generate electricity [Xiang *et al*, 2010]. Figure 2.2 is a basic coal gasification scheme:

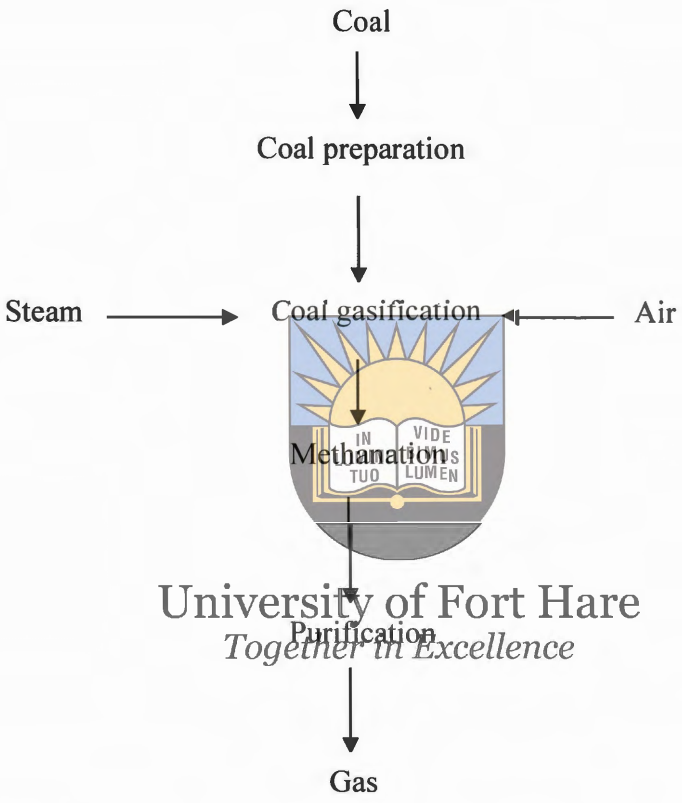

Figure 2.2: Basic schematic for coal gasification [adapted from Duret et al, 2005]

2.4. CO-GASIFICATION OF BIOMASS AND COAL

Global electricity demand is increasing at an enormous rate, whilst the industry is expected to reduce CO_2 emissions due to global warming. As a result, there is a demand to improve the efficiency of energy use through changes in technology and to produce energy vectors that have almost zero emissions of greenhouse gases. Co-gasification of biomass and coal can be considered as a possible fuel-base for gasification and syngas production. Combined gasification of biomass and coal gives effective constancy, decreasing the impact on the environment and most advantageous thermal efficiency for the process [Chmielniak and Sciazko, 2003, and Collot, 2006].

Co gasification of woody biomass and coal offer several advantages such as; the addition of woody biomass to coal gasification does not only reduce CO_2 emissions but also reduce the problems caused by sulphur and ash found in coal, this is because the woody biomass has almost no sulphur and has low ash content. Biomass and coal are essentially chemical opposites, coal contains a lot of sulphur and ash, and biomass contains more oxygen and nitrogen and is more prone to producing tar. Coal contains many transition metals, while biomass contains more alkali and alkaline-earth metals, usually in the form of salts (especially sodium and potassium.) Biomass is also more likely to produce ammonia, which is useful as a cleaning agent, but can be emitted as a deadly pollutant if not properly contained. Biomass also has generally higher volatile content than coal [Kumabe *et al*, 2007, and Long III and Wang, 2011].

Gasification begins with an endothermic process known as pyrolysis, where the small amount of carbon-based feedstock is burned; giving heat that is essential to drive out moisture and volatiles, and all this takes place in the absence or poor presence of oxygen. After pyrolysis, more heat is then needed to thermally break the volatiles and the long hydrocarbon chains into lighter gases. The remaining carbon left in the feedstock is then gasified giving syngas as the product. The chemical form of syngas usually consists mostly of CO and H_2 with trace amounts of CH_4 as fuel and also CO_2, N_2, and water vapour as non-combustible gases [Long III and Wang, 2011].

The syngas also consists of H_2S, COS, HCN, HCl, Hg, and other contaminants that will have to be removed before utilizing the syngas for power generation. Unlike combustion, the aim of gasification is to produce syngas that can then be separated into components and used for different applications in a more efficient way, which makes up for the initial energy investment necessary to produce the syngas. All of this occurs inside the gasifier. After the volatiles leave the feedstock, what is left in the gasifier is char, which is basically pure carbon. Once this occurs, then the char is reacted using air/oxygen and steam to produce carbon monoxide (CO), carbon dioxide (CO_2), and hydrogen (H_2) [Long III and Wang, 2011]. Figure 2.3 shows the basic step wise processing for the co-gasification of coal and biomass:

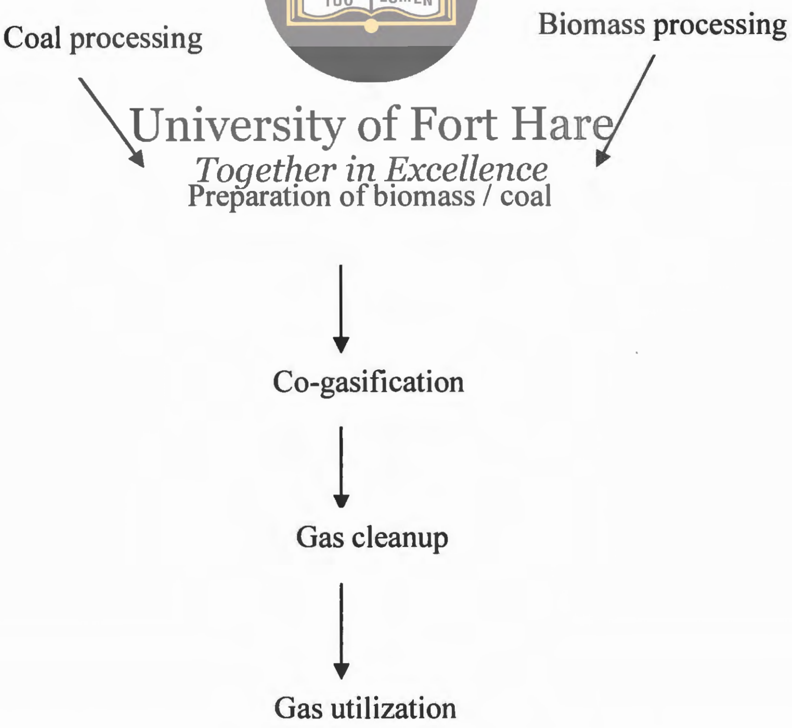

Figure 2.3: Basic step wise processing for the co-gasification of coal and biomass [adapted from Brar et al, 2012]

Biomass and coal processing (separately) involve size reduction and drying in preparation for the gasification process. Size reduction is necessary to attain suitable particle sizes; however, drying is necessary to achieve moisture content appropriate for gasification operations. During the co-gasification process, there is heating involved and chemical reactions taking place, in the clean-up step the tar and other particulates are removed from the syngas [Brar *et al*, 2012]. Coal gasification follows a combination of the following reactions:

Oxidation reaction

$$C + O_2 \longleftrightarrow CO_2 \qquad (+393\ \text{MJ/kg/mole}) \qquad (1)$$

Methanation reaction

$$C + 2H_2 \longleftrightarrow CH_4 \qquad (+75\ \text{MJ/kg mole}) \qquad (2)$$

Water-gas shift reaction

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad (+122.6\ \text{MJ/kg mole}) \qquad (3)$$

Steam reforming reaction

$$H_2 + \frac{1}{2}O_2 \longleftrightarrow H_2O \qquad (+241.1\ \text{kJ/mol}) \qquad (4)$$

Water gas reaction

$$C + H_2O \longleftrightarrow CO + H_2 \qquad (+42.3\ \text{MJ/kg/mole} \qquad (5)$$

Boudouard reaction

$C + CO_2 \longleftrightarrow 2CO$ (-164.9 MJ/kg/mole) (6)

[Pinto *et al*, 2003]

During gasification of biomass / coal, slight oxidation and major pyrolysis take place. During pyrolysis biomass/coal produces char condensable volatiles and tar, and gaseous products. Char is mostly carbon and it follows reactions 1 to 6 (above) during gasification. All of the volatiles and some tars are thermally broken down into simple gaseous products during gasification. The remaining tar and some other alkali minerals leave with the product gases [Brar *et al*, 2012]. Biomass gasification process is in a single equation as follows.

$CH_xO_yN_zS_s$ + Air (79%N_2 and 21% O_2) + H_2O (water vapour) (7)

$\downarrow$

$CH_4 + CO + H_2 + H_2O$ (unreacted water vapour) + C (Char) + Ash + Tar (8)

The bottom line of this reaction scheme is that both coal and biomass go through pyrolysis without interacting before entering into the gasification. During the pyrolysis, removal of volatile material of coal and biomass takes place and condensable volatiles as well as tar rise along with air or steam away from the gasification zone leaving char behind. Since methane and ethylene formation does not take place at atmospheric pressure, their presence in the product syngas is the result of pyrolysis [Brar *et al*, 2012]

2.5 FACTORS GOVERNING THE CO-GASIFICATION OF BIOMASS AND COAL

There are a number of factors that influence the co-gasification process and the composition of the product gas. Factors such as the type of gasifier used, gasification temperature, oxidizing agent used, the type and quality of catalyst used, proportion of biomass in the coal-biomass blend, the properties and type of biomass used.

2.5.1 The type of gasifier used

A number of biomass gasifier types have been developed. Their range is from lower temperature and pressure, and larger grain size to designs both size and higher flow rates. They can be classified according to the relative movement of the fuel and the gasifying intermediate into groups as either: the fixed bed gasifier, which is divided into down-draft, up-draft and cross draft gasifiers or fluidized beds which are divided into bubbling, circulating, spouted and swirling gasifiers.

2.5.1.1 The up-draft gasifier

Figure 2.4 illustrates a schematic diagram of a fixed bed up-draft gasifier

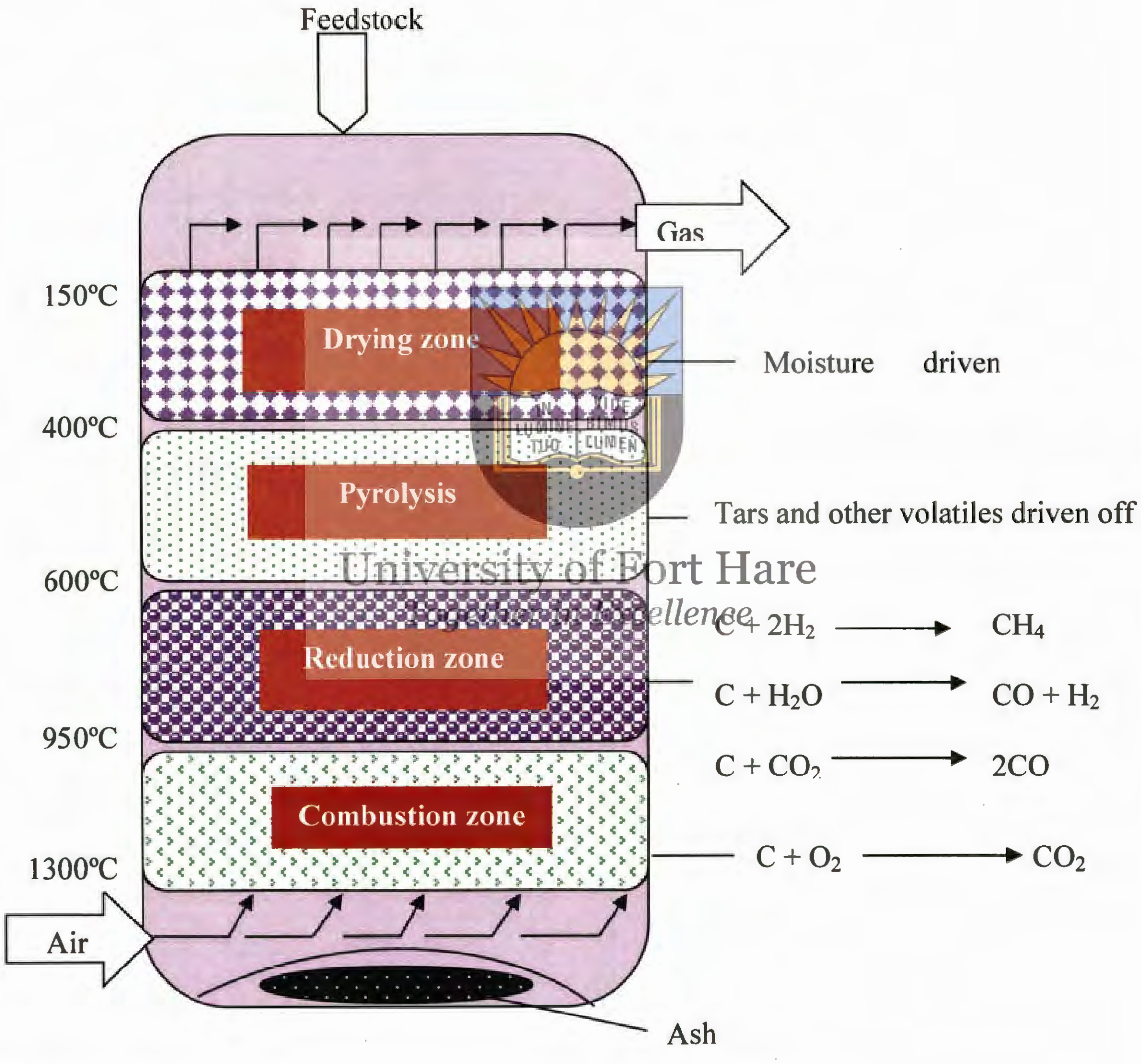

Figure 2.4: Schematic of the updraft gasifier [adapted from Ganesh, 2006]

The up-draft gasifier is designed for the gasification agent such as oxygen or air to enter from the bottom of the gasifier. The feedstock is fed from the top of the gasifier, this type of gasifier is also called the counter-flow or counter current gasifier, because of the change in the flow direction; and the origin of the input air has severe effects on the gasifier performance. For instance, the air or oxygen enters from the bottom of the gasifier acts as a cooling agent for the hotter syngas leaving from the same universal location. In addition, after gasification, the hot air that is left, because it blows past the input feedstock entrance, may be used as a built-in dryer for the fuel. Therefore, there will be less wasted heat. This then gives this gasifier design an efficiency boost. However, because of the drying effect, fuels with much higher moisture content can be utilized in an up-draft gasifier, especially certain types of biomass [Long III and Wang, 2011]. The advantage of the updraft gasifier is that it is a low cost process. It is also able to handle biomass with high moisture contents. Its disadvantage is that the syngas contains about 10 – 20% tar by weight, which then requires extensive syngas clean up.

2.5.1.2 The down-draft gasifier

Figure 2.5 illustrates a schematic diagram of a fixed bed up-draft gasifier

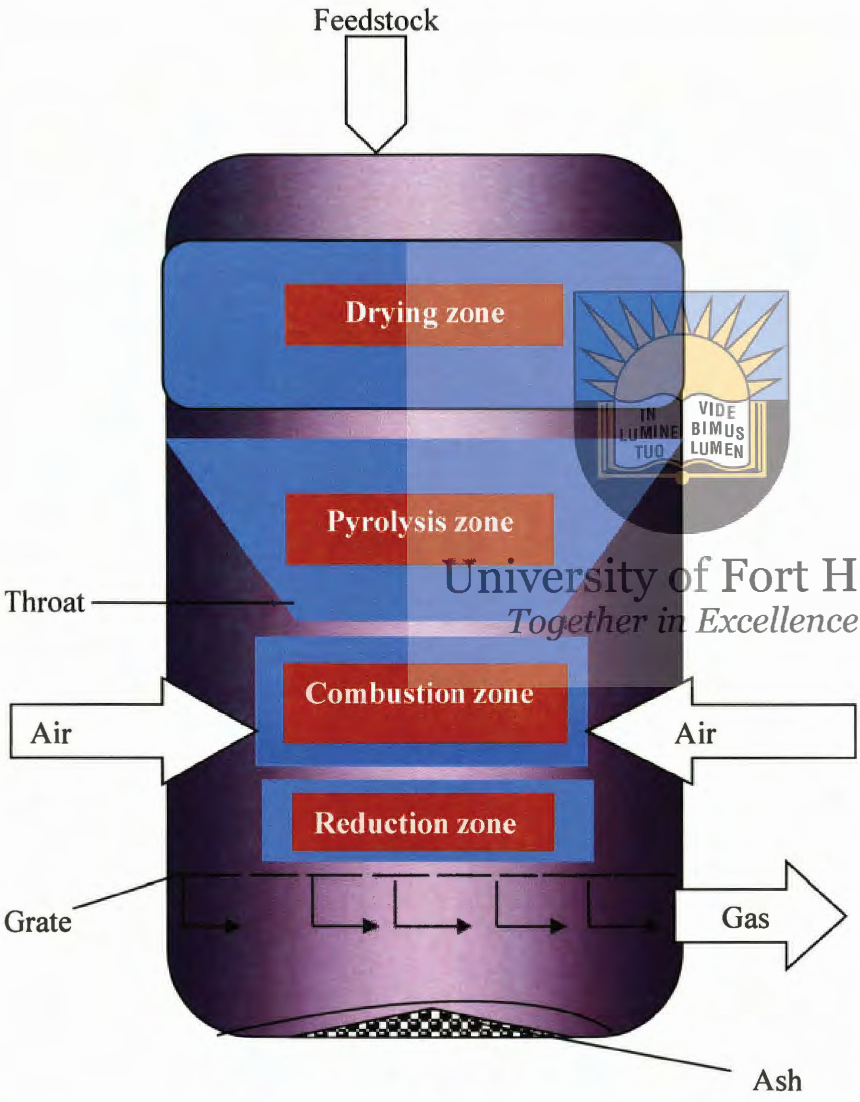

Figure 2.5: Schematic of the downdraft gasifier [adapted from Warnecke, 2000 and Ganesh, 2006]

In this gasifier the air or oxygen which is a combusting agent is injected into the top of the gasifier and flows towards the bottom. Because the typical feedstock is also fed from the top of the gasifier this then results in both the input air and feedstock flowing in the same direction. The internal temperature of a typical down-draft gasifier is between about 427 and 649°C. The pyrolysis and thermal cracking stages take place in this high-temperature zone. The result is that there is lower tar and ash production compared to other gasifier types, and, as such, there is less syngas clean-up necessary [Nilsson *et al*, 2012].

The advantages of a downdraft gasifier are that, about 99% of the tar is consumed which then require minimal or no tar clean-up. Also, the minerals remain with the char or ash, and it is a proven simple and low cost process. Its disadvantages are that; it requires drying to low moisture content, some of the carbon remains unconverted and the syngas exiting the reactor is at high temperatures.

2.5.1.3 The Fluidized Bed Gasifier

Figure 2.6 illustrates a schematic diagram of a fluidized bed gasifier

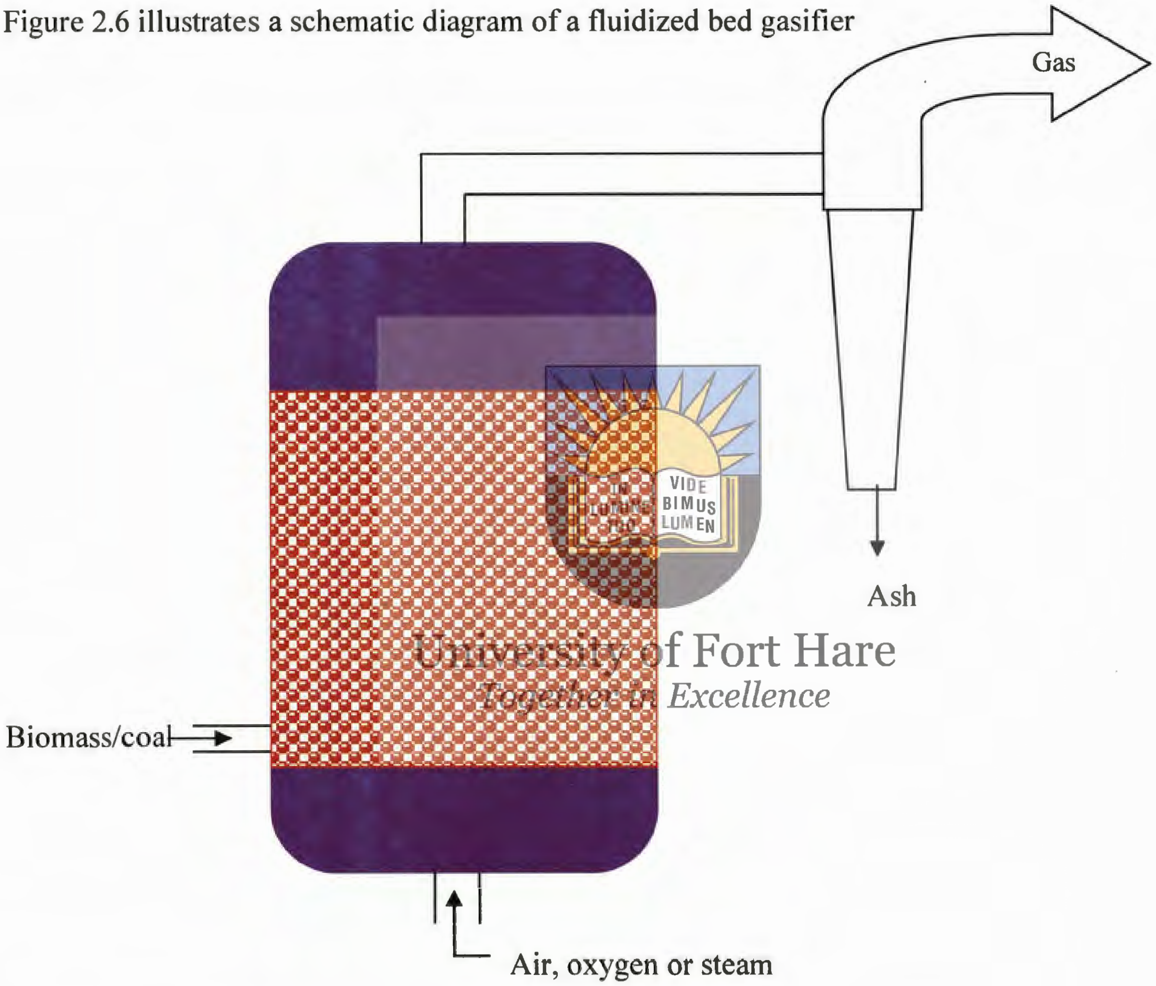

Figure 2.6: Schematic of a fluid bed gasifier [adapted from Xiao et al, 2010]

This type of gasifier uses fluidization to move the feedstock particles. Basically, the gasifier is packed with a bed of solid, dry feedstock particles that may or may not actually be fuel particles. At times, sand or gravel forms the bed and the fuel that enters the bed with the gasifying agent which is then met with a moving stream of fluid particles that are allowed to pass through the pores and cracks in the solid medium. When the fluid flow rate reaches a certain critical point, the solid particles become fully suspended in the fluid. They begin to grow freely and effectively and then they begin to behave as a fluid themselves; hence, they have been fluidized. Fluidized bed gasifiers are not suitable for very small-scale applications because of their high heat transfer rates, which results from the high amount of exposed feedstock surface area [Long III and Wang, 2011].

Gasification in a fluidized bed (FB) consists of numerous advantages over fixed/moving bed or entrained-flow. When processing biomass or waste in fluidized-bed gasifiers (FBG) whose ash limits the operating temperature because of the risk of clustering, the gasification efficiency may be low due to the high amount of carbon in the produced fly-ash. If the ash content of the fuel is high, extensive bed extraction is necessary to maintain the pressure, lowering the process efficiency further because of the carbon that did not burn and sensible heat carried by the extracted material from the bed. Also, the low temperatures of the gasifier yields a gas with a high concentration of tars, which then limits the application of the gas in the cases where it is used without cooling [Nilsson *et al*, 2012]

2.5.1.4 Circulating fluidized bed gasifier.

This type of gasifier, has been extensively used in coal and biomass combustion and gasification processes. External circulation processes build upon lumping, and use complex separation and return equipment, which then increases control problems and investment costs. However, internal circulation processes are more economical and require only a relatively simple fluidized bed structure to produce a well-regulated internal circulation route within the bed to improve mixing and heat transfer between the bed material and the biomass. Internal circulating fluidized bed technology has been recently used for the combustion and gasification of coal, biomass and municipal solid waste [Zhou *et al*, 2009].

2.5.1.5 The Entrained Flow Gasifier.

Figure 2.7 illustrates a schematic diagram of an entrained flow gasifier

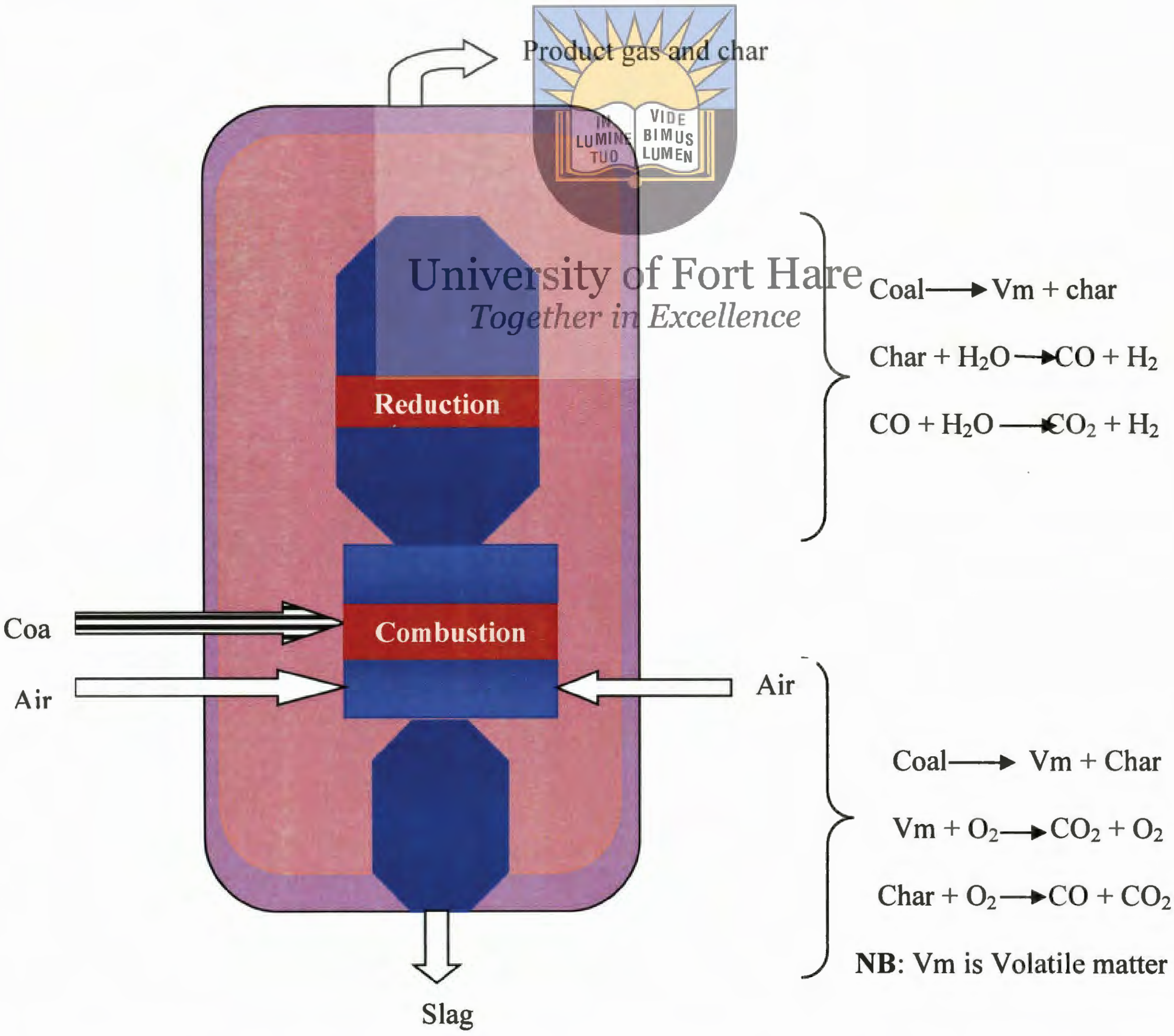

Figure 2.7: Schematic of an entrained flow gasifier [adapted from Watanabe and Otaka, 2006]

This type of gasifier gets its name from the fact that the feedstock particles and the gasification agent are the part of the same stream once within the gasifier. Furthermore, the solid particles or liquid droplets of feedstock that have been trapped inside the gas stream form an entrainment. This allows for a more temperature distribution and a more stable reaction rate. Entrained flow gasifiers are very common in very big power plants since they can carry out very high syngas mass flow rates higher than any other gasifier type. All entrained flow gasifiers produce slag.

Most of the slag that is produced forms a protective coating along the sides of the gasifier, which protects the walls from more corrosive substances that may form during gasification. Entrained flow gasifiers are capable of undergoing gasification at very high temperatures; this then means that almost no tar will form inside the gasifier. Even though for all of their strengths, entrained flow gasifiers have a few drawbacks. For example, the necessary average feedstock particle size is extremely small. This is not a problem for liquid feedstocks, but solids like coal and biomass need to be pre-treated before they can be used in an entrained flow gasifier [Long III and Wang, 2011].

2.5.2 Gasification temperature

Gasification temperature is one of the most important operating parameters that affect the performance of gasification due to the balance between endothermic and exothermic reactions involved. [Lee *et al*, 2010]. The temperature alongside the gasifier greatly influences the product gas composition. The temperature inside the directly-heated co-gasification reactor is also influenced by the proportion of biomass in the coal-biomass mixtures; hence, the temperature is specific to a particular coal-biomass mixture and the type of biomass used. High temperature in the reduction zone reduces the tar content in the product gas; which is why high temperature in the combustion zone might causes sintering problems and de-fluidization of the bed. [Brar *et al*, 2012]. Increase in bed temperature increases the rate of feedstock and tar cracking and reforming reactions [Aznar *et al*, 2006].

2.5.3 Oxidizing agents such as air and/or steam

When air and steam are used as gasifying agents, they show accurate flow rates and they do not only create proper stoichiometric gasification conditions but also provide sufficient reaction time for heavy molecular weight volatiles and tar particles to break down into gaseous species [Brar *et al*, 2012].

2.5.4 The type and quality of catalysts

The use of a suitable catalyst does not only reduce the reaction temperature but it also improves the gasification rates. The catalysts also reduce tar formation. There are several catalysts that are used, for example; $Rh/CeO_2/SiO_2$, dolomite or olivine catalyst, and nickel-based catalysts etc. It was reported that a higher ratio of H_2/CO can be obtained by using dolomite and nickel-based catalysts, also tar yields are reduced. Dolomite as a catalyst is known to be better than Ni-dolomite and Zinc Oxide in terms of sulphur and chlorine retention. Catalysts have proven effects on gasification and quality of syngas. [Brar *et al*, 2012].

The use of alkaline-earth mineral catalysts has been reported to be a low-cost option, resulting in reduction in the rate of tar formation with respect to the no catalytic processes. Dolomite, which is used separately or in combination with other reforming catalysts, has been assayed extensively for its catalytic performance. Nickel-based catalysts, which include noble metals supported on $Ni/CeO_2/Al_2O_3$, $Ni/CeO_2/Al_2O_3$, Ni/Al_2O_3, Ni/Dolomite and Ni/Olivine. In either single or two-stage reactors, these catalysts generally lead to increased H_2 and CO content in the gasified product, and to a significant reduction in the hydrocarbon content as a result of the reforming of methane and other, potentially present light hydrocarbons [Corujo *et al*, 2010].

2.5.5 Proportion of biomass in the coal-biomass mixture

The amount of biomass in the co-gasification process influences product gas composition. Besides proportion of biomass, co-gasification is also dependent on the type of coal used in the mixtures [Brar *et al*, 2012].

2.5.6 The properties and type of biomass

Table 2.1 shows the proximate and ultimate analysis of a typical biomass material.

Table 2.1: Properties found in a typical biomass material [Ganesh, 2006]

Properties	Biomass
Volatile matter (dry basis)	60 – 90 %
Fixed carbon (dry basis)	<5 – 25%
Ash (dry basis)	<1 – 25%
C (d. m. m. f)	About 50%
H (d. m. m. f)	About 10 %
O (d. m. m. f)	About 40%
Calorific value (MJ/kg)	16 – 19

Moisture content of the biomass is the most important parameter. The moisture content higher than 30% can cause the ignition of the gasifier complicated and also it reduces the calorific value of the producer gas. Significant heat is required to evaporate the moisture prior to gasification. Higher moisture content also reduces the temperature of the combustion zone of the gasifier that has lead to incomplete cracking of hydrocarbons or tars released during pyrolysis. Thus, direct hydrogenation of carbon in biomass can occur resulting in the production of methane. Therefore, the production of carbon monoxide is then reduced. Since the combined heat of combustion of H_2 and CH_4 is lesser than the heat of combustion of CO, the net calorific value of the producer gas decreases [Buragohain *et al*, 2010].

2.6 PROPERTIES OF LIGNOCELLULOSE BIOMASS

Biomass is an organic material that comes from plants and animal remains. The lignocellulose biomass store energy from sunlight by photosynthesis using the bonds of carbon, hydrogen and oxygen molecules. They are characterised into four main types known as woody plants, herbaceous plants/grasses, aquatic plants and manures. Currently, biomass contributes approximately 10–14% of the world's energy supply. The sources of biomass are specially grown energy crops, agricultural wastes, forestry residues and the organic fraction of municipal wastes. Its energy is converted to heat, power or chemical feedstock mainly by thermo-chemical conversions [Ryu *et al*, 2006].

Biomass is composed of biopolymers that consist of various types of cells and the cell walls are built of cellulose, hemicelluloses and lignin. Cellulose and hemicelluloses form mostly volatile products during pyrolysis due to the thermal cleavage of the sugar units. The lignin forms mainly char since it is not readily cleaved to lower molecular weight fragments [Zhou *et al*, 2006]. Lignocellulosic biomass is composed mostly of several chemical constituents such as:

2.6.1 Cellulose

Cellulose is the major structural component of plants, especially of wood and plant fibers. It is a linear homogeneous polymer made up of β - (1, 4) glycosidic bonds linked D-glucose units; it is the most abundant biopolymer on earth. Partial oxidation of cellulose constitutes one of the most versatile transformations since it provides access to various novel products and intermediates with valuable properties. There are a number of ways of oxidizing cellulose. However, only some methods are suitable for a regioselective oxidation of the chain units, while the glycosidic linkages remain intact [Aimin *et al*, 2005; and Heinze and Liebert, 2001]. Figure 2.8 shows the molecular structure of cellulose

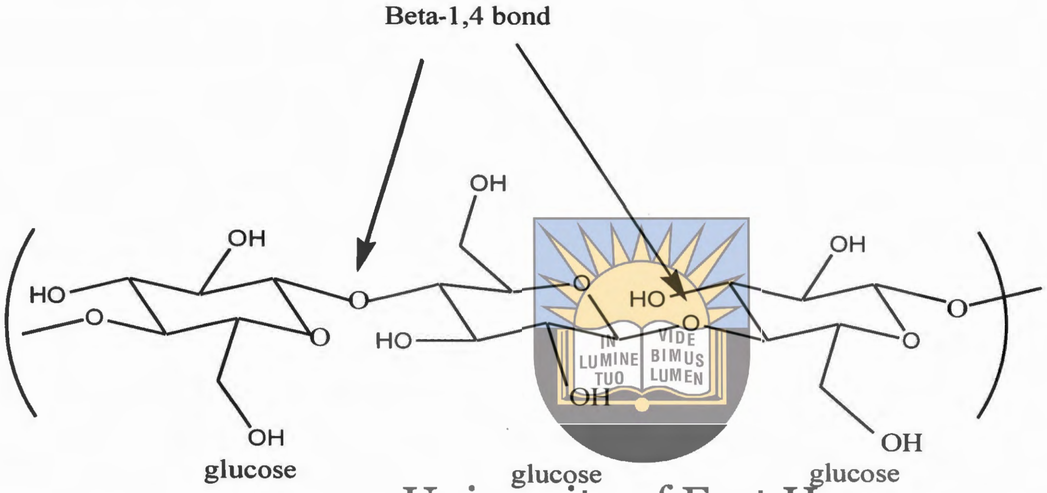

Figure 2.8: The molecular structure of cellulose [adapted from Aimin et al, 2005 and Heinze and Liebert, 2001]

2.6.2 Hemicellulose

Hemicellulose is a polysaccharide found in plant cell walls. Hemicelluloses include xyloglucans, xylans, mannans and glucomannans, and also β-(1→3, 1→4)-glucans. These types of hemicelluloses are found in the cell walls of all terrestrial plants, except for β-(1→3,1→4)-glucans, which are restricted to Poales and a some other groups. The most significant biological role of hemicelluloses is that they contribute to the strengthening of the cell wall by interacting with cellulose and also with lignin in some other walls [Scheller and Ulvskov, 2010]. Hemicellulose consists of shorter chains than cellulose. Figure 2.9 shows the molecular structure of hemicellulose

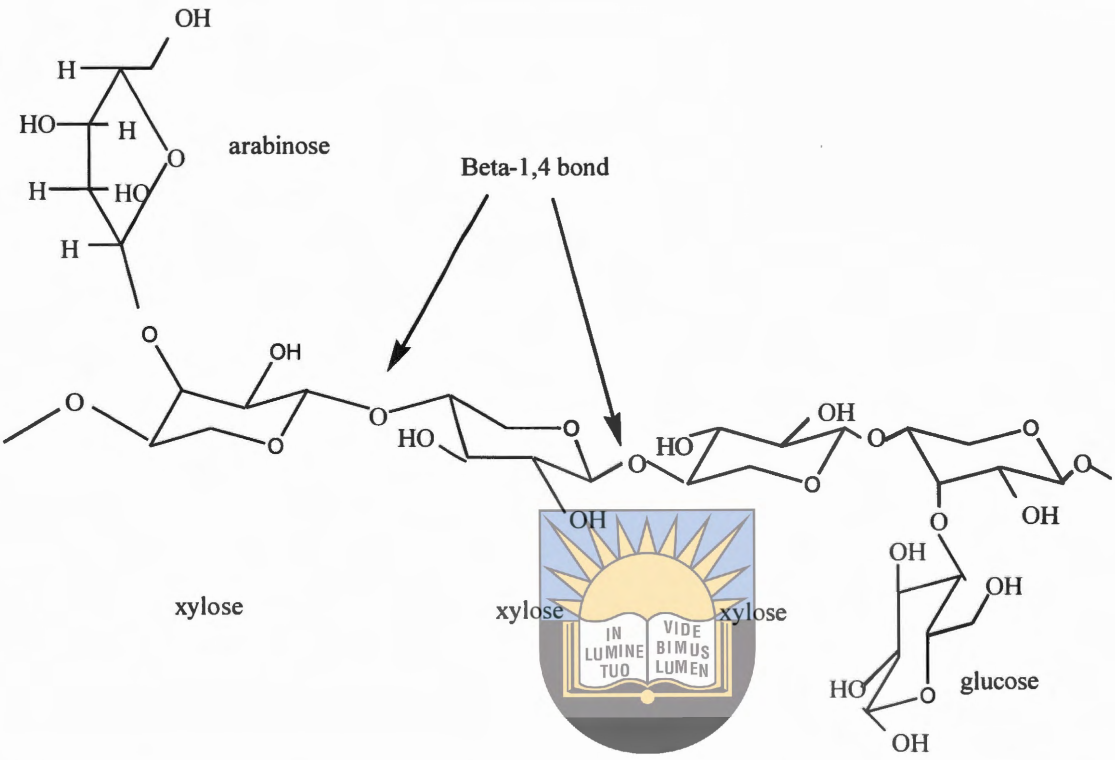

Figure 2.9: The molecular structure of hemicellulose [adapted from Scheller and Ulvskov, 2010]

2.6.3 Lignin

Lignin, which is present in all vascular plants, represents about 25% of the terrestrial plant biomass. It is a complex phenolic heteropolymer that result from the oxidative polymerization [Rastogi and Dwivedi, 2008]. When burned it yields more energy than cellulose. Figure 2.10 shows a molecular structure of lignin

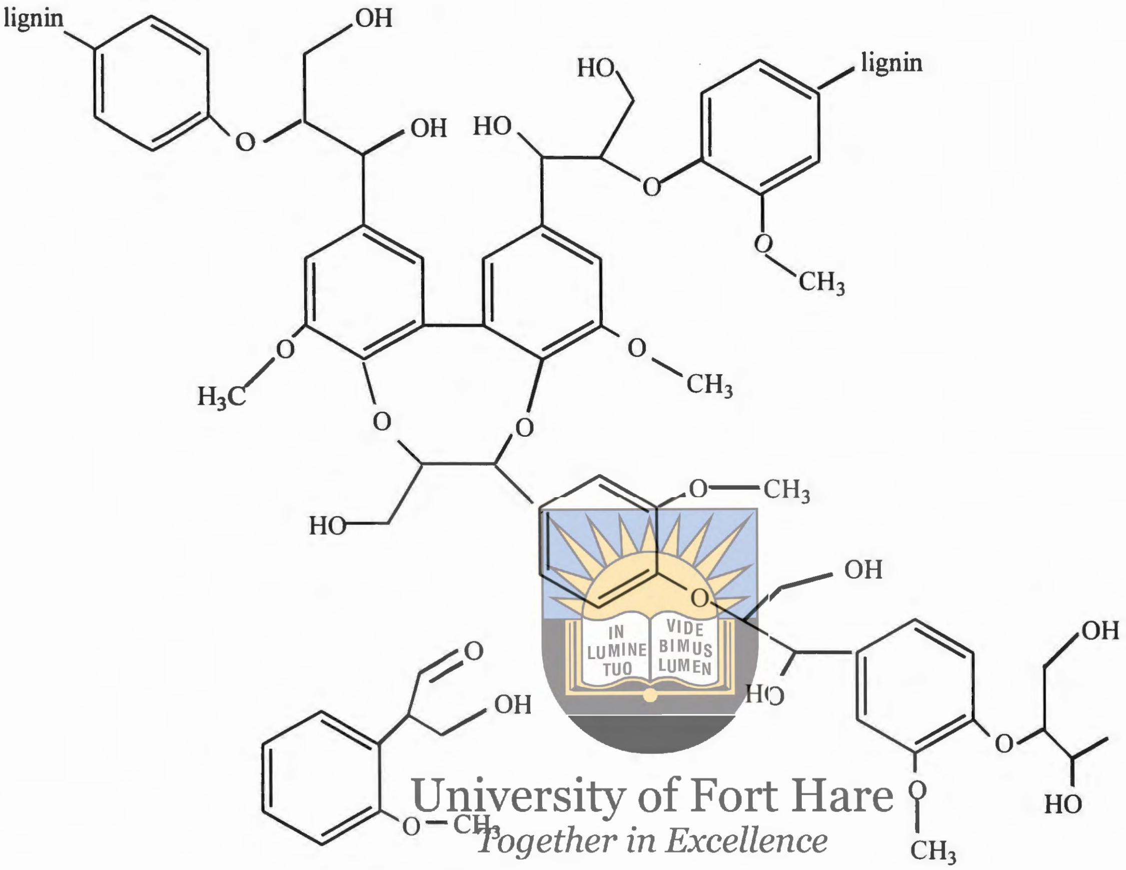

Figure 2.10: The molecular structure of lignin [adapted from the International Lignin Institute, 2012]

There are also other minerals present; the amount of these chemical species influences the composition of the gasification products to a great extent.

2.7 PROPERTIES OF COAL

Coal is a black carbonaceous black sedimentary rock occurring in workable quantities. It is made up of carbon (about 50 – 98%), hydrogen, oxygen, nitrogen and some smaller amounts of sulphur and other trace elements. It is formed from the accumulations of plant remains modified by chemical, biological and physical processes during and after burial [RockTalk, 2005 and Willamson, 1967].

The degree of alteration which such deposits have attained determines their position or rank in the coalification series commencing at peat and extending through lignites to bituminous coal and finally anthracite. Organic material, small quantities of inorganic and incombustible minerals are also present in almost all coals where the degree of compaction and alteration is relatively slight, as in peat and some brown lignite; the sediments are not regarded as true coals. Nonetheless, they are the first members of the coalification series [Williamson, 1967].

2.7.1 Peat

Peat occurs as a soft unconsolidated deposit near the surface in beds rarely more than about 30 feet thick. Most deposits are waterlogged and one of the most notable characteristics of the material is its high moisture content, which undrained deposits are between 90 and 95 % of the total weight. This may be reduced by air-drying technique to about 35 %. Although the calorific value the calorific value of peat when calculated on a dry basis is about 9500Btu/1b the value of air dried peat is only about 6000Btu/1b [Williamson, 1967].

2.7.2 Lignite

Most lignites are of late cretaceous or tertiary age, except the lower carboniferous seams of the Moscow basin. Individual seems are commonly tens of feet in thickness and many occur within relatively unconsolidated sands and clays at shallow depths below the surface. More rarely lignites may exceed 100 ft as in Victoria, Australia where the thickest continuous seam in the world was proved in a borehole at Loy Yang to be 757 ft thick and to occur beneath only about 90 ft of overburden [Williamson, 1967].

The term lignite is defined differently in various countries. For example, in Britain the terms brown coal and lignite are usually regarded as synonyms where as in Germany lignite is restricted to district fragments of wood enclosed in brown coal. In North America brown coal is an unconsolidated deposit whereas lignite is consolidated and much of the brown coal of Germany would be classified as sub-bituminous. Brown lignites vary from yellowish to dark brown in colour and possess a predominantly dull earthy lustre, and black lignites which are also called sub-bituminous coals are dark brown to black in colour and their lustre is often silky and may sometimes be indistinguishable from that of the bituminous coals [Williamson, 1967]. Lignite is the softest and has the least amount of carbon.

2.7.3 Sub-bituminous

Sub-bituminous coal is a type of coal with properties that range from those of lignite to those of bituminous coal and are used primarily as fuel for steam-electric power generation. Their relatively low density and high water content renders some types of sub-bituminous coals susceptible to spontaneous combustion if not packed densely during storage in order to exclude free air flow [Wikipedia, 2012].

2.7.4 Bituminous

Bituminous coal is a relatively soft coal, and it was usually formed as a result of high pressure on lignite. It is of higher quality than lignite coal but of poorer quality than anthracite [Wikipedia, 2012].

2.7.5 Anthracite

Among all, anthracite is the hardest and has the most carbon with the fewest impurities; it has the highest calorific content of all types of coals. It differs from other coals by its greater hardness, higher relative density and lustre which are often [illegible] metallic with a mildly brown reflection. It contains a high percentage of fixed carbon and a low percentage of volatile matter [Wikipedia, 2012]. Different types of coal are characterized by their unique properties [RockTalk, 2005]. Table 2.2 shows the proximate and ultimate analysis of a typical coal material.

Table 2.2: Properties of coal [Ganesh, 2006]

Properties	Coal
Volatile matter (dry basis)	< 20 – 50 %
Fixed carbon (dry basis)	About 40 – 80 %
Ash (dry basis)	About 10 – 45 %
C (d. m. m. f)	About 80 %
H (d. m. m. f)	About 5 – 10 %
O (d. m. m. f)	About 10 – 20 %
Calorific value	16 – 34 MJ/kg

Coals that are highly reactive supply high carbon conversion at moderate gasifier temperatures improving overall system efficiency. The reactivity of coal chars under gasification conditions is a most important determinant of the gasifier size and design. Reactive coals can be gasified at lower temperatures and therefore at higher cold gas efficiency, while less reactive coals may need higher gasification temperatures in order to achieve sufficient conversion efficiencies. At the same time, the temperature must be high enough to yield a tappable slag. Therefore, the preferred operating strategy for a coal is always a balance between reactivity and slag tapping considerations [Collot, 2006].

2.8 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric Analysis is a technique in which the mass loss of a certain material is monitored as a function of temperature or time as the sample is subjected to a controlled temperature program in a controlled atmosphere [Wikipedia, 2013].

2.8.1 Applications of Thermogravimetric analyzer

Thermogravimetric analyzer is used for the determination of temperature and weight change of decomposition reactions, which often allows quantitative composition analysis. It may be used to determine the amount of water content. It allows analysis of reactions with air, oxygen, nitrogen or other reactive gases such as helium. It can also be used to measure some evaporation rates, such as to measure the volatile emissions. It allows the determination of temperatures of magnetic transitions by measuring the temperature at which the force exerted by a nearby magnet disappears on heating or reappears on cooling. It helps to identify plastics and organic materials by measuring the temperature of bond scissions in inert atmospheres or of oxidation in air or oxygen. It is used to measure the weight of fiberglass and inorganic fill materials in plastics, laminates, paints, primers, and composite materials by burning off the polymer resin. [Wikipedia, 2013].

CHAPTER 3: RESEARCH METHODOLOGY

3.1 INTRODUCTION

This chapter presents the various methods used to gather the required data for this research. It was found necessary to first determine the moisture content, volatile matter content, fixed carbon content and ash content of the materials using a muffle furnace. The energy values of the materials were determined using a CAL 2K - ECO bomb calorimeter. The elemental analysis was carried out using a Vario EL CUBE CHNS analyzer and PANanalytical Epsilon 3 XRF analyzer. The thermal degradation of the material was assessed using a Perkin Elmer TGA 4000 thermogravimetric analyzer, the kinetic analysis and simulations were then carried out. Figure 3.1 shows the methodology followed for this study.

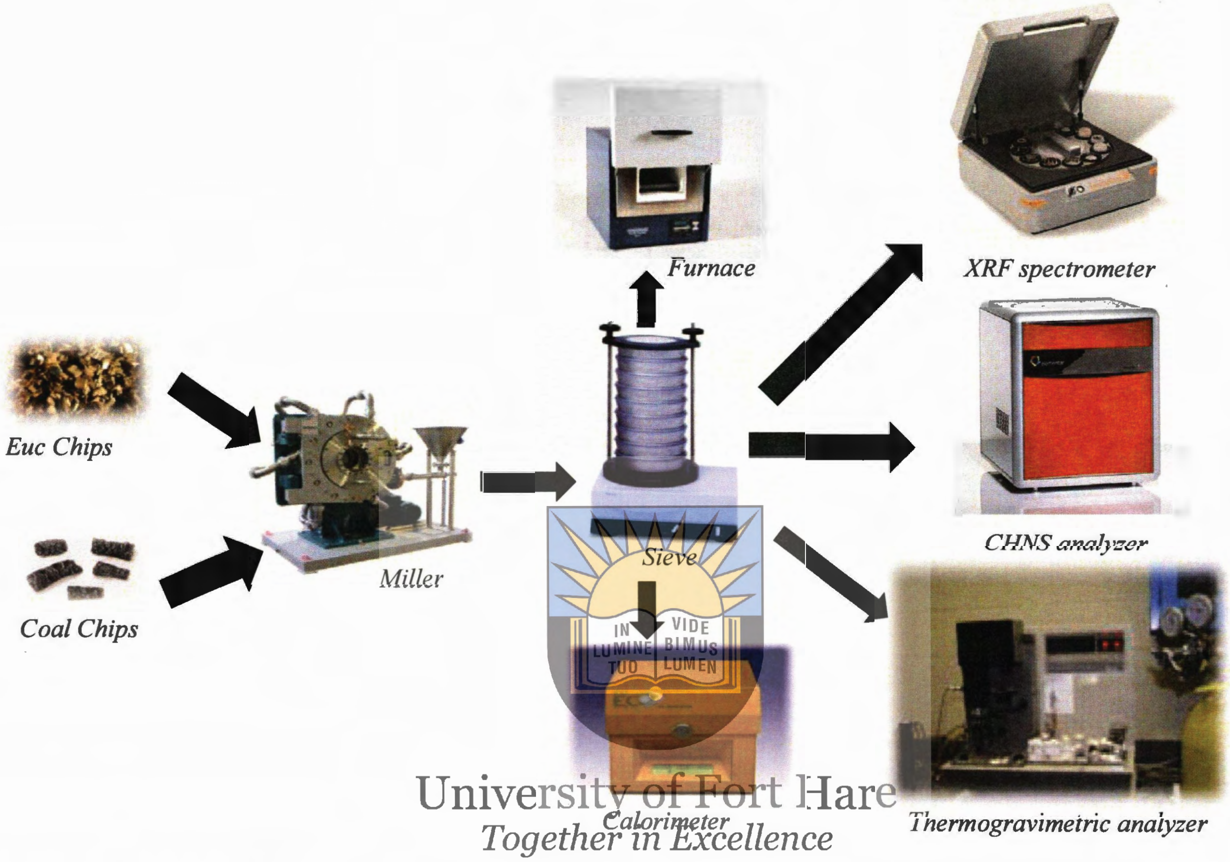

Figure 3.1: Methods employed for sample analysis

3.2 SAMPLE PREPARATION

The coal used for this study is a typical low grade with high ash content South African coal, and the biomass samples used are: eucalyptus (camaldulensis), pine (pinus) wood and corn cob (obtained in the Eastern Cape). All the samples were prepared using the coning and quartering method. The cone-and-quartering method was applied subsequent to size reduction to obtain a more representative sample. Chips were then milled using a Condux-Werk Wolfgang bei Hanau mill to reduce the chips to a size of approximately 10 mm (with the largest dimension being 10 mm). The 10mm samples were milled using a Retsch ZM200 mill equipped with a 1 mm circular blade to produce samples of approximately ±425 µm, which were further milled to approximately ±250 µm. The samples were screened in a Retsch AS200 shaker to obtain fractions between 250 and 425 µm, where the ±250 µm were used for analyses. All the three biomass samples showed the same behaviour and so it was necessary to report using one biomass material. For this reason eucalyptus was chosen, since it is not seasonal unlike corn cob it is the most available in the Eastern Cape. The eucalyptus wood for this study used was collected from a plantation in Stutterheim.

3.3 PROXIMATE ANALYSIS

There are large variations for the characteristics determined by the proximate analysis of biomass/coal samples. However, these variations are mostly due to the moisture contents and ash yields, which vary in the greatest intervals. When the measured parameters are recalculated on dry and dry ash-free basis their variations are in more narrow ranges for biomass groups and sub-groups. The moisture content and ash yield are important parameters of the biomass/coal system and require a more detail discussion [Vassilev *et al*, 2010]. Moisture content, volatile matter content, fixed carbon content and ash content were obtained using the Standard Biomass Analytical Methods provided by the National Renewable Energy Laboratory ("NREL"), [NREL/TP-510-42621, NREL/TP-510-42622, Vassilev *et al*, 2010 and Garcia *et al*, 2012]. Calorific values were determined using a CAL 2K - ECO bomb calorimeter. Calorific values are also amongst the most important aspects for gasification since they give an idea of whether the material will be suitable or not.

3.3.1 Determination of the calorific values

A bomb calorimeter (CAL 2K - ECO model) was used to determine the calorific values of the samples. It is the experimental procedure used to determine higher heating values. A calorific value is the amount of energy per unit mass released upon complete combustion. The gross calorific value is measured in a bomb calorimeter for solid fuels. The definition of the gross calorific value at constant volume given in different standards or technical specifications is almost the same. According to the technical specification it is defined as the absolute value of the specific energy of combustion, in joules, for unit mass of a solid biofuel burned in oxygen in a bomb calorimeter under specified conditions. The products of combustion are assumed to consist of gaseous oxygen, nitrogen, carbon dioxide and sulphur dioxide, liquid water in equilibrium with its vapour saturated with carbon dioxide under the conditions of the bomb reaction, also of solid ash [Llorente and Garcia, 2008].

3.3.2 Determination of the moisture content

To determine the moisture content the crucibles were marked for identification using a marker, and then they were placed in the muffle furnace, and brought to constant weight by burning at 105°C for about one hour. The crucibles were then cooled in a desiccator, and were used for the determination of moisture content.

Approximately 1.0 g of the sample (for each material) was weighed; the samples were then placed into a muffle furnace at 105°C for one hour. The samples were removed from the furnace and allowed to cool to room temperature in a desiccator. The crucibles containing the oven-dried samples were weighed. The samples were placed back into a muffle for thirty minutes furnace at 105°C and dried to constant weights [Sluiter *et al*, 2008]. The percent total solids were calculated using equation 9 and the moisture content using equation 10

$$\%Totalsolids = \frac{(weight_{drycrucible+drysample} - weight_{drycrucible})}{weight_{sample}} \times 100\% \qquad (9)$$

Where

Weight$_{drycrucible+drysample}$ = mass of the burnt crucible with the sample

Weight$_{drycrucible}$ = mass of the burnt crucible

Weight$_{sample}$ = mass of the sample

$$\%Moisturecontent = 100 - \%Totalsolids \qquad (9)$$

[Sluiter *et al*, 2008]

3.2.3 Determination of Volatile matter content

This test method analyzes the percentage of gaseous products which are released during the experiment in the sample. It is determined by heating an initial mass of the material at 950±20°C in a muffle furnace for seven minutes. The mass of the sample left is recorded as the final mass.

The calculation is usually obtained as a percent by mass of the total mass of the sample. The volatile matter content in biomass varies in the interval of 48–86% and normally decreases in the order: herbaceous and agricultural grass >wood and woody biomass > herbaceous and agricultural biomass> herbaceous and agricultural straw>herbaceous and agricultural residue >contaminated biomass >animal biomass. In contrast, the volatile matter value in coal is commonly in the larger range of 12–68%. The extremely high volatile matter value is a characteristic of some wood and woody biomass, sugar cane bagasse, and paper waste. The volatile matter yield of biomass commonly includes light hydrocarbons, CO, CO_2, H_2, moisture, and tars [Vassilev *et al*, 2010]. The weight loss is calculated using the following formula:

$$Weightloss\% = A = \left(\frac{W_o - W}{W_{so}}\right) * 100 \qquad (10)$$

Where W_0 is the initial weight of the sample plus crucible with top, W is the resulting weight of the crucible plus sample waste, and W_{SO} is the initial sample weight [Garcia *et al*, 2012].

3.2.4 Determination of Fixed carbon content

It is a solid, combustible residue that is determined by the final calculation of the amount present in a biomass or coal sample after the percentages of moisture, ash, and volatile matter have been determined. It is determined using the following formula:

$$\% FC = 100 - (\% moisture + \% Ash + \% VM) \qquad (11)$$

Where FC is the percentage value of fixed carbon and VM is the previously obtained volatile matter content during the experiment [Garcia *et al*, 2012].

3.3.5 Determination of the ash content

To determine the ash content the crucibles were placed in the furnace at 1000°C for three hours. The crucibles were then removed and placed in a desiccator to cool to room temperature and then weighed. After weighing the crucibles were returned to the furnace for one hour at 1000°C, cooled again in the desiccator, reweighed, and used for the determination of ash content. Approximately 1.0 g of the sample (for each material) was weighed; the samples were then placed into a muffle furnace at 750±20°C for two hours.

The samples were removed from the furnace and allowed to cool to room temperature in a dessicator. The crucibles containing the ash were weighed. The samples were placed back into a muffle furnace at 750±20°C and reheated to constant weights [Sluiter *et al*, 2008]. The oven dry weight (ODW) was calculated using equation 12 and the ash content calculated using equation 13:

$$ODW = \frac{weight_{airdrysample} \times \%Totalsolids}{100} \qquad (12)$$

Where

$Weight_{airdry\ sample}$ = mass of the sample

$$\%Ash = \frac{weight_{crucible+ash} - weight_{crucible}}{ODW} \times 100\% \qquad (13)$$

Where

Weight $_{crucible+ash}$ = mass of the crucible with ash

Weight $_{crucible}$ = mass of the burnt crucible

[Sluiter *et al*, 2008]

The conditions used for the determination of proximate analysis were that of coal since coal is a stronger material than biomass and the research intends on blending the two materials for co-gasification; using the biomass conditions results in incomplete analysis for coal.

3.4 ULTIMATE ANALYSIS

Ultimate analysis is a quantitative analysis whereby the quantities of all the elements present in the material are determined. Carbon is anticipated to have values between 45% and 55%, hydrogen is expected to range from 5.6% to 7%, oxygen from 40% to 44%, nitrogen from 0.1% to 0.5% and sulphur near 0.1%. When compared with coal, biomass shows high reactivity due to its highly volatile content, and higher reactive chars, but lower C and H levels give it lower higher heating value [Garcia *et al*, 2012]. The ultimate analysis was undertaken using a Vario EL CUBE CHNS analyzer and PANanalytical Epsilon 3 XRF analyzer.

3.4.1 CHNS analysis

CHNS Analysis is the determination of the amount of Carbon, Hydrogen, Nitrogen and Sulphur present in the material. Oxygen is determined by difference. These are the major elements found in coal and biomass. This technique involves combustion of the sample in an oxygen rich environment. The products of combustion in a CHNS analysis (CO_2, H_2O, N_2 and SO_2) are carried through the system by Helium carrier gas. The combustion products are measured quantitatively by means of a non-dispersive IR absorption detection system, except for the N_2 which is determined through a thermal conductivity (TC) detector. [Wikipedia, 2014].

3.4.2 XRF analysis

XRF analysis is an analytical tool for the spectrochemical determination of the elements present in a sample. The XRF method depends on fundamental principles that are most common to numerous other instrumental methods that involve interactions between electron beams and x-rays with samples. The analysis of major and trace elements using XRF is made possible by the behavior of atoms when they interact with X-radiation. An XRF spectrometer works because if a sample is illuminated by an intense X-ray beam, known as the incident beam, some of the energy is scattered, but some is also absorbed inside the sample in a way that depends on the chemistry of the sample. The incident X-ray beam is normally produced from a Rh target, although W, Mo, Cr and others can also be used, depending on the application.

When this primary X-ray beam illuminates the sample, the sample is said to be excited. The excited sample then releases X-rays along a spectrum of wavelengths characteristic of the types of atoms present in the sample. The atoms in the sample absorb X-ray energy by ionizing, ejecting electrons from the lower (usually K and L) energy levels. The ejected electrons are then replaced by electrons from the outer, higher energy orbital. When this occurs, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. This energy release is in the form of emission of characteristic X-rays indicating the type of atom present.

If a sample has many elements present, as in most minerals and rocks, the use of a Wavelength Dispersive Spectrometer more like that in an Electron probe micro-analyzer (EPMA) which allows the separation of a complex emitted X-ray spectrum into characteristic wavelengths for each element present. Various types of detectors (gas flow proportional and scintillation) are used to measure the intensity of the emitted beam. The flow counter is commonly utilized to measure long wavelength (>0.15 nm) X-rays that are usually of K spectra from elements lighter than Zn.

The scintillation detector is commonly used to analyze shorter wavelengths in the X-ray spectrum (K spectra of elements from Nb to I; L spectra of Th and U). X-rays of intermediate wavelength (K spectra produced from Zn to Zr and L spectra from Ba and the rare earth elements) are generally measured by using both detectors in. The intensity of the energy measured by these detectors is proportional to the abundance of the element in the sample. The exact value of this proportionality for each element is derived by comparison to mineral or rock standards whose composition is known from prior analyses by other techniques. [Wikipedia, 2014].

3.6 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis (TGA) is one of the most common techniques used to investigate thermal events and kinetics during pyrolysis of solid raw materials such as coal and biomass. It gives a measurement of weight loss of the sample as a function of time and temperature. The kinetics of these thermal events has been determined by the application of the Arrhenius equation corresponding to the separate slopes of constant mass degradation [Zhou *et al*, 2006].

Thermogravimetric Analysis (TGA) is an analytical technique that measures the quantity and rate of change in the weight of a material as a function of temperature or time in a controlled environment. Measurements are mostly used to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. This technique can distinguish materials that display weight loss or gain due to decomposition, oxidation, or dehydration.TGA can tell the following:

- Composition of multicomponent systems
- Thermal stability of materials
- Oxidative stability of materials
- Estimated lifetime of a product
- Decomposition kinetics of materials

- The effect of reactive or corrosive atmospheres on materials
- Moisture and volatile content of materials

[Thermogravimetric Analysis (TGA), 2012]

The data was obtained by analysing the samples using Perkin Elmer TGA 4000. All samples were analyzed by purging with Nitrogen at a flow rate of 20 mL/min. All the samples were heated from 35 °C to 900 °C. The 20°C/min heating rate was chosen because this is the typical heating rate in a biomass gasification process.

3.6.1 Rate law and kinetics analysis

TGA is one of the most common techniques used to investigate thermal events and kinetics during pyrolysis of coal or coal / biomass mixtures. It gives a measurement of weight loss of the sample as a function of time and temperature. The kinetics of thermal decomposition reactions of carbonaceous materials is complex; in that decomposition of carbonaceous materials it involves a large number of reactions in parallel and in series.

A number of procedures for evaluating devolatilization kinetic parameters of solid fuels from the data derived from non-isothermal thermogravimetric analysis (TGA) have been developed, and the enormous majority of them can be classified as either model-free or model-fitting. The conventional approach for estimating kinetic parameters, which are the activation energy, pre-exponential factor and the reaction order from TGA data via model-fitting analysis generally involves assuming a certain reaction order, and then manipulating the differential or integral form of the resultant rate equation until a straight line plot can be obtained from where the remaining unknown parameters can be obtained by linear regression [Aboyade *et al*, 2012].

Another approach to kinetic analysis is to use model-free methods that allow the evaluation of the Arrhenius parameters without choosing the reaction model. The best known representatives of the model-free approach are the iso-conversional methods. These methods give the effective activation energy as a function of the extent of conversion. Knowledge of the dependence *E*a on α assists in both detecting multi-step processes and drawing certain mechanistic conclusions [Jankovi´c *et al*, 2007]. This study applied the model free kinetic method (Kissinger), which does not take into consideration the reaction model. The activation energy (Ea) and the pre-exponential factor were determined from the following equation:

$$\ln\left(\frac{\beta}{T^{2}\,m}\right)=\ln\left(\frac{AR}{Ea}\right)-\frac{Ea}{RTm} \tag{14}$$

Where β is the heating rate and Tm is the maximum peak temperature

In general, the kinetic parameters are obtained through minimization of the square of the deviations between experimental data and calculated values using traditional optimization techniques and direct and gradient-based search methods. However, the direct search methods are normally slow and involve many functions. They are strongly dependent on initial estimations and not efficient in handling nonlinear models [Saha and Ghoshal, 2005]. Although TGA provides general information on the overall reaction kinetics, rather than individual reactions, it could be used as a tool for providing comparison of kinetic data of various reaction parameters. The kinetics of these thermal events has been determined by the application of the Arrhenius equation corresponding to the separate slopes of constant mass degradation as follows:

$$\frac{dx}{dt} = \frac{A}{\Phi} e^{-\frac{E}{R}\left(\frac{1}{T}\right)} - (1-\alpha)^{n} \qquad (15)$$

where α is the conversion of reactant, t is the time (min), A is the pre-exponential factor (min–^{1}), Φ is the heating rate (°C), E is the activation energy (J/mol), R is the universal gas constant (J/mol/K) (8.314), T is the temperature (K) and n is the reaction order [Vuthaluru, 2004].

The rate of a solid state reaction may be described by:

$$d\alpha/_{dt} = k(T) f(\alpha) \qquad (16)$$

Where t is the time, T is the temperature, α is the extent of reaction and f (α) is the reaction model. The explicit temperature dependence of the rate constant is introduced by replacing k (T) with the Arrhenius equation which then gives the following equation:

$$d\alpha/_{dt} = A \exp\left(\frac{-Ea}{RT}\right) f(\alpha) \qquad (17)$$

Then,

$$g(\alpha) = A \exp\left(\frac{-Ea}{RT}\right) t \qquad (18)$$

Where A is the pre-exponential factor and Ea is the activation energy. They are both the Arrhenius parameters and R is the gas constant. The Arrhenius parameters together with the reaction model are sometimes called the kinetics triplet. Under non-isothermal conditions in which the sample heated at a constant rate, the explicit temporal in equation (17) is eliminated through the trivial transformation:

$$d\alpha/_{dt} = \frac{A}{\beta}\exp(\frac{-Ea}{RT})f(\alpha) \tag{19}$$

Where β is the heating rate. The integration of equation (19) gives:

$$g(\alpha) = \frac{A}{\beta}\int_{0}^{T}\exp(\frac{-Ea}{RT})dT \tag{20}$$

If Ea/RT is replaced by x and the integration limits are transformed, then equation (20) becomes:

$$g(\alpha) = \frac{AEa}{RT}\int_{x}^{\infty}\frac{e^{-x}}{x^{2}}dx \tag{21}$$

Kinetics parameters can be obtained from non-isothermal rate laws by both model-fitting and model-free methods. Model-fitting methods involve fitting different models to α-temperature curves and simultaneously determining the activation energy (Ea) and frequency factor (A) [Kahrizsangi *et al*, 2007].

3.7 SIMULATION PROGRAME

The computer software used for the simulation was essentially a model developed for the downdraft wood gasifiers to study the effects of operating and design parameters on reactor performance [Chen, 1986]. It consists of two sub-models, namely flaming pyrolysis and gasification zone sub-models. Flaming pyrolysis zone sub model is used to determine the product concentration and temperature of gas leaving the flaming pyrolysis zone. The gasification zone sub-model is used to predict the output of the product gas and the length of the gasification zone at any given time step [Jayah, 2002]. The principle of mass and energy balance was also used.

3.7.1 Flaming pyrolysis zone sub model

In the flaming pyrolysis zone, the general equation of the reaction of the material can be expressed by equation 21:

$$CH_aO_b + wH_2O + m(0.21O_2 + 0.79N_2) \rightarrow x_{char}Char + x_{tar}Tar + x_1CO + x_2H_2 + x_3CO_2 + x_5CH_4 + x_6N_2 \quad (21)$$

Where char was taken as carbon and ultimate analysis of tar as $CH_{1.03}O_{0.03}$ [Adams, 1980]. From equation 22 and 23 we can obtain the equilibrium equation and the corresponding equilibrium constant respectively.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{22}$$

$$K_3 = \frac{x_3 \times x_2}{x_1 \times x_4} \tag{23}$$

The correlation between the temperature and equilibrium constants for the above is given by equation 24 [Gumz, 1950].

$$Log(K_3) =$$

$$-36.72508 + \frac{3994.704}{T} - 4.46241 \times 10^{-3}T + 6.71814 \times 10^{-7}T^2 +$$

$$12.2228 \log(T)$$

(24)

Where T is the temperature in Kelvin.

By mass balance the following equations 25 – 28 can be obtained:

Carbon: $1 = x_{char} + x_{tar} + x_1 + x_3 + x_5$ (25)

Hydrogen: $a + 2w = 1.03x_{tar} + 2x_2 + x_1 + 2x_4 + 4x_5$ (26)

Oxygen: $b + w + 0.42m = 0.03x_{tar} + x_1 + 2x_3 + x_4$ (27)

Nitrogen: $0.79m = x_6$ (28)

The energy balance in flaming pyrolysis zone is given by equation 29:

$$H_c wood = H_c Char + H_c Tar + H_c Gas + H_s Char + H_s Tar + H_s Gas + Heatloss \tag{29}$$

The number of moles of water *(w)*, including fuel moisture, air moisture, and water or steam addition can be calculated by the following relationship [Chen, 1987]:

Moisture in fuel = dry matter in fuel × moisture content on dry basis as follows:

$$w = (12 \times 1 + 1 \times a + 16 \times b) \times mc_{db} kg \qquad (30)$$

The values of a and b have been given. Heat loss and *m* (number of moles of oxygen input) are obtained from the experiment, x_5, x_{char} and x_{tar} are assumed, x_1, x_2, x_3, x_4, x_6 and T are solved by using the successive approximation method with a Fortran program. The higher heating value (MJ/kg) of wood, char and tar are calculated from the equation as follows (Gaur and Reed, 1998).

$$H_C Wood = 0.3491 f_C + 0.1783 f_H - 0.1034 f_O \text{ (N}_2\text{ and ash content are neglected)} \qquad (31)$$

$$H_C Char = 0.3491 \times f_{C,char} \qquad (32)$$

$$H_C Tar = 0.3491 \times f_{C,tar} + 0.1783 f_{H,tar} - 0.1034 f_{O,tar} \qquad (33)$$

The chemical energy content of output gas, and sensible energy of char, tar and output gases are calculated as follows:

$$H_C Gas = 241000 x_1 + 283000 x_2 - 802300 x_5 \qquad (34)$$

$$H_S Char = 12.15 x_{char} \times (T - 300) \qquad (35)$$

$$H_S Tar = 21.95 x_{tar} \times (T - 300) \qquad (36)$$

$$H_S Gas = x_1 H_{CO} + x_2 H_{H2} + x_3 H_{CO2} + x_4 H_{CO2} + x_4 H_{H2O} + x_5 H_{CH4} + x_6 H_{N2} \qquad (37)$$

3.7.2 Sub – model of gasification zone

The gasification zone is modeled by following a particle along the axis of the reactor. The computer program has been formulated using FORTRAN language to calculate the characteristic profiles along the reactor axis. The profile includes temperature, concentrations, efficiency and distance the particle travelled. The length co-ordinate is coupled with a time variable through the solid phase velocity. A small time increment approach is used in calculating the product composition of the zone. It involves the use of a step procedure starting from the gasification zone and marches axially through the reactor in appropriate time increments. The output values of the flaming pyrolysis zone are used as inputs for modeling the gasification zone [Jayah, 2002]. The wood to producer gas conversion efficiency [illegible] biomass downdraft gasifier was estimated using equation 33.

$$CGE = \frac{CV_{gas} \times W_w}{CV_{fuel} \times G_q} \times 100 \qquad (38)$$

CHAPTER 4: RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter presents the results obtained using the methods discussed in chapter three. The results are presented and discussed in relation to the existing theories and existing literature. The need for the methods employed in data collection are justified and used to answer the research questions and objectives presented in chapter one. The research started by looking at a number of biomass materials, namely, corn cob, eucalyptus wood and pine wood. All the biomass materials showed a similar behaviour during the analysis due to the fact that they are all Lignocellulosic materials, and for this reason only one biomass material was chosen to report on, which is eucalyptus. It was chosen because of its high productivity compared to others.

4.2 PROXIMATE ANALYSIS

This section presents the calorific values as well as the moisture content, volatile matter content, fixed carbon content and ash contents of the material used for this study.

4.2.1 Calorific values

This subsection presents the calorific values of the material used for this study. The type of coal used was a very low grade coal with very high ash content and low calorific value, whereas the biomass materials used were of low ash. The low grade coal was chosen because it is the most commonly used coal in South Africa for power generation, while most of the high quality coal is exported.

Table 4.1 shows the energy values of coal and eucalyptus *camaldulensis*. This data was necessary to establish the baseline in terms of calorific values against which the calorific values of the blends would be compared. This would also assist in determining whether the blending of coal with the biomass significantly affected the energy value of the material.

Table 4.1: Calorific values of coal and eucalyptus wood (MJ/Kg)

Sample ID	Test 1	Test 2	Test 3	Average	Standard deviation
Coal	17.78	17.31	18.24	17.78	0.379678226
Eucalyptus	17.16	19.06	19.93	18.72	1.156613832

The values presented in table 4.1 are the average values of three measurements on each material. From table 4.1 it was observed that the coal has a lower energy value of about 18 MJ/kg which is far less than the amount found in high grade coals of more than 24 MJ/kg [Ganesh, 2006], however this value is acceptable since it is more than 15 MJ/kg reported to be the lowest calorific value of low grade coal. The eucalyptus was observed to have the energy value of about 18 MJ/kg, which is for a typical biomass Lignocellulosic material.

Table 4.2 presents the calorific values of the eucalyptus / coal blends. These were measured to establish the impact of blending the two materials on the energy value of the blends.

Table 4.2: Calorific values of the eucalyptus / coal blends (MJ/Kg)

Sample ID	Test 1	Test 2	Test 3	Average	Standard deviation
Euc$_{10\%}$-Coal$_{90\%}$	17.97	17.92	17.33	17.74	0.290631496
Euc$_{20\%}$-Coal$_{80\%}$	17.52	16.91	17.2	17.21	0.249131826
Euc$_{30\%}$-Coal$_{70\%}$	17.92	17.56	18.25	17.91	0.281780056
Euc$_{40\%}$-Coal$_{60\%}$	17.57	18.39	18.12	18.03	0.341207008
Euc$_{50\%}$-Coal$_{50\%}$	17.44	18.1	18	17.85	0.290440279
Euc$_{60\%}$-Coal$_{40\%}$	18.39	17.64	17.54	17.86	0.379326889
Euc$_{70\%}$-Coal$_{30\%}$	18.44	17.86	17.65	17.98	0.340816014
Euc$_{80\%}$-Coal$_{20\%}$	17.7	18.07	17.8	17.86	0.156276109
Euc$_{90\%}$-Coal$_{10\%}$	17.51	17.79	17.61	17.64	0.115854315

Euc – eucalyptus

It is evident from table 4.2 that there is no significant difference between the calorific values of the blends and that of the pure coal and eucalyptus wood. Although the calorific values of the materials did not differ significantly, the rate of thermal degradation and energy released was different due to the high carbon content in coal and the blends with higher carbon content. This is further discussed during the analysis of thermal degradation (TG).

4.2.2 Moisture content

Moisture content is one of the most important parameters that need to be determined when the material is going to be converted through gasification and power production. The amount of moisture is mostly influenced by how the material was handled before the analysis was carried out. Table 4.3 shows the moisture content of coal and eucalyptus.

Table 4.3: Moisture content of coal and eucalyptus wood (%)

Sample ID	Test 1	Test 2	Test 3	Average	Standard deviation
Coal	2.352	2.272	2.310	2.311	0.032668355
Eucalyptus	2.029	2.127	2.020	2.059	0.048652715

The moisture content of the samples was kept below 11% before analysis, which is within the acceptable moisture level for gasification in a downdraft gasifier. Very high moisture content evaporates and condenses against the walls of the gasifier, even though some gasifiers consist of an internal condensate trap. Excess moisture could lower the temperatures in the combustion zone thereby affecting the thermochemical reactions leading to poor gas quality [Mamphweli and Meyer, 2009]. The moisture content for the two materials was also kept at almost the same level (approximately 2%) for it not to have a huge impact on the variations in terms of thermal behavior of the blends and the other parameters.

4.2.3 Volatile mater

Table 4.4 shows the volatile content of coal and eucalyptus. A muffle furnace was used for the determination of the quantity of volatile matter present in the material. It was necessary to establish the percentage amount of volatiles when the material has been heated at high temperatures (±950ºC).

Table 4.4: Volatile matter content of coal and eucalyptus wood (%)

Sample ID	Test1	Test 2	Test 3	Average	Standard deviation
Coal	23.98	24.68	24.16	24.27	0.297880852
Eucalyptus	78.98	77.99	78.99	78.65	0.469073941

According to Ganesh, 2006 a typical biomass material has volatile matter content in the range from 60% to 90% and a typical with coal having volatile matter ranging from 20% to 50%. From table 6 the volatile matter of the coal used for this study is 24.27% and the volatile matter of the eucalyptus is 78.75%, both these values are within the acceptable ranges. Generally the volatile matter is a mixture of short and long chain hydrocarbons, aromatic hydrocarbons and some sulfur. The bonds between these hydrocarbons are strong in coal and medium to light in the biomass materials, which explains the high volatile matter content in eucalyptus and low content in coal. This is further discussed in section 4.5. Table 4.5 presents the percentage volatile matter of the eucalyptus / coal blends and figure 4.1 shows the difference in the volatile matter content of eucalyptus and coal blends.

Table 4.5: Volatile matter content of the eucalyptus / coal blends (%)

Sample ID	Test1	Test 2	Test 3	Average	Standard deviation
$Euc_{10\%}$-$Coal_{90\%}$	23.02	22.89	24.01	23.31	0.500529859
$Euc_{20\%}$-$Coal_{80\%}$	29.79	29.97	28.87	29.54	0.481102445
$Euc_{30\%}$-$Coal_{70\%}$	37.98	37.68	36.97	37.54	0.423210226
$Euc_{40\%}$-$Coal_{60\%}$	43.78	43.99	42.99	43.59	0.431156406
$Euc_{50\%}$-$Coal_{50\%}$	51.12	50.20	50.12	50.48	0.452162517
$Euc_{60\%}$-$Coal_{40\%}$	55.68	54.99	54.98	55.22	0.327634118
$Euc_{70\%}$-$Coal_{30\%}$	61.89	60.99	61.99	61.63	0.449941258
$Euc_{80\%}$-$Coal_{20\%}$	69.98	68.89	68.99	69.29	0.491366991
$Euc_{90\%}$-$Coal_{10\%}$	73.98	74.43	74.53	74.32	0.238569026

Euc – eucalyptus

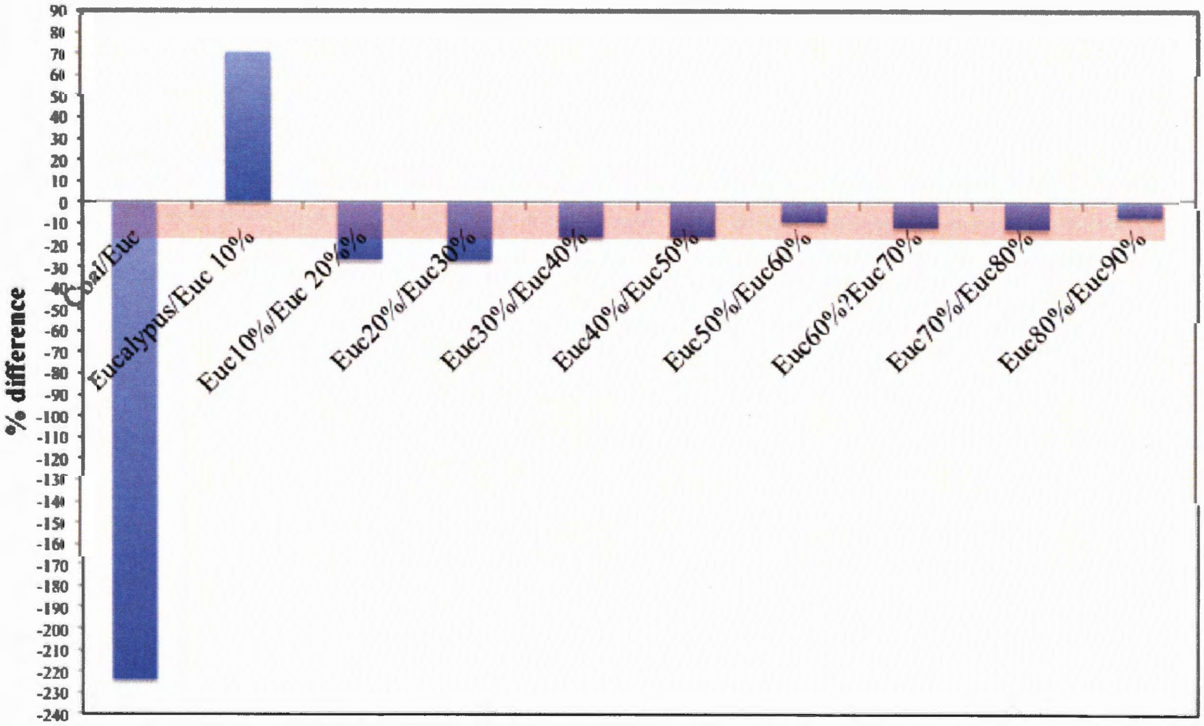

Figure 4.1: % difference in the volatile matter content of eucalyptus and coal

From table 4.5 it observed that the blends with the high content of coal have low volatile matter content and the blends with high eucalyptus content have high volatile matter content, which then implies that there is a synergy that exists between eucalyptus and coal during thermochemical conversion, and this synergy is further explained in the TGA section.

4.2.4 Fixed carbon

Table 4.6 shows the fixed carbon content of coal and eucalyptus. The fixed carbon is a solid, combustible residue remaining after the removal of moisture, volatile, and ash materials, and it is expressed in a percentage.

Table 4.6: Fixed carbon content of coal and eucalyptus wood (%)

Sample ID	Test1	Test 2	Test 3	Average	Standard deviation
Coal	25.94	26.04	25.83	25.94	0.085624937
Eucalyptus	18.18	19.12	18.22	18.51	0.434365008

The fixed carbon content of the material is the carbon that is left in the material after volatiles have been driven off. It differs from the ultimate carbon content of the coal because some carbon is lost in hydrocarbons with the volatiles. The fixed-carbon value is one of the parameters used in conducting computer simulations. Table 4.7 presents the fixed carbon content of the eucalyptus coal / blends and figure 4.2 shows the difference in fixed carbon content of eucalyptus and coal blends.

Table 4.7: Fixed carbon content of the eucalyptus / coal blends (%)

Sample ID	Test1	Test 2	Test 3	Average	Standard deviation
$Euc_{10\%}$-$Coal_{90\%}$	24.21	24.39	23.29	23.96	0.482362579
$Euc_{20\%}$-$Coal_{80\%}$	23.96	22.86	23.86	23.56	0.4942669
$Euc_{30\%}$-$Coal_{70\%}$	22.46	21.42	22.11	22.00	0.431876672
$Euc_{40\%}$-$Coal_{60\%}$	22.75	22.70	22.83	22.76	0.055065844
$Euc_{50\%}$-$Coal_{50\%}$	20.60	20.09	20.88	20.52	0.327635069
$Euc_{60\%}$-$Coal_{40\%}$	20.62	20.22	20.15	20.33	0.207662969
$Euc_{70\%}$-$Coal_{30\%}$	19.92	19.92	19.64	19.83	0.129919385
$Euc_{80\%}$-$Coal_{20\%}$	19.11	19.50	19.36	19.32	0.159172309
$Euc_{90\%}$-$Coal_{10\%}$	18.91	18.51	18.18	18.53	0.299963409

Euc – eucalyptus

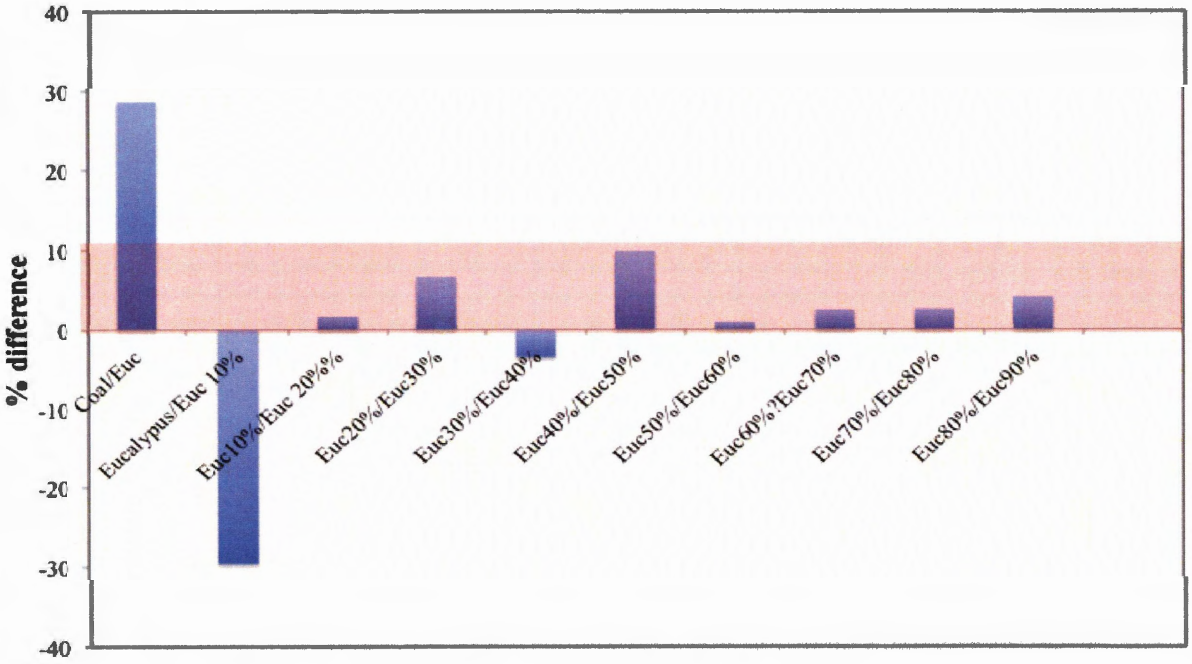

Figure 4.2: % difference in fixed carbon of eucalyptus and coal blends

From table 4.7 it was observed that the fixed carbon content of the blends with high content of coal is more than the blends with high content of eucalyptus, due to the strong carbon bonds in coal and due to the fact that eucalyptus act as a catalyst for coal gasification. This is further discussed section 4.5.

4.2.5 Ash content

Table 4.8 shows the ash content of coal and eucalyptus which was determined by heating the material in a muffle furnace at 750°C for 2 hours. Ash content is one of the parameters that need to be considered for the material before gasification, since the material with high ash content can cause serious problems to the equipment, problems such as blockages which can then lead to expensive maintenance and at times explosion.

Table 4.8: Ash content of coal and eucalyptus wood (%)

Sample ID	Test 1	Test 2	Test 3	Average	Standard deviation
Coal	46.89	47.71	47.83	47.48	0.417718672
Eucalyptus	0.774	0.822	0.728	0.775	0.038378235

From table 4.8 it is evident that the coal used for this study is a low grade coal with very high ash content of 47.73%. The eucalyptus on the other hand has low ash content of 0.775%. This implies that this type of coal is not good for gasification because it can cause blockages, slagging in the rector and excessive tar formation depending on its chemical composition. This high ash content in coal is also the reason for the low calorific value of the coal [Mamphweli and Meyer, 2009]. The blending of this type of coal with eucalyptus could thus lead to the low ash content in the blend and reduce some of the latter risks. Table 4.9 shows the ash content of the eucalyptus / coal blends and figure 4.3 shows the difference in the ash content of eucalyptus and coal blends.

Table 4.9: Ash content of the eucalyptus / coal blends (%)

Sample ID	Test 1	Test 2	Test 3	Average	Standard deviation
$Euc_{10\%}$-$Coal_{90\%}$	43.21	42.52	41.79	42.50	0.579508482
$Euc_{20\%}$-$Coal_{80\%}$	33.95	34.03	35.13	34.37	0.53839267
$Euc_{30\%}$-$Coal_{70\%}$	34.58	35.26	36.02	35.28	0.592339992
$Euc_{40\%}$-$Coal_{60\%}$	27.08	28.02	27.15	27.42	0.427577154
$Euc_{50\%}$-$Coal_{50\%}$	21.59	19.89	20.87	20.78	0.69632368
$Euc_{60\%}$-$Coal_{40\%}$	17.12	16.02	17.30	16.81	0.565295235
$Euc_{70\%}$-$Coal_{30\%}$	14.12	12.99	13.65	13.59	0.463489182
$Euc_{80\%}$-$Coal_{20\%}$	8.50	9.250	7.850	8.535	0.5719421
$Euc_{90\%}$-$Coal_{10\%}$	7.234	5.942	6.622	6.599	0.527637875

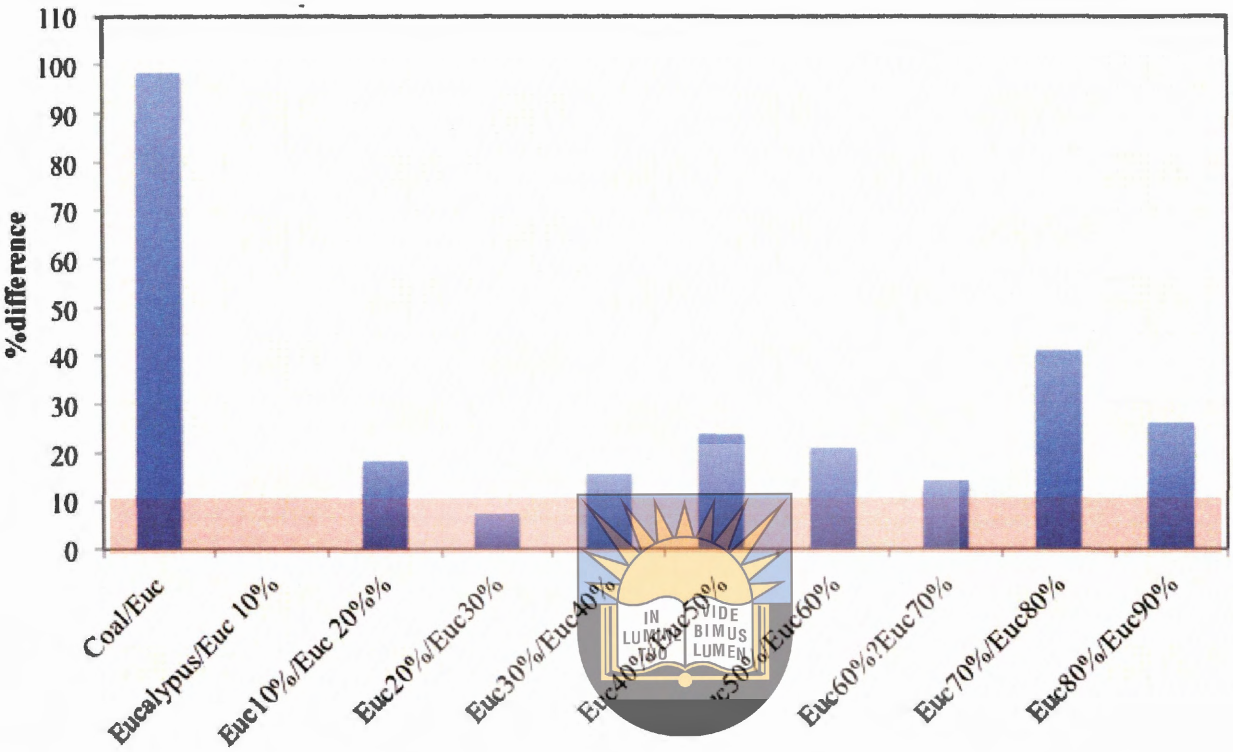

Figure 4.3: % difference in the ash content of eucalyptus and coal blends

From table 4.9 it was observed that blending this type of coal with eucalyptus reduces the ash content. The more eucalyptus added the lower the ash content. Adding 50% eucalyptus to the coal reduces the ash from 42% to 20% implying a 50% decrease in ash content. It is well known that there is a correlation between the ash content and the calorific value of the fuel. Lower ash content should imply higher calorific value; however the results recorded in this study do not suggest a change in the calorific value after blending.

4.3 ULTIMATE ANALYSIS

This section presents the elemental composition of the material used for this study. This data was necessary to establish the variations in the elemental composition after blending the coal with eucalyptus wood and the implications for these variations during gasification as determined through computer simulation of the gasification process.

Table 4.10 shows the CHNS (carbon, hydrogen, nitrogen, sulphur and oxygen was determined by difference) analysis of coal and eucalyptus wood and table 4.11 shows the XRF analysis of coal and eucalyptus. This data was necessary to establish the elemental composition of pure eucalyptus and coal to obtain the basis for comparison of the data on the blends, and draw inferences on the impact of blending the two materials on the elemental composition of the final product.

Table 4.10: CHNS composition of coal and eucalyptus wood (%)

Sample ID	%C	%H	%N	%S	%O
Coal	55.90	3.900	1.250	0.400	38.55
Eucalyptus	45.30	5.500	0.070	1.000	48.13

C – carbon, H – hydrogen, N – nitrogen, S – sulphur, O – oxygen

*O was determined by difference

Table 4.11: XRF analysis of coal and eucalyptus wood (%)

Sample ID	%Mg	%Al	%Si	%P	%S	%Cl	%K	%Ca	%Ti	%Fe	%Cu	%Zn
Coal	0.412	17.85	57.12	0.220	11.55	0.729	3.213	5.439	4.612	8.350	0.030	0.018
Eucalyptus	0.000	1.049	10.36	7.831	1.150	12.14	7.406	34.19	2.829	6.993	0.343	0.644

Mg – magnesium, Al – aluminium, Si – silicon, P – phosphorus, S – sulphur, Cl – chlorine, K – potassium, Ca – calcium, Ti – titanium, Fe – iron, Cu – copper, Zn – zinc

The amount of chemical elements in the fuel influences the ash content of the fuel. The slagging behaviour of ash depends to a large extent on the ash melting temperature which is influenced by the presence of trace elements which increases the formation of low melting point eutectic mixtures [Mamphweli and Meyer, 2009]. The quantity of carbon in coal was found to be higher than that of eucalyptus as expected (about 55.90%).

Elements such as magnesium, aluminium, silicates and sulphur are involved in the reactions that lead to ash fouling and slagging. The eucalyptus was found to have less amounts of these elements as compared to coal. Silicon is a problematic element that can melt at gasification temperature and cause agglomeration. During combustion sulphur quantitavely oxides and some of it reacts with alkali materials to form sulphates. Alkali sulphates are unstable at typical combustion temperatures of about 900°C. These sulphates can stimulate agglomeration. [Mamphweli and Meyer, 2009].

It is clear from table 4.10 and table 4.11 that eucalyptus and coal have some considerable differences in their chemical composition, thereby requiring different gasifier designs and gasification conditions. The blending of the two materials resulted in some synergy, discussed in detail in section 4.5

Table 4.12 and table 4.13 shows the elemental composition of the eucalyptus / coal blends. The data presented in this table was meant to investigate the impact of blending coal with eucalyptus on the elemental composition and gasification characteristics of the two feedstocks.

Table 4.12: CHNS analysis of the eucalyptus / coal blends (%)

Sample ID	%C	%H	%N	%S	%O
Euc$_{10\%}$-Coal$_{90\%}$	53.39	3.980	1.150	0.340	41.14
Euc$_{20\%}$-Coal$_{80\%}$	53.01	4.100	1.120	0.398	41.37
Euc$_{30\%}$-Coal$_{70\%}$	51.49	4.000	1.100	0.465	42.94
Euc$_{40\%}$-Coal$_{60\%}$	52.26	4.250	0.980	0.473	42.04
Euc$_{50\%}$-Coal$_{50\%}$	51.03	4.429	0.850	0.500	43.19
Euc$_{60\%}$-Coal$_{40\%}$	49.69	4.320	0.543	0.702	44.74
Euc$_{70\%}$-Coal$_{30\%}$	48.82	5.201	0.220	0.798	44.96
Euc$_{80\%}$-Coal$_{20\%}$	47.55	4.730	0.099	0.990	46.63
Euc$_{90\%}$-Coal$_{10\%}$	46.71	4.900	0.089	0.975	47.33

C – carbon, H – hydrogen, N – nitrogen, S – sulphur, O – oxygen

*O was determined by difference

Table 4.13: XRF analysis of the eucalyptus / coal blends (%)

mple ID	%Mg	%Al	%Si	%P	%S	%Cl	%K	%Ca	%Ti	%Fe	%Cu	%Zn
c$_{10\%}$-Coal$_{90\%}$	0.310	16.33	54.86	0.789	5.079	0.877	3.273	4.657	4.360	8.501	0.046	0.028
c$_{20\%}$-Coal$_{80\%}$	0.291	16.94	58.34	0.629	2.390	-	3.323	4.349	4.358	8.319	0.035	0.027
c$_{30\%}$-Coal$_{70\%}$	0.223	15.72	54.83	0.947	4.692	1.681	3.438	4.573	4.333	8.514	0.036	0.032
c$_{40\%}$-Coal$_{60\%}$	0.279	16.094	52.78	0.800	5.001	1.648	3.438	5.769	4.303	8.851	0.038	0.039
c$_{50\%}$-Coal$_{50\%}$	0.290	15.59	50.66	1.192	5.113	2.463	3.820	6.468	4.238	9.76	0.039	0.052
c$_{60\%}$-Coal$_{40\%}$	0.197	14.80	49.48	1.543	5.016	3.427	3.660	8.332	4.041	8.384	0.045	0.103
c$_{70\%}$-Coal$_{30\%}$	0.247	15.15	48.87	1.495	5.662	3.108	3.499	8.641	4.087	8.105	0.045	0.074
c$_{80\%}$-Coal$_{20\%}$	0.012	12.73	43.54	2.927	5.394	6.072	4.399	12.22	3.626	7.437	0.058	0.142
c$_{90\%}$-Coal$_{10\%}$	0.147	11.14	33.00	3.650	5.726	7.431	4.874	17.71	3.663	10.73	0.073	0.201

Mg – magnesium, Al – aluminium, Si – silicon, P – phosphorus, S – sulphur, Cl – chlorine, K – potassium, Ca – calcium, Ti – titanium, Fe – iron, Cu – copper, Zn – zinc

From table 4.12 it is evident that the carbon content of all the eucalyptus / coal blends is lower than that of coal and it decreases with an increase in the quantity of eucalyptus in the blend. This is because of some dilution effect caused by the low carbon content in eucalyptus. This may have an impact on the energy value of the feedstock; however it might not be a challenge as it may be complemented by the reactivity of eucalyptus that would act as a catalyst for full conversion of coal thereby resulting in more energy released, this can be clearly observed when a high grade coal is used. From table 4.13, the trace elements such as magnesium, aluminium, silicates and sulphur are then diluted when higher quantities of eucalyptus are present in the blends and this would reduce the risk of slagging during gasification of the material.

4.5 THERMOGRAVIMETRIC ANALYSIS (TGA)

This sub-section presents the thermal degradation of the material as well as their derivatives. This data was necessary to establish the rate of thermal degradation of pure biomasses and coal to obtain the basis for comparison of the data on the blends. Lignocellulosic biomass consists of cellulose, hemicellulose and lignin.

Cellulose is the major structural component of plants, especially of wood and plant fibres. It is a linear homogeneous polymer and degrades at higher temperatures (around 300–900°C). Hemicellulose is a polysaccharide found in plant cell walls and it normally decomposes at temperatures above 160°C up to around 300°C. Lignin is found in all vascular plants, and represents about 25% of the terrestrial plant biomass. It is a complex phenolic heteropolymer that results from oxidative polymerization [Kumabe *et al*, 2007]. It is normally lost at a slow rate respectively. This implies that coal requires higher gasification temperature than biomass for complete gasification to take place. Figure 4.6 and figure 4.7 presents the mass loss and derivative mass loss of the eucalyptus / coal blends, respectively in relation to temperature and time.

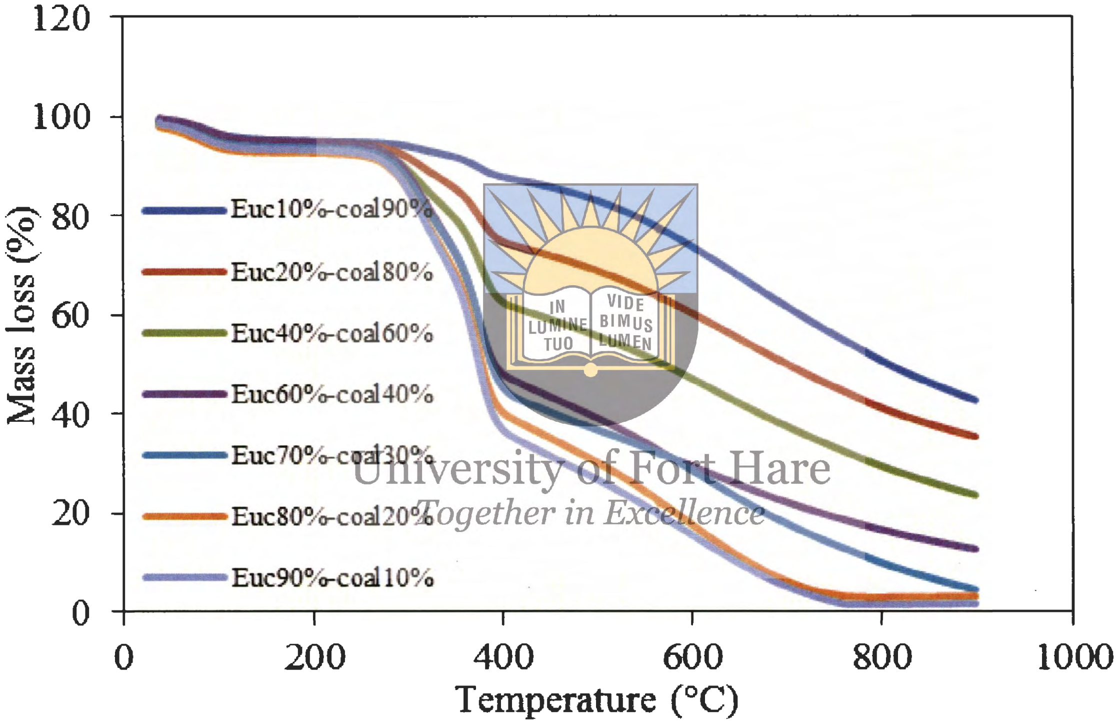

Figure 4.6: TG plots of the eucalyptus / coal blends

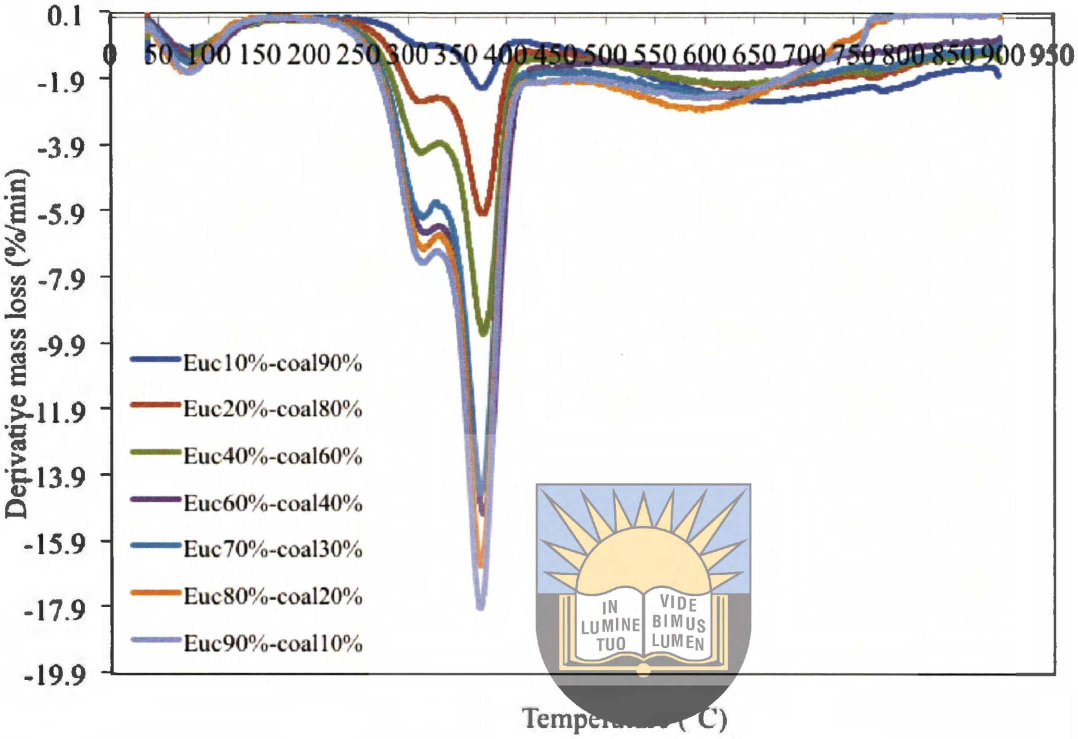

Figure 4.7: DTG plot of the eucalyptus / coal blends

It is evident from figure 4.6 that the addition of eucalyptus results in higher rate of devolatilization of the blend even at lower temperatures, the more the eucalyptus added to the blend the faster the reaction. The moisture content was observed to be almost the same for all the blends and the differences are clear in stage B where volatile matter is released and rapid devolatilization is taking place. This proves that there is a synergistic effect between coal and eucalyptus with eucalyptus acting as a catalyst for coal degradation due to its high volatile matter content, and the amount of ash left decreasing with the increase in the addition of eucalyptus. Although the two materials have almost the same energy content, eucalyptus wood releases the energy faster at lower temperatures making that energy available for the conversion of coal at higher temperatures, this synergy is very important during the conversion of the blends.

This therefore lowers the gasification temperature of the coal / biomass blend. Even figure 4.7 shows that the 90%euc-10%coal blend had the fastest degradation rate and 10%euc-90%coal had the slowest as previously stated than the devolatilization of coal alone.

4.5.1 Rate law and kinetic analysis

The kinetic parameters, activation energy and pre-exponential factor were determined from the TG data using the Kissinger method. Table 4.14 shows the kinetic parameters of coal, eucalyptus and their blends.

Table 4.14: kinetic parameters of coal, eucalyptus and their blends

Sample ID	Activation energy (kJmol^{-1})	Pre-exponential factor (min^{-1})
Coal	77.5222302	$7.5333\text{X}10^{71}$
Eucalyptus	71.6783196	$1.364\text{X}10^{74}$
Euc$_{10\%}$-coal$_{90\%}$	77.3422321	$0.832\text{X}10^{76}$
Euc$_{20\%}$-coal$_{80\%}$	75.901354	$0.851\text{X}10^{76}$
Euc$_{40\%}$-coal$_{60\%}$	75.430187	$0.930\text{X}10^{75}$
Euc$_{60\%}$-coal$_{40\%}$	73.701634	$0.98\text{X}10^{76}$
Euc$_{70\%}$-coal$_{30\%}$	73.018254	$1.250\text{X}10^{75}$
Euc$_{80\%}$-coal$_{20\%}$	72.407332	$1.28\text{X}10^{75}$
Euc$_{90\%}$-coal$_{10\%}$	71.515327	$1.360\text{X}10^{74}$

Activation energy is the amount of energy required to break bonds during the reaction. Therefore, it is assumed that the hydrocarbons in coal are more strongly bound together than eucalyptus hydrocarbons based on the activation energies and slower decomposition rates [Oba *et al*, 2002]. From table 4.14 it is evident that the kinetic analysis is in agreement with the chemical analysis since the activation energies also proved that the more biomass material added to the blend the faster the reaction as compared to coal alone. This is in agreement with the synergistic effect observed through TG and DTG graphs.

4.6 *SIMMULATIONS*

Table 4.15 shows the parameters of coal, eucalyptus and the eucalyptus / coal blends used for the simulation.

Table 4.15: Simulation parameters of coal, eucalyptus and their blends

	Coal	Eucalyptus	10%Euc-90%C	20%Euc-80%C	30%Euc-70%C	40%Euc-60%C	50%Euc-50%C	60%Euc-40%C	70%Euc-30%C	80%Euc-20%C	90%Euc-10%C
Carbon	55.90	45.46	53.08	53.10	53.49	52.88	51.30	48.87	48.84	47.39	46.71
Hydrogen	3.9	5.5	3.98	4.1	4.2	4.25	4.29	4.32	4.67	4.73	4.9
Oxygen	31.22	46.71	32.46	34.49	35.57	40.73	47.51	47.14	47.56	47.62	47.72
Nitrogen	8.143	9.64	7.85	8.083	7.913	9.507	9.15	9.41	9.69	9.11	9.75
Fixed carbon	25.94	18.51	23.96	23.56	22.00	23.76	20.52	20.33	19.83	19.32	18.53
Bulk density	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Diameter of wood particle	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Throat diameter	30	30	30	30	30	30	30	30	30	30	30
Throat angle	35	35	35	35	35	35	35	35	35	35	35
Insulation thickness	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5
Thermal conductivity (Insulating material)	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Moisture content	2.311	2.058	2.221	2.562	2.372	2.227	2.35	2.814	2.215	2.136	2.387
Temperature of input air	300	300	300	300	300	300	300	300	300	300	300
Feed input	40	40	40	40	40	40	40	40	40	40	40
Air input	45	45	45	45	45	45	45	45	45	45	45
Heat loss	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5

Euc – eucalyptus wood, C - carbon

Figure 4.8 shows the maximum efficiency plot of coal, eucalyptus and the eucalyptus / coal blends. The data presented in this figure was obtained through computer simulation of the gasification of these blends in a downdraft biomass gasifier.

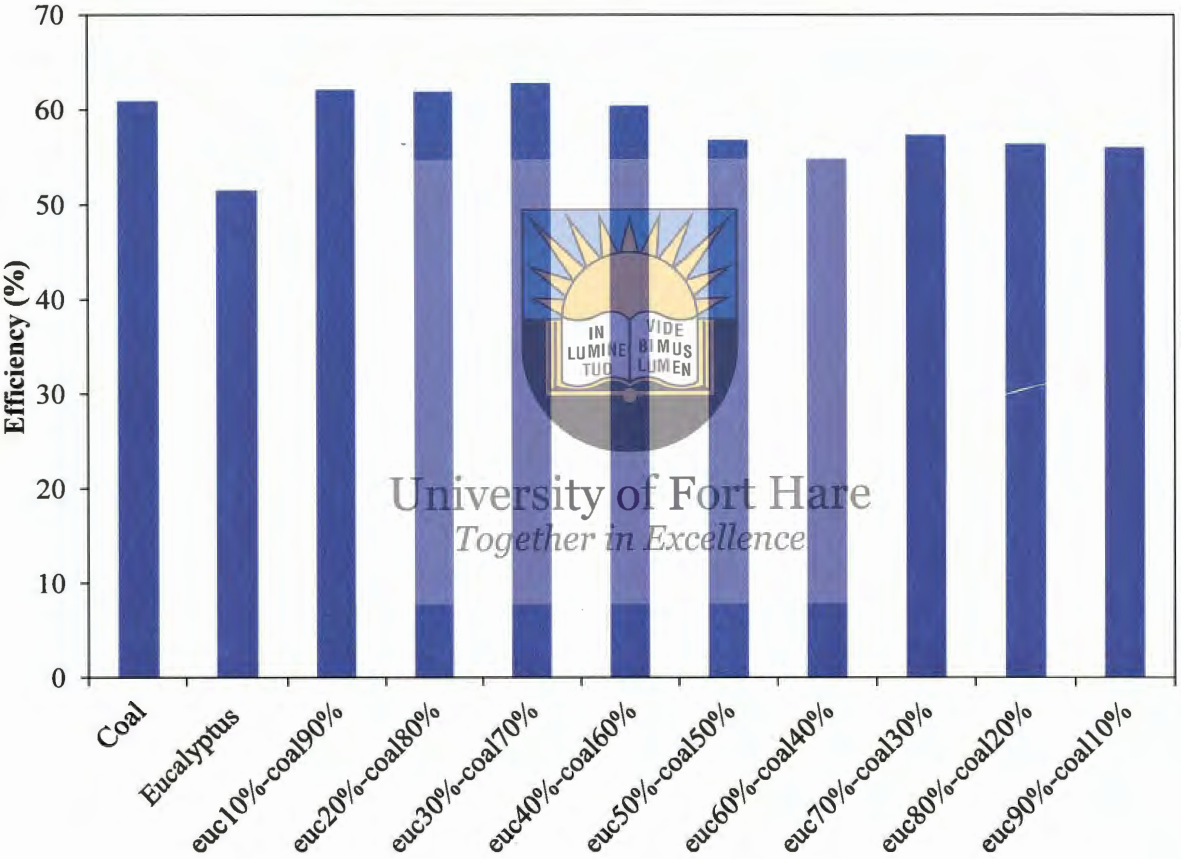

Figure 4.8: Maximum efficiency plot of coal, eucalyptus and their blends

From figure 4.8 it was observed that all the blends with the high content of coal have high conversion efficiency. The euc10%-coal90% blend have a conversion efficiency of 62.1%, euc20%-coal80% blend has a conversion efficiency of 61.9%, euc30%-coal70% blend has a conversion efficiency of 62.8% and the euc40%-coal60% blends having the conversion efficiency of 60.4%. While, the blends with high biomass material have quite lower conversion efficiency around 57%, with pure coal having the conversion efficiency of 60.9% and eucalyptus wood having the conversion efficiency of 51.5%.

4.7 ANOVA ONE WAY TEST

Analysis of variance (ANOVA) is a general method that is used for studying sampled-data relationships. This method permits the difference between two or more sample means to be analyzed. Its purpose is to test for significant differences between means, and this is done by analyzing the variances. ANOVA was conducted on the TGA data. Table 4.16 shows the summary of the ANOVA one way test.

Table 4.16: Summary of ANOVA one way test analysis

Groups	Count	Sum	Average	Variance
100%coal	5291	324928.8	61.4116	1450.958
100%euc	2655	202252.9	76.17812	559.9832
Euc10%-coal90%	2655	211696.3	79.73494	309.1994
Euc20%-coal80%	2655	191909.1	72.28214	448.6637
Euc40%-coal60%	2655	170741.2	64.30929	676.4141
Euc60%-coal40%	1640	125490.8	76.5188	584.7107
Euc70%-coal30%	1640	122984.1	74.99028	606.9891
Euc80%-coal20%	1640	118116.3	72.02214	728.5802
Euc90%-coal10%	1640	116588.7	71.09069	828.5033

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	956083.7	8	119510.5	153.6287	$4.8477X10^{-253}$	1.938824
Within Groups	17473589	22462	777.9178			
Total	18429673	22470				

Euc – eucalyptus

The p value was found to be $4.8477X10^{-253}$, which is far less than 0.05, therefore there is a significant difference between coal, eucalyptus and their blends, in terms of thermal degradation.

CHAPTER 5: SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY OF MAJOR FINDIGS

Gasification of carbon-based resources such as coal or any other biomass residues is a useful conversion technology that adds flexibility to the energy systems. However, gasification of coal has shown several disadvantages such as the release of greenhouse gases such as sulphur to the atmosphere. Whereas biomass is an environmentally friendly resource even though it has a low calorific value than high grade coals. Co-gasi[illegible] and biomass does not only reduce the global warming risks but also give clean energy with syngas having high calorific value.

This research carried out the proximate analysis, elemental analysis, thermal degradation, kinetic analysis and tested the data using ANOVA one way test, for coal, eucalyptus and their blends. From the proximate analysis it was found that both materials had low calorific values, which is acceptable for the gasification process. Coal had very high ash content; this is due to the fact that the coal used for this study was a very low grade coal. This high ash content could cause problems such as blocking the gasifier. However, the eucalyptus had low ash content and blending the two materials resulted in lower ash content.

Both materials have almost the same calorific values, which then leads to no much difference in the blends in terms of calorific values. However, even though the calorific values were low they were still in the acceptable range. From the elemental analysis it was observed that the coal had higher carbon content that eucalyptus wood, which then implied that it can still release the same quantity of energy slowly due to the strong carbon bonds that require higher temperatures to break. The eucalyptus had higher oxygen content as expected, which then make it a good catalyst for coal gasification.

Thermogravimetric analysis and derivative mass loss showed that eucalyptus burns faster that coal and at lower temperatures (about 200 to 600°C) whereas coal burns very slowly and require higher temperatures (about 500 to 900°C). From the blends it was observed that the more biomass added to coal the faster the reaction rate and the lower the activation energy. This implies that blending the two materials will also reduce the temperature required for complete gasification to take place, as coal on its own requires temperatures of above 1000°C for complete gasification.

The kinetic analysis was also in agreement, because the activation energy of coal was higher than that of eucalyptus (77KJ/mol and 71KJ/mol respectively), and the more eucalyptus added the lower the activation energy which implies that the faster the reaction. The ANOVA one way test was conducted on the TGA data and it also showed the two materials are really different (with the p value being $4.8477X10^{-253}$, which is far less than 0.05) as well as to their blends. This means that blending the two materials could lead to clean efficient energy.

5.2 SUMMARY OF THE CONTRIBUTIONS

Coal gasification is a well-known technology for syngas production. Biomass gasification on the other hand has been the focus of research in recent years to evaluate the efficiency and performance of the gasification process using various types of lignocellulosic biomass such as sugarcane bagasse, pine wood sawdust and many others. There has been some substantial research interest in co-gasification of various biomass and coal mixtures to improve the carbon footprint of the fossil fuels technologies.

This research undertook chemical analysis and kinetic analysis of various biomass / coal blends for co-gasification in a downdraft gasifier. The results gave an insight on what to expect during co-gasification. A paper on the synergistic evaluation of biomass / coal blends for co-gasification purposes was presented at the South African Institute of Physics conference 2012, with the paper viewed as having some relevant contributions to the field. Another paper on the chemical analysis of the biomass / coal blends for co-gasification is under corrections to be considered for publication with Fort Hare Papers Journal. The research also revealed that the blending of coal and biomass results in a synergy during gasification and this was evident from the kinetic analysis of the blends.

5.3 CONCLUSIONS

The coal and eucalyptus wood used for this study were found to have an insignificant variation in the energy values, this was due to the fact that the coal used was a low grade coal with high ash content. It can therefore be concluded that for systems that use low grade coal for energy production it would be better if they can switch directly to eucalyptus wood to avoid the adverse environmental impacts associated with coal conversion. It can also be concluded that it is possible to combine coal and biomass for gasification in low temperature downdraft biomass gasifier. The higher conversion efficiency was also obtained when the coal and biomass were blended.

There was a significant variation in the chemical composition of the two materials used with coal having higher quantities of carbon as opposed to eucalyptus wood. The chemical elements of the two materials were found to get diluted with the blending of the materials giving rise to the synergy that occur during conversion. This synergy results in eucalyptus acting as a catalyst for coal gasification. This was also established through kinetic analysis of the blends.

The trace elements such as magnesium, aluminium, silicates and sulphur are then diluted when higher quantities of eucalyptus are present in the blends and this would reduce the risk of slagging during gasification of the material, which could be a challenge is coal is gasified alone in the downdraft gasifier.

Buragohain B., Mahanta P. and Moholkar V. S. Biomass gasification for decentralized power generation: The Indian perspective, Renewable and Sustainable Energy Reviews, **14,** (2010), pp 73–92.

Chen J. S. Kinetic engineering modeling of co-current moving bed gasification reactors for carbonaceous material. Cornell University, New York, USA. (1986).

Chmielniak T. and Sciazko M. Co-gasification of biomass and coal for methanol synthesis. Applied Energy, **74**, (2003), pp. 393–403.

Collot A. Matching gasification technologies to coal properties. International Journal of Coal Geology, **65**, (2006), pp 191– 212.

Corujo A., Yerman L., Arizaga B., Brusoni M. and Castiglioni J. Improved yield parameters in catalytic steam gasification of forestry residue; optimizing biomass feed rate and catalyst type. Biomass and Bioenergy, **34**, (2010), pp 1695 – 1702.

Duret A., Friedli C. and Marechal F. Process design of Synthetic Natural Gas (SNG) production using wood gasification. Journal of Cleaner Production, **13**, (2005), pp 1434 – 1446].

Fan L., Li F. and Ramkumar S. Utilization of chemical looping strategy in coal gasification processes. Particuology, **6**, (2008), pp 131–142.

Ganesh A., Biomass Resources, Characterisation and Technologies, Energy Systems Engineering, IIT Bombay, 21st September 2006.

Garcia R., Pizarro C., Lavin A. G. and Bueno J. L. Characterization of Spanish biomass wastes for energy use. Bioresource Technology, **103**, (2012), pp 249–258.

Gaur S. and Reed T.B. Thermal data for natural and synthetic fuels. Marcel Dekker Inc, New York, USA, (1998).

Gumz W.G. Gas producers and blast furnaces: Theory and Methods of Calculation. John Wiley and Sons, New York, USA, (1950).

Heinze T. and Liebert T. Unconventional methods in cellulose functionalization. Progress in polymer science, **26**, (2001), pp 1689 – 1762.

Howaniec N., Smolinski A., Stanczyk K. and Pichlak M. Steam co-gasification of coal and biomass derived chars with synergy effect as an innovative way of hydrogen-rich gas production, International Journal of Hydrogen Energy, **36**, (2011), 14455 -14463.

Jankovi´c B., Adnadevi´c B. and Jovanovi´c J. Application of model-fitting and model-free kinetics to the study of non-isothermal dehydration of equilibrium swollen poly (acrylic acid)hydrogel: Thermogravimetric analysis, Thermochimica Acta,**452**, (2007), pp 106–115.

Jayah T. H. Evaluation of a downdraft wood gasifier for tea manufacturing in Sri Lanka. Melbourne University, Victoria, Australia, (2002).

Kahrizsangi E., Reza, H. A. M. and Ali S. Model - Fitting Approach to Kinetic Analysis of Non-Isothermal Oxidation of Molybdenite, Department of Materials Engineering Isfahan University of Technology IsfahanI. R. IRAN, **26**, (2), (2007).

Kirkels A. F. and Verbong G. P.J. Biomass gasification: Still promising? A 30 - year global overview. Renewable and Sustainable Energy Reviews, **15**, (2011), pp 471–481.

Kumabe K., Hanaoka T., Fujimoto S., Minowa [illegible] and Sakanishi K. Co-gasification of woody biomass and coal with air and steam. Fuel **86** (2007), pp 684–689.

Lee S. H., Yoon S. J., Ra H. W., Son Y. Il, Jai C. H. and Lee J. G. Gasification characteristics of coke and mixture with coal in an entrained-flow gasifier. Energy, **35**, (2010), pp 3239 – 3244.

Llorente M.J. Fernandez J.E. and Garcia C. Suitability of thermo-chemical corrections for determining gross calorific value in biomass. Thermochimica Acta, **468**, (2008), pp 101–107.

Long H. A. and Wang T., Case Studies for biomass/coal co-gasification in IGCC applications, Proceedings of ASME Turbo Expo,Vancouver, Canada, 2011.

Mamphweli N. S. and Meyer E. L. Implementation of the biomass gasification project for community empowerment at Melani village, Eastern Cape, South Africa. Renewable Energy, (2009), **34**, pp 2923 – 2927.

McMurry J. 2008, Organic Chemistry, 7th edition, Thomson Learning Academic resource centre, 423-25.

Nilsson S., Gómez-Barea A., Fuentes-Cano D. and Ollero P. Gasification of biomass and waste in a staged fluidized bed gasifier: Modeling and comparison with one-stage units. Fuel, **97**, (2012), pp 730 – 740.

Oba M., Mita H. and Himoyama A. Determination of activation energy and pre-exponential factor for individual compounds on release from kerogen by a laboratory heating experiment. Geochemical Journal, **36**, (2002), pp. 51 to 60,

Pan Y. G., Velo E. and Puigjaner L. Pyrolysis of blends of biomass with poor coals. Fuel, **75**, (4), (1996), pp. 412-418.

Pinto F., Franco C., Andre R. N., Tavares C., Dias M., Gulyurtlu I. and Cabrita I. Effect of experimental conditions on co-gasification of coal, biomass and plastics wastes with air/steam mixtures in a fluidized bed system. Fuel, **82,** (2003), pp 1967–1976.

Rajvanshi A. K. Alternative Energy in Agriculture. Biomass Gasification, **2** (1986), pg 83-102.

Rastogi S. and Dwivedi U. N. Manipulation of lignin in plants with special reference to O-methyl transferase. Plant Science, **174**, (2008), pp 264–277.

Ryu C., Yang Y. B., Khor A., Yates N. E, Sharifi V. N. and Swithenbank J. Effect of fuel properties on biomass combustion: Part I. Experiments—fuel type, equivalence ratio and particle size. Fuel, **85**, (2006), pp 1039–1046.

Saha B. and Ghoshal A. K. Hybrid Genetic Algorithm and Model-Free Coupled Direct Search Methods for Pyrolysis Kinetics of ZSM-5 Catalyzed Decomposition of Waste Low-Density Polyethylene. Ind. Eng. Chem. Res., **46**, (2007), pp [illegible]85-5492.

Scheller H. V. and Ulvskov P. Hemicelluloses, Annual Reviews. Plant Biology, **61**, (2010), pp 263-289.

Shen L., Gao Y. and Xiao J. Simulation of hydrogen production from biomass gasification in interconnected fluidized beds. Biomass and Bioenergy, **32,** (2008) pp 120 – 127.

Sluiter A., Hames B., Hyman D., Payne C., Ruiz R., Scarlata C., Sluiter J., Templeton D., and Wolfe J., Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid Process Samples, Laboratory Analytical Procedure (LAP), National renewable energy, Revised March 2008, NREL/TP-510-42621.

Sluiter A., Hames B., Ruiz R., Scarlata C., Sluiter J., and Templeton D., Determination of Ash in Biomass, Laboratory Analytical Procedure (LAP), National renewable energy ,revised January 2008, NREL/TP-510-42622.

Toonssen R., Sollai S., Aravind P.V., Woudstra N. and Verkooijen A. H.M. Alternative system designs of biomass gasification SOFC/GT hybrid systems. International Journal of Hydrogen Energy, **36,** (2011), pp 10414 - 10425.

Vassilev S. V., Baxter D., Andersen L. K. and Vassileva C. G., An overview of the chemical composition of biomass. Fuel, **89**, (2010), pp 913–933.

Vuthaluru H.B. Investigations into the pyrolytic behaviour of coal/biomass blends using thermogravimetric analysis. Bioresource Technology, **92**, (2004), pp 187–195.

Warnecke R. Gasification of biomass: comparison of fixed bed and fluidized bed gasifier. Biomass and Bioenergy, **18,** (2000), pp 489 – 497.

Watanabe H. and Otaka M. Numerical simulation of coal gasification in entrained flow coal gasifier. Fuel, **85**, (2006), pp 1935–1943.

Williamson I. A. coal mining geology, London Oxford University press, New York, Toronto, 1967, pp 218 – 239.

Xiang W., Chen S., Xue Z. and Sun X. Investigation of coal gasification hydrogen and electricity co-production plant with three-reactors chemical looping process. International Journal of Hydrogen Energy, **35**, (2010), pp 8580 - 8591.

Xiao X., Le D. D.., Morishita K., Zhang S., Li L. and Takayuki T. Multi-stage biomass gasification in Internally Circulating Fluidized-bed Gasifier (ICFG): Test operation of animal-waste-derived biomass and parametric investigation at low temperature. Fuel Processing Technology, **91**, (2010), pp 895–902.

Yin C., Prediction of higher heating values of biomass from proximate and ultimate analyses. Fuel, **90**, (2011), pp 1128–1132.

Zhang Y., Wang Y., Cai L., Yao C., Gao S., Li C. and Xu G. Dual bed pyrolysis gasification of coal: Process analysis and pilot test, Fuel, (2012).

Zhou L., Wang Y., Huang Q. and Cai J. Thermogravimetric characteristics and kinetic of plastic and biomass blends co-pyrolysis. Fuel Processing Technology, **87**, (2006), pp 963 – 969.

Zhou Z., Ma L., Yin X., Wu C., Huang L. and Wang C., Study on biomass circulation and gasification performance in a clapboard-type internal circulating fluidized bed gasifier, Biotechnology Advances, **27**, (2009), pp 612–615.

WEBSITES

Excerpts from RockTalk,**8**, (2), (2005), http://www.geotech.org/survey/geotech/coal.pdf, last accessed in February 2012.

http://en.wikipedia.org/wiki/Anthracite, last accessed in February 2012.

http://en.wikipedia.org/wiki/Bituminous coal, last accessed in February 2012.

http://en.wikipedia.org/wiki/Sub-bituminous_coal, last accessed in February 2012.

http://www.intertek.com/analysis/thermogravimetric/, Thermogravimetric Analysis (TGA), last accessed in February 2012.

The international learning institute, about Lignin, http://www.ili-lignin.com/aboutlignin.php last accessed in February 2012.

http://www.perkinelmer.com/CMSResources/Images/44-74556GDE_TGABeginnersGuide.pdf, last accessed October 2013.

http://www.andersonmaterials.com/tga.html, last accessed in October 2013 http://serc.carleton.edu/research_education/geochemsheets/techniques/XRF.html, last accessed on January 2014

http://www.science.saf.kuniv.edu/index.php?page=facility_chns, last accessed on January 2014

APPENDICES

APPENDIX A: RESEARCH OUTPUTS ASSOCIATED WITH THE WORK

A1. CONFERENCE PROCEEDINGS

S Gaqa, S Mamphweli, D Katwire and E Meyer, Synergistic evaluation of biomass / coal blends for the purpose of co-gasification, *57th SAIP Conference*, University of Pretoria, South Africa, 9 - 13 July 2012. (**Paper under review**).

A2. CONFERENCE PRESENTATIONS

S Gaqa, S Mamphweli, D Katwire and E Meyer, Chemical analysis of the biomass / coal blends for co-gasification, *1st National Global Change Conference,* Birchwood hotel in Boksburg, Johannesburg, South Africa, 26 – 28 November 2012.

S Gaqa, S Mamphweli, D Katwire and E Meyer, The properties and suitability of various biomass/coal blends for co-gasification in a downdraft biomass gasifier, *58th SAIP Conference,* University of Pretoria, South Africa, 08 - 12 July 2013.

A3. JOURNAL PAPERS

S Gaqa, S Mamphweli, D Katwire and E Meyer, Synergistic evaluation of biomass / coal blends for the purpose of co-gasification (Paper accepted to be published with the International Journal of Energy and Environment (IJEE), reference number IJEE-1096-09012014).

S. Gaqa, S. Mamphweli, D. Katwire and E. Meyer, The properties and suitability of various biomass/coal blends for co-gasification in a downdraft biomass gasifier. (Paper accepted to be published with the Journal of Sustainable Bioenergy Systems (JSBS) - manuscript ID: 2210094).

S Gaqa, S Mamphweli, D Katwire and E Meyer, Analysis of the biomass / coal blends for co-gasification. (Paper submitted under review for consideration to be published with Fort Hare Papers).