CHARACTERIZATION AND COMPUTER SIMULATION OF CORN STOVER / COAL BLENDS FOR CO-GASIFICATION IN A DOWNDRAFT GASIFIER

University of Fort Hare
Together in Excellence

A dissertation submitted in fulfilment of the requirements for the degree of

Master of Science in Physics

By

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Year: 2014
DEDICATIONS

To my mother, father (late), siblings, wife (Primrose Nosicelo Njingana - Mabizela) and kids.
ACKNOWLEDGEMENTS

It has been possible to produce this dissertation due to significant contributions many people have made. Notwithstanding the fact that it is not possible to list here the names of all those I am indebted to in this regard, I want them to know that I really deeply appreciate their contributions. In particular the following:

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- Special thanks to my wife – Primrose Nosicelo Njingana-Mabizela, my mother and siblings who constantly encouraged me throughout the project
DECLARATION

I declare that this dissertation is not one for which a degree has been or will be conferred by any other university or institution. It is not one for which a degree has already been conferred by this University. The work for this dissertation is my own work and, all non-original material have been duly acknowledged.

DATE: 1 JUNE 2014
SUMMARY

The need for sustainable alternative energy technology is becoming more urgent as the demand for clean energy environment increases. For centuries, electricity in South Africa has been derived mostly from coal with results growing in multifold annually due to concerns about the impact of fossil fuel utilization related to emission of greenhouse gasses. It is practically impossible at the moment to replace coal with biomass resources because of the low energy value of biomass. However, the conversion of coal has experienced some challenges especially during its gasification which includes, but are not limited to a high reaction temperature exceeding 900°C which most gasifiers cannot achieve, and if achieved in most cases, combustion of the resulting syngas usually occur, leading to low conversion efficiency and the risk of reaching extremely high temperatures that may result in pressure build up and explosion may also occur. Therefore, this study sought to investigate the possibility of co-gasifying corn stover with coal with the ultimate aim establishing the best mixing ratio that would result in optimum co-gasification efficiency after computer simulation. Proximate and ultimate analysis, including energy values of corn stover and coal as well as their blends were undertaken and results showed significant differences between the two feedstocks and narrow range composition between their blends in terms of properties and energy value. Corn stover showed a higher fraction of volatile matter and lower ash content than coal, whereas those of their blends vary considerably in terms of physical properties. Differences in chemical composition also showed higher fraction of hydrogen and oxygen, and less carbon than coal while those of their blends vary according to the ratio of corn stover to coal and vice versa in the blends. The thermal stability of corn stover and coal as well as their blends were also established and the maximum temperature reached for thermal degradation of their blends was 900°C as depicted by TGA analysis. The SEM
results revealed no changes in morphology of the pure samples of corn stover and coal which was due to the fact that a pre-treatment of the samples were not undertaken, whereas the blends showed significant changes in morphology as a result of blending. However, luminous and non-luminous features were noticed in both SEM images of the blends with the 10% coal/90% corn stover blend having higher percentages of luminosity as a result of higher quantities of coal in the blend. The energy density of the samples were also measured and found to be 16.1 MJ/kg and 22.8 MJ/kg for corn stover and coal respectively. Those of their blends varied from 16.9 to approximately 23.5 MJ/kg. These results were used to conduct computer simulation of the co-gasification process in order to establish the best blend that would result in maximum co-gasification efficiency. The blend 90% corn stover/10% coal was found to be the most suitable blend for co-gasification resulting in an efficiency of approximately 58% because its conversion was efficiently achieved at a temperature that is intermediate to that of coal and biomass independently. The simulation results were, however, compared with experimental data found in the literature and results showed only slight variation between them.

**Keywords:** Biomass, coal, co-gasification, blend, efficiency.
DEFINITION OF TERMS

Biomass – It is defined as any organic matter which is available on a renewable basis (agricultural crops, agricultural wastes, municipal wastes and animal waste) [Tumuluru et al., 2011].

Coal - It is defined as a combustible black or dark brown rock consisting chiefly of carbonized plant matter found mainly in underground seams [Tumuluru et al., 2011].

Co-gasification – It involves blending of coal and biomass, which results in reduction of gasification temperature and decreasing the environmental impact because biomass is carbon neutral [Tumuluru et al., 2011].

Thermogravimetric analysis (TG) – It is defined as a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of temperature (f (T)) or as a function of time (f (t)) [Wikipedia, 2014].

Differential thermogravimetric analysis (DTG) – It is defined as a rate of thermal degradation (weight loss) as the temperature changes with time [Wikipedia, 2014].

Greenhouse gas – It is defined as a gas that absorbs infrared radiation (IR) and radiates heat in all directions [Wikipedia, 2014].

Efficiency – It is defined as the ratio of output power generated divided by input power [Mamphweli and Meyer, 2009].
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CR &amp; W</td>
<td>Combustible renewable and waste</td>
</tr>
<tr>
<td>HHV</td>
<td>Highest heating value</td>
</tr>
<tr>
<td>CS</td>
<td>Corn Stover</td>
</tr>
<tr>
<td>RRDB</td>
<td>Renewable Resource Database</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
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<tr>
<td>N₂</td>
<td>Nitrogen</td>
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<tr>
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<td>Sulfur oxides</td>
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<tr>
<td>SO₂</td>
<td>Sulfur Dioxide</td>
</tr>
<tr>
<td>SCN</td>
<td>Thiocyanide</td>
</tr>
<tr>
<td>H₂SO₃</td>
<td>Sulfurous acid</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammonia</td>
</tr>
<tr>
<td>H₂CO</td>
<td>Synthetic gas</td>
</tr>
<tr>
<td>GHG</td>
<td>Green House Gas</td>
</tr>
<tr>
<td>GHGI</td>
<td>Green House Gas Index</td>
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<tr>
<td>SNG</td>
<td>Synthetic Natural Gas</td>
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<thead>
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<th>Unit</th>
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<tbody>
<tr>
<td>cm³</td>
<td>cubic centimeter</td>
</tr>
<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>GWh</td>
<td>Gigawatt hours</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>MJ/kg</td>
<td>Mega joules per kilogram</td>
</tr>
<tr>
<td>KPa</td>
<td>kilopascal</td>
</tr>
<tr>
<td>MJ/Nm³</td>
<td>Megajoule per Newton cubic meter</td>
</tr>
<tr>
<td>kJ/m³</td>
<td>kilojoules per cubic meter</td>
</tr>
<tr>
<td>Kg/s</td>
<td>kilograms per second</td>
</tr>
<tr>
<td>m³/s</td>
<td>cubic meter per second</td>
</tr>
<tr>
<td>kJ/kg °K</td>
<td>kilojoules per kilogram per Kelvin</td>
</tr>
<tr>
<td>°C/min</td>
<td>Degrees centigrade per minute</td>
</tr>
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</table>
CHAPTER ONE: INTRODUCTION

1.1 BACKGROUND

Gasification of biomass has been reported to have attracted enormous interest for the past several years within thermochemical conversion technologies as it has been shown to offer higher efficiency in relation to combustion. Fuels obtained from biomass are considered to be a remedy to greenhouse gas emission. Biomass gasification is defined as the conversion of unprocessed raw biomass materials into gaseous energy carriers known as producer or synthetic gas (syngas).

The producer gas is a mixture of various gases such as carbon monoxide (CO), hydrogen (H₂), methane (CH₄), carbon dioxide (CO₂), nitrogen (N₂) and steam (H₂O). The producer gas is used for heating, electricity generation and fine chemicals production. Biomass is a renewable energy source which is not only has a potential to meet the energy demands of both developed and developing countries throughout the world on unprocessed and processed biomass materials, but also mitigate proliferation of carbon dioxide (CO₂) reduction [Anon, 1997]. Biomass fuel can be converted to energy through thermochemical processes (combustion, pyrolysis, and gasification) and biological means (enzyme/fermentation) [Maniatias, 1999].
Biomass materials can either be thermochemically converted or biochemically converted or by extraction. Each route discussed have sub-routes until final products are produced. Figure 1.1 shows a schematic summary of possible different biomass conversion routes.

![Diagram of biomass conversion routes]

Figure 1-1: Different routes of biomass conversion [Devi, 2005]

The path followed in this research was from biomass characterization, then thermochemical conversion rate, gasification, syngas production through computer simulation. In as much as there are numerous advantages associated with biomass, a number of disadvantages have also been noted to exist. Reported biomass disadvantages are bi-production of alkali-chloride, seasonal and scattered (transportation costs, drying, milling, storage, and hazard). The latter problem makes direct utilization prohibitive and expensive. The use of waste fuels may represent an alternative to waste disposal and a consequent valid exploitation as an energy source [Robinson et al., 1998].
Coal is classified as follows: anthracite (highest rank), bituminous, sub-bituminous and lignite (lowest rank). The chemical composition of coal has a strong influence on its combustibility. The properties of coal are broadly classified as chemical and physical. Lignite has been widely used for electricity generation and heat, besides producing various refined chemicals. Structural characterization of lignite coal was reported to present major challenges because of the extreme complexity and heterogeneity (different phases) of low ranked coal. Morphological analysis of lignite is complex and complicated. Thermogravimetric analysis (TGA) is one of the techniques used for different coal analysis. In coal gasification process for production of synthetic gas, coal is converted into gases that can be converted into quality gas having a higher heating value and with the greatest efficiency [Meuzelaar et al, 1996].

The biomass–coal co–combustion is the most promising short term option for renewable fuels. The existing coal – fuelled power plants may be generally used with very little modification. The technical challenges associated with co – combustion have been explored [Baxter, 2005]. Sliethoff et al reported that in the gas phase, the biomass nitrogen preferable form ammonia (NH₃) in contrast to the second (SCN) formed during co – gasification. The highly volatile matter yield of biomass fuels is an important aspect of the co – gasification, another process for utilization of residual fuels [Sliethoff et al., 2000].

Biomass is a renewable energy source with a potential to meet the energy needs have developed and developing countries throughout the world [Anon, 1997]. The unprocessed biomass material is plant matter, namely wood, twigs, straw, animal dung / waste, vegetable matter and agricultural waste. Processed biomass materials include charcoal, methane, sawdust and alcohol produced from fermentation (enzyme catalysis) process [Hall et al.,
1991]. Biomass fuel can be converted to energy through thermochemical (chemical reaction rate kinetics) and biological (enzyme catalysis kinetics) processes [Maniatis, 1999].

Biomass gasification has also been defined as the conversion of wood charcoal, sawdust and other biomass into gaseous energy carriers known as producer gas [Hoss et al., 1987]. Producer gas (syngas) is defined as a mixture of carbon monoxide (CO), hydrogen (H₂), methane (CH₄), carbon dioxide (CO₂), nitrogen (N₂) and steam (H₂O). The producer gas is used for heating and electricity generation.

1.2 THE SOUTH AFRICAN CONTEXT OF RENEWABLE ENERGY

The bulk of South African energy is derived from coal. Coal is the largest source of electrical energy in South Africa and about 92% of coal consumed on the African continent is produced in South Africa [International Energy Outlook, 2009]. There are other sources of energy such as nuclear, wind power, hydropower, tidal power, hydrothermal, biomass. Biomass contributes 10.2%. Actually; it is the second largest energy source. The pie graph in Figure 1.2 clearly depicts this fact.
Figure 1-2: Pie graph showing various energy sources in South Africa [International Energy Agency, 2007]

The white paper on energy policy for South Africa is largely driven by a 10 000 GWh target of energy derived from renewables which will contribute to final consumption by 2013 and sets up a target of 40% electricity generation from renewable energy by the year 2030 [Edkins et al., 2010]. Small scale gasification has been active in the Republic of South Africa (RSA) for the past number of years [DME, 1998].

1.3 OVERVIEW OF THE GASIFICATION PROCESS

Figure 1-3 shows an overview of the gasification process together with its products and by-products.
Various thermochemical processes take place in a limited supply of oxidizer (air or oxygen) in a specially designed reactor commonly known as biomass gasifier. The biomass particles undergo drying, pyrolysis, oxidation and char reduction to generate a gaseous mixture of combustibles such as carbon monoxide (CO), hydrogen (H$_2$), methane (CH$_4$) and diluents [Sharma, 2008].

In the drying zone, biomass materials are dried at temperature above 100 °C, carbonization takes place above the heath zone at a temperature between 600 – 800 °C converting biomass materials into charcoal while giving off nitrogen (N$_2$), methane (CH$_4$) and some tar. In the oxidation/heath zone, the combustion of biomass takes place resulting in the release of carbon dioxide (CO$_2$) and water vapour (H$_2$O) [Mamphweli and Meyer 2009]. Various high temperature chemical reactions take place in the reduction zone below the oxidation zone. The carbon dioxide from combustion reacts with carbon and gets reduced to carbon monoxide and water vapour. The hydrogen also reacts with carbon to form methane. It is the zone where a large proportion of producer gas is formed [Beall and Eickner, 1970].

Figure 1-3: Overview of the gasification process [Mamphweli and Meyer, 2009]
1.4 PROBLEM STATEMENT

All biomass materials including coal are well established feedstocks with potential as fuel for energy production. However, there are various technical issues related to analysis of the biomass materials for blending with coal for the purpose of co-gasification. The ratio of biomass or coal in the co-gasification process is one of these issues. The type and ratio of fuel in the mixture of both feedstock influences some factors such as the conversion efficiency of the co-gasification process, the syngas and tar yield, as well as the yield of impurities. Another practical issue with regard to the analysis of corn stover and coal for co-gasification purposes is that of the particle size of both feedstocks. The particle size of the biomass and coal must be uniform for optimum co-gasification efficiency.

1.5 RESEARCH OBJECTIVES

The aim of this research was to investigate the physical and chemical properties of corn stover blended with coal to establish the best mixing ratio that results in enhanced conversion efficiency during gasification. The following aspects were investigated to accomplish this aim:

i. Preparation of various blends of corn stover and coal

ii. Characterization of corn stover and coal and their blends in terms of proximate and ultimate analysis as well as energy values

iii. Conduct computer simulation of the co-gasification process of the various blends of corn stover and coal in order to determine the best blend that would result in optimum efficiency under normal gasifier operating conditions/parameters.
1.6 DELINEATION AND LIMITATIONS

The biomass material that has been chosen for this study is corn stover, because of its availability within the Eastern Cape Province. The coal used was a sub-bituminous one, which was also readily available than other types of coal. This study sought to investigate corn stover and coal blends with the aim of selecting a blend for co-gasification in a downdraft biomass gasifier system. Determination of the physical and chemical properties as well as energy values of corn stover and coal including their blends were undertaken so as to guide in the proper selection of the particular blend for the purpose of co-gasification. The actual co-gasification of the materials was not conducted, instead, the study relied on computer simulation of the co-gasification process.

1.7 RESEARCH QUESTIONS

i. What are the properties of corn stover and coal as well as the properties of their blends?

ii. What is the best corn stover/coal blend that results in enhanced conversion efficiency during gasification in a downdraft gasifier?

1.8 RATIONALE OF THE STUDY

Many co-conversion studies related to co-gasification of biomass and coal have focused on parametric studies of the gasifier and the feasibility in feedstock availability and supply, omitting the mechanisms by which mixtures of biomass and coal interact including how they
thermally degrade during co-conversion. This interaction is an issue yet to be solved. The interaction occurring between biomass and coal during thermal conversion have not been sufficiently investigated. This require further evaluation to clarify the mechanism and conditions by which the two fuels interact when blended and co-gasified.

1.9 DISSERTATION OUTLINE

This dissertation provided an elucidation on the characterization of various biomass and coal with the aim of selecting a particular biomass material for co-gasification with coal employing computer simulation. It has been arranged into the following chapters:

Chapter 1 - This chapter provides an overview of the basic theory behind this work. The chapter covers the background of the study, the problem statement and rationale of the study as well as research objectives including delineation and limitation of the study. Research questions and definition of terms were also covered in this chapter.

Chapter 2 – This chapter provides a synthesis of literature that is relevant to the study. Here, we looked at published information by various researchers on similar studies.

Chapter 3 – This chapter describes the research methodologies and techniques adopted in carrying out this research, and justification for the choice and use of the techniques, providing guidance to achieve the objectives of the research.

Chapter 4 - Presents the results, data analysis, including discussion of findings. The results were presented and discussed in relation to existing theories and literature.
Chapter 5 – This chapter outlines the summary and conclusion drawn from the foregoing as well as the summary of the drawbacks and limitations, ending with some recommendations for future work that was beyond the scope of this study.

Appendix A – This provides the research outputs associated with this project in form of submitted papers for review in peer reviewed journals and conference proceedings.
CHAPTER TWO: LITERATURE REVIEW

2.1 INTRODUCTION

This chapter contains a synthesis of literature on biomass (corn stover, eucalyptus, cow dung, chicken litter and pinewood) and coal (coal properties, availability in South Africa as well as gasification of the two materials separately) and in (c) combination (co – gasification).

2.2 BIOMASS

Properties of biomass and coal relevant to co-gasification are briefly reviewed. It is important to understand the fuel properties of biomass in order to be able to estimate its energy output or performance in conversion systems [Anukam et al., 2014].

2.2.1 BIOMASS CHARACTERISATION

Characterization of biomass involves obtaining sufficient information about a specific fuel to be used before gasification processes. Biomass contains various amounts of lignocellulose (cellulose, hemicelluloses, and lignin) and a small amount of other extracts.

2.2.1.1 CELLULOSE

Cellulose is generally the largest fraction of the secondary cell wall in wood, representing about 40–50 weight percentage of the biomass and hemicelluloses portion represents 20–40
weight % of the material. Cellulose is defined as a glucose \((C_6H_{12}O_6)\) polymer (many monomer units), consisting of linear long chain of \((1,4) – D – \text{glucopyranose unit}\) in which the units are linked \(1– 4 \beta – \text{configuration}\), with an average molecular weight of approximately 100 000. A simplified structure of cellulose is given in Figure 2.1:

![Beta-1,4 bond](image)

**Figure 2-1: Molecular structure of cellulose [Bossel, 1980 and Jenkins et al., 1998]**

It has been reported that cellulose has a net calorific value of approximately 17.52 MJ/kg [Bossel, 1980].

### 2.2.1.2 HEMICELLULOSE

Hemicellulose is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, manose, xylose, methylglucuronic and galaturonic acids, with an average molecular weight of not less than 30 000. Hemicellulose is heterogeneous branched polysaccharides that
bind tightly, but non-covalently, to the surface of each cellulose microfibril. The molecular structure of hemicelluloses is presented in Figure 2-2 below.

Figure 2-2: Molecular structure of hemicelluloses [Fengel and Wegener, 1984]

### 2.2.1.3 LIGNIN

Lignin can be classified as a group of amorphous, high molecular – weight, chemically related compounds. The building blocks of lignin are three - carbon atoms, called phenyl propanes. These may have zero, one or two methoxyl groups attached to the ring. Lignin is the second largest structural component of biomass after cellulose. Lignin is the adhesive and aromatic component of wood, which is insolvent [White and Plaskett, 1981]. It has been reported by White and Plaskell (1981) that lignin has an energy content of 25.5 MJ/kg, which is higher than cellulose. Molecular structure of lignin is presented in Figure 2.3 represents the lignin structure of softwood.
It is mainly the properties of the biomass source that determines the choice of the conversion route and any subsequent processing difficulties that may arise. Each type of biomass source has specific properties that determine its performance as a fuel in gasification or combustion devices. These properties include moisture content, volatile matter content, and elemental composition, heating value, bulk density, nitrogen content, sulfur and chlorine content. Biomass properties dictate the form of energy conversion route [Safriti, 2005].

Table 2.1 shows the biomass composition and chemical properties.
Table 2-1: Biomass composition and chemical properties derived from ultimate analysis

[Stretcher, 1984]

<table>
<thead>
<tr>
<th>Fuel</th>
<th>VM (%)</th>
<th>CV (MJ/kg)</th>
<th>Ash</th>
<th>C</th>
<th>O</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD</td>
<td>15.68</td>
<td>67.50</td>
<td>26.84</td>
<td>3.96</td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ch-L</td>
<td>12.68</td>
<td>43.78</td>
<td>50.34</td>
<td>5.89</td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS</td>
<td>15.81</td>
<td>39.61</td>
<td>52.79</td>
<td>6.74</td>
<td>0.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CL</td>
<td>15.68</td>
<td>67.50</td>
<td>26.85</td>
<td>3.96</td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PI</td>
<td>17.69</td>
<td>45.22</td>
<td>48.02</td>
<td>6.65</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EU</td>
<td>17.28</td>
<td>48.05</td>
<td>-</td>
<td>6.38</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charcoal</td>
<td>23.00</td>
<td>30.10</td>
<td>0.70</td>
<td>71.00</td>
<td>11.00</td>
<td>3.00</td>
<td>0.10</td>
</tr>
</tbody>
</table>

VM = Volatile matter, CV = Calorific value, C = Carbon, O = Oxygen, H = Hydrogen, N = Nitrogen.

It was reported that wood has the lowest ash content of various biomass types, but compared to other carbon-based fuels, it also has low energy content. The chemical composition of biomass, especially the carbon content, determines the energy and ash content. Biomass feedstocks have different combustion characteristics that are basically depending on their moisture content and chemical characteristics. It is necessary to dry the biomass either in a kiln or in the air, in order to increase its energy content. Rain protected and well aerated systems should be used to store biomass [Stretcher, 1984].

Biomass fuels have large differences with respect to physical (moisture content and bulk density), chemical (volatile content and ash content) and morphology (size and size distribution) characteristics. These fuel characteristics affect the choice of conversion technology. Easy fuels such as charcoal or wood block can be made to work in a large variety
of equipments. Difficult fuels such as rice husks or sugar cane bagasse require very specific and expensive equipments or in fuel preparation facilities. Biomass materials contain very few components that can cause environmental problems. Sulfur and chlorine may be present in small amounts, and contribute to the formation of acid rain (H$_2$SO$_3$) when they are converted into SO$_2$ and HCl during combustion. For nitrogen content determination, nitrogen oxides (NO and NO$_2$, collectively referred to as NO$_x$) also contribute to the formation of acid rain. Two types of NO$_x$ formation takes place during combustion namely

- **A thermally NOx formation** which takes place at temperatures above 950 °C from the nitrogen contained in the combustion air.
- **A fuel NOx formation** which occurs at lower temperatures from the nitrogen contained in the fuel [Quaack et al., 1999].

### 2.2.2 THE PROPERTIES OF BIOMASS

The use of any biomass for conversion to energy will be affected by the values of its physicochemical properties. These values will not only determine the conversion process but in general the investment evaluation, as a whole. The dependence of those properties on the different biomass resources which they come from is great and the in-depth understanding of them is essential before the thermochemical conversion process can be considered [Anukam et al., 2014].

In general, the biomass properties that are of the greatest importance in energy processes are moisture content, ash content, volatile matter content and heating value as well as bulk density and alkali metal content. These properties are usually described in terms of proximate
and ultimate analysis. The following sub-sections attempts to describe these concepts in detail.

2.2.2.1 PROXIMATE ANALYSIS

Proximate analysis indicates the percentage by weight of the fixed carbon, volatiles, ash, and moisture content in biomass or coal. The amounts of fixed carbon and volatile combustible matter directly contribute to the heating value of coal [Anukam et al., 2014]. The following sub-sections describes the composition of biomass and/or coal in terms of proximate analysis.

2.2.2.1.1 MOISTURE CONTENT

The moisture content (MC) of the biomass is defined as the quantity of water in the material. It is expressed as a percentage of the material’s weight. The weight can be referred to on wet basis, on dry basis, and on a dry and ash free basis. (Quaack, Peter; Harrie and Stassen, Hubert., 1999). Biomass have high moisture content. The moisture is nomarly evaluated on dry basis according to the following mathematical expression:

\[
\%MC_{db} = \left( \frac{W_{water \ vapour}}{W_{biomass \ db}} \right) \times 100\% \tag{2.1}
\]

Where:

\[
\%MC_{db} = \text{Percentage of Moisture Content in dry bases}
\]

\[
W_{water \ vapour} = \text{Weight of water vapour(g)}
\]

\[
W_{biomass} = \text{Weight of biomass material on dry bases(g)}
\]

The above equation allows determination of moisture content on dry basis. It has been reported that the moisture content of pure corn stover is within the range 12.7 – 17.15%
[Rene et al., 2013] on an air dried basis. That of eucalyptus was reported as between 9 – 11 %, cow dung between 10 – 15 % and chicken litter 18.68 – 51.8% [de Olivier et al., 2013] all also on an air dried basis. Lynch et al., 2013 reported moisture content of pinewood to be beween 0.1 – 2 % on a dry basis.

2.2.2.1.2 VOLATILE MATTER

Volatile matter (VM) refers to the part of the biomass that is released when biomass is heated (up to 400 °C to 500 °C. During the heating process, the biomass decompose into volatile gases and solid char [Mamphweli, 2009]. Biomass material has a high volatile matter content (up to 80%), whereas, coal has a low volatile matter (less than 20%). It comprises of all liquid and tarry residues not fully driven off in the carbonization process [Chen and Azeredo, 2005]. VM can be mathematically determined by the following expression [Mamphweli, 2009]:

\[
\% VM_{db} = \left( \frac{W_{t_0} - W_{t_x}}{W_{t_x}} \right) \times 100\% \tag{2.2}
\]

Where:

\% VM_{db} = Percentage of Volatile matter in dry bases

\[ W_{t_0} = Weight \ of \ initial \ mass \ of \ cut – off \ sample \ (g) \]

\[ W_{t_x} = Weight \ of \ cut – off \ sample \ at \ a \ particular \ temperature \ (g) \]
2.2.1.3 ASH CONTENT

Ash is typically the inorganic component of the biomass. Ash content on dry bases is usually determined using the gravimetric method or the microwave digestion method. It can also be determined using the expression:

\[
\%AC_{\text{biomass}} = \left( \frac{W_{\text{ash}}}{W_{\text{biomass}}} \right) \times 100\% \tag{2.3}
\]

Where:

\(\%AC\) = percentage ash content of biomass

\(W_{\text{ash}}\) = Mass of the ash(g)

\(W_{\text{biomass}}\) = Mass of the biomass material before burning(g).

The total ash content in the biomass and the chemical composition of the ash affects its behavior under high temperatures of gasification. For example, melted ash may cause problems in both combustion and gasification reactors. These problems may vary from clogged ash – removal caused by slagging ash to severe operating problems when fluidized – bed systems are used. Similarly, it can also be experimentally obtained through TGA at Temperature beyond 600 °C.

2.2.1.4 FIXED CARBON

It is defined as the solid combustible material that remains after all the moisture is removed (loss) after complete combustion.

\[
FC = 100 - (MC + VM + Ash) \tag{2.4}
\]
Where

\[ FC = \text{Fixed Carbon} \]

\[ MC = \text{Moisture Content} \]

\[ VM = \text{Volatile Matter} \]

\[ AC = \text{Remainder of burnt mixture (Ash content)} \]

### 2.2.2.1.5 EXTRACTABLES

Extractables are the non-structural materials present in the biomass that can be easily extracted.

### 2.2.2.1.6 BULK DENSITY

Biomass feedstocks exhibit a wide range of physical and chemical properties. Bulk density is defined as the weight per unit volume of a material, expressed in kilograms per cubic metre \((\text{kg/m}^3)\) or pounds per cubic foot \((\text{lb/ft}^3)\) [Clarke and Preto, 2011]. For biomass, the bulk density is commonly expressed on an oven-dry-weight basis (moisture content = 0\%) or as-received basis, with a corresponding indication of moisture content \((MC_w)\). Most biomass feedstocks generally exhibit low bulk densities and also show extreme variation from lows of 150 to 200 kg/m\(^3\) for cereal grain straws and shavings to highs of 600 to 900 kg/m\(^3\) for solid wood [Nordin, 1994]. Together, the heating value and bulk density of biomass determine its energy density which are approximately one-tenth that of fossil fuels such as coal [Biomass Energy Technologies, 1987]. The bulk density of a biomass material can be calculated by the following equation [Zhang et al., 2012]:

\[
\rho_b = \frac{w_2 - w_1}{v} \quad [2.5]
\]
Where:
\( P_b \) = The bulk density of the biomass material (g/cm\(^3\))
\( W_2 \) = The weight of the container and biomass material (g)
\( W_1 \) = The weight of the container (g)
\( V \) = the volume of the container (cm\(^3\))

**2.2.2.2 ULTIMATE ANALYSIS**

The ultimate analysis indicates the various elemental constituents such as carbon, hydrogen, oxygen, nitrogen, sulfur, etc. It is useful in determining the quantity of air required for combustion and the volume and composition of the combustion gases as well as the heating performance of the fuel.

**2.3 ENERGY CONTENT**

The energy content of a fuel is the amount of energy stored per unit volume or mass. Only the useful or extractable energy is measured, which means that chemically inaccessible energy such as rest mass energy of the fuel is ignored [Aigner *et al.*, 2011]. This is somewhat different for the heating value (HV), which is an indication of the energy chemically bound in the fuel with reference to a standardized environment. The standardization involves temperature, state of water (vapour or liquid), and combustion products (CO\(_2\), H\(_2\)O, etc.). These standard conditions are widely available in the literature on the measurement of heating values. The energy chemically bound in the fuel is given by the heating value of the fuel in energy per amount of matter (J Kg\(^{-1}\)). This energy cannot be measured directly, but only with respect to a reference state. Reference states may differ, so a number of different
heating values exist. The best known are the lower heating value (LHV) and higher heating value (HHV). For the LHV, the reference state water is its gaseous state. For the HHV, the reference state of water is its liquid state.

Bulk density refers to the weight of material per unit volume. For biomass, this is commonly expressed on an oven-dry-weight basis (moisture content (MC = 0%), or an as–is basis with corresponding indication of moisture contents (MCw). The heating value and bulk density, together, determine the energy density (potential energy available per unit volume of the biomass). In general, biomass energy densities are approximately one-tenth that of fossil fuels such as petroleum or high quality coal [Quaack, 1999]. The energy is determined from calorific value measurements. The energy content of biomass is dictated by the amount of carbon and hydrogen present. Biomass fuels contain more oxygen and less carbon, which leads to lower calorific values per unit of biomass [Unger, 1994] The energy content of fully dried biomass is between 15 – 20 MJ/kg. The energy content decreases with increasing moisture content [Malatji, 2009].

2.4 PROPERTIES OF CORN STOVER

Corn stover is a broad term which describes all of the above ground biomass from the corn crop except the grain. It is composed of structural components including stalks, leaves, tassel, husk, and cob, and classified as lignocellulosic biomass with cellulose, hemicellulose and lignin as its main constituents [Barten, 2013]. It is one crop residue with potential as alternative fuel source as it could simply be burned or transformed into higher energy intermediates through gasification. Early settlers often burned corn stover as a heat fuel source. More recently, this practice has been tried and proven to be a viable practice. A
project was undertaken by Pordesimo et al. (2005) to evaluate the combustion energy of
different stover fractions. Another was undertaken by Deere & Co., ADM, and Monsanto Co.
which showed corn stover burned in lieu of coal as 10% of the burner fuel on a dry basis was
feasible in operation of a power plant employing the fluidized bed boiler. The process varied
greatly with the quality of corn stover, particularly with the concentration of moisture in the
stover.

Corn stover has differing botanical fractions with each having its compositional
characteristics. The stalk fraction accounts for more than half of the total stover fraction. This
is followed by leaves, cobs, and husk. Most of the stalk tissue is concentrated in the rind, a
mixture of densely packed vascular bundles embedded in the outer periphery of the
internodes. This tissue accounts for less than 20% of the cross sectional area of the stalk, but
more than 80% of the stalks dried mass [Dhugga, 2007]. Table 2-2 shows the properties of
corn stover.
The calorific value of corn stover on a moisture free basis was recorded as 17.9 MJ/kg which falls in the range of 17.7 to 18.5 MJ/kg as reported by Hoskinson et al., 2007. The ash content and ultimate analysis of corn stover as evident from Table 2-2 are consistent with the values reported by other researchers. The ultimate analyses will provide useful input for modeling of combustion and gasification of corn stover [Morey et al., 2009].
2.5 AVAILABILITY AND USE OF BIOMASS RESOURCE

In Africa, most of the biomass used is harvested informally and only a small part is commercialized. Wood is the largest energy source of biomass. Contributors include timber industry, agricultural crop and raw materials from the forest. Waste energy is the second largest source of biomass energy. The main contributors are municipal solid waste and manufacturing waste. Alcohol fuels are largely contributor and are mainly derived from corn. Any source can be used to fuel biomass energy production. Rubbish, manure, animal waste, wood chips, seaweed, corn stalk and other waste, livestock manure, human waste (faeces). Traditional technologies predominate.

In many parts of Asia and Latin America, on the other hand, modern and commercial bioenergy options are readily available and significant. The Brazilian ethanol programme, based largely on sugar cane, is well established and provides alternative fuel to the transportation sector at highly competitive prices. In addition to wood fuels, other biomass fuels such as forest and crop residues, as well as animal waste, are a common source of bio-energy. Many countries still have land available for energy plantations. Integrating biomass harvesting for energy purpose with forestry and agricultural activities is another option. In most regions, the use of biomass still needs to be sustainable, this being true both where traditional and modern technologies are applied [Siveria and Foster, 2008].

In South Africa, renewable energy has been reported to account approximately 9% (1999) of total energy consumption whereby most of this energy is generated from fuel wood and dung and not modern renewable energy technologies [DME, 2003]. Figure 2.4 shows the South African Renewable Energy Resource Database (RRDB) and was based on the analysis of a
comprehensive data set, which covered the whole of South Africa [DME, Eskom and CSIR, 2001].

Figure 2-4: Total biomass energy potential for South Africa [DME, Eskom and CSIR, 2001]

The total potential biomass energy in South Africa is represented as modelled by Renewable Resource Database (RRDB). High Energy densities are found around sugar, wood and pulp mills. It is at these mills where the potential lies for Independent Power Producers (IPP) [DME, Eskom and CSIR, 2001].
2.6 TYPES AND SOURCES OF BIOMASS

The main source of biomass is fuel wood in the rural domestic sector, bagasse in the sugar industry, energy crops such as maize (corn stover), sunflower and Jatropha tree for bio-fuel production, and pulp and paper waste in the commercial forestry industry for in-house heat and electricity generation. Wood is one of the most important biomass. Trees collected from forest can be logged or cut into appropriate size for direct use as fuel. Woodworking industries are able to make trees by processing them into construction materials. Debris of wood from construction is also used as fuel. Residues such as bark, sawdust and odd sized pieces are economically used as fuel. Many agricultural residues can be used as fuel. These include straws from grain, husks from rice, coconut or coffee, stalks from maize or cotton, bagasse from sugar cane. Energy cropping from cultivated biomass (poplar, willow, sugar cane, sweet sorghum) is also used as fuel. Electricity generated from bagasse contributes some 60% of Mauritius electricity needs during the 9-month harvesting season [DME and DANCED, 2001].

Fuel wood is the main source of energy for most rural households. Demand exceeds supply in many rural areas of South Africa, resulting in environmental degradation caused by unsustainable harvesting practice and past clearance of land for residential and agricultural purpose. Targeted intervention in these areas to manage woodlands for the benefit of rural household is recognized in the White Paper on Energy Policy. The Department of Water Affairs and Forestry (DWAF) is responsible for community forestry and as such, is currently preparing a strategy for managing wood supply in the rural areas. According to DWAF, the key biomass resources in terms of renewable energy are invasive aliens (e.g. exotic acacia species like black wattle and Port Jackson), commercial plantation and the wood industry,
woodlots, trees in the urban environment, woodland and indigenous and trees cultivated as a fuel crop [DWAF, 2003]. The potential exists to utilize the manure and litter from livestock to generate methane gas through anaerobic fermentation in biogas plants for electricity generation. Cattle farms in South Africa are free range and the poultry and pigs have large amount of manure available on site [DME, Eskom and CSIR, 1999].

2.7 THERMAL DEGRADATION OF BIOMASS COMPONENTS

When biomass are subjected to high temperatures, changes occur in its chemical structure and the major components are degraded. These changes are heavily dependent on the form of the material, as well as process parameters, such as heating rate. When biomass such as wood is progressively heated to a higher temperature, various degradation products are produced. Loss of water and volatile components takes place in temperature below 140 °C, the production of CO₂ and CO can be detected [Hill, 2006]. Hemicelluloses are known as the most thermally unstable biomass components. The degradation of hemicelluloses increases with temperature and heat residence time and happens between 100 °C and 200 °C [Bourgeois et al., 1989]. Cellulose degradation, on the other hand, occurs at significantly higher temperature, because of crystalline structure of cellulose. It degrades in a temperature range of 300 – 340 °C [Kim et al, 2001].

Lignin is accepted as the most thermally stable, although lignin degradation stretches over a wide temperature range starting at 180 °C [Hill, 2006]. Generally, all volatile matter is released at temperature above 450–500 °C. The remaining material is char [Beall and Eickner, 1970].
2.8 ADVANTAGES AND DISADVANTAGES OF BIOMASS AS A FUEL SOURCE

Climate change, global warming conditions and changes in the atmospheric concentration of sulfur and carbon compounds are leading to an expanding interest towards alternatives to fossil fuels. Fossil fuel stocks are limited and have a detrimental effect on the environmental conditions due to pollution caused by emission of greenhouse gases because they cause the following problems:

i. Increased extremes in climatic conditions
ii. Increase in global temperature
iii. Loss of biodiversity
iv. Increased desertification
v. Changes in sea water level

In the latter mentioned context, biomass could be used as an alternative energy resource, because it is composed of environmental friendly, renewable compounds [Bezzon and Cortez, 1999; Strehler, 1998]. The biomass definition encompasses numerous materials that may be converted into efficient fuels. These materials can be divided into the following:

i. Woody biomass (wood, branches, leaves and waste)
ii. Agricultural biomass and residues
iii. Industrial processing residues
iv. Dedicated energy crops
v. Animal wastes (manure, poultry litter)
In this context, biomass is defined as all renewable organic material, whether in the form of plant materials, animal manure, food processing, forest material or urban waste [Scane, 1993; Kitani and Hall, 1989].

2.8.1 ADVANTAGES OF BIOMASS AS A FUEL

Biomass materials have many benefits as a fuel. The advantages associated with the use of biomass as a fuel include the following:

i. Clean combustion

ii. Compact burning equipment

iii. High thermal efficiency

iv. A good degree of control

v. Provides energy security

vi. Generates local employment in the rural sector

In locations where biomass were already available at reasonable low prices (e.g. rice mill) or in industries using fuel wood, gasifier system offers definite economic advantages. Biomass gasification technology is also environment-friendly, because of the firewood savings and reduction in CO₂ emissions.
2.8.2 DISADVANTAGES OF BIOMASS AS A FUEL

The disadvantages associated with biomass as a fuel according to White and Paskell (1981) includes:

i. Its low calorific value compared to fossils

ii. The high moisture content, which inhibits the immediate combustion, because of dehydration requirements

iii. The low density

iv. Heterogeneous size, weight and shape

2.9 THEORY OF BIOMASS GASIFICATION

Biomass gasification was intensively used to operate the farm and transportation systems during the World War 2. It can be described as a process that involves the incomplete combustion of biomass to produce combustible gases, which include carbon monoxide, hydrogen, methane and tar, this blend is called producer gas, which can be utilized to run internal combustion engines, to substitute furnace oil in direct heat applications or to produce methanol for industrial or heat engines [Rajvanshi, 1986]. Historically, gasification was conducted at low temperatures whereby biomass was partially combusted or oxidized. Partial oxidation yields low energy content gas compared to gasification. The quality of gas derived was usually poor, as it contained impurities, and too much fuel was required to power any system. Over the decades, gasification has been improved and is now a high efficient thermochemical technology of converting biomass into energy. If conducted according to system specifications, the technology is capable of performing at more than 70% cold gas
efficiency. The producer gas retains 70 – 80% of the original biomass energy [Demirbas, 2004].

Walker (2006) reported that the process of gasification occurs by heating biomass to high temperature (1200 – 1400 °C) by combustion in an oxygen deprived environment, therefore limiting combustion. The combustion gases are then reduced by being passed through an incandescent bed of charcoal. The chemical processes occurring in four stages/ zones can be distinguished namely drying zone, pyrolysis (devolatization) / carbonization zone, reduction zone and hearth zone. The first phase of heating and drying (drying zone) is unproductive in terms of energy output, as the energy is used to evaporate remaining moisture content of biomass. In the second stage (pyrolysis zone), volatile components of the biomass are removed. The temperature range at this stage is 450 – 600 °C. Volatile materials that are pyrolysed comprised of water, carbon monoxide, hydrogen, methane, volatile tars and carbon monoxide. The remaining biomass is a carbonized solid fuel – charcoal with 10 – 25% of original fuel mass. The final stage at temperature between 700 - 1200°C involves the conversion of char into producer gas that constitutes about 16% CO, 20% H₂, 50% N₂, 12% CO₂ and 2% CH₄ and products such as ash and powder slag [Malatji, 2009].

The gasifier is divided into four zones according to chemical reactions taking place. Combustion occurs in the oxidation zone. Introduced air in the oxidation zone contains inert gases such as nitrogen and argon (besides oxygen and water vapor). These inert gases are non-reactive to fuel constituents. The oxidation takes place at the temperature of 700 – 2000 °C. Heterogeneous (different phases) reaction takes place between oxygen in the air and solid carbonized fuel (charcoal), producing carbon monoxide. Hydrogen in the fuel reacts with
oxygen in the air blast, producing steam. Combustion is described by the following chemical formulas [Kumar et al., 2009]:

\[
\text{CH}_x\text{O}_y\text{N}_z\text{S}_s + \text{Air (79 N}_2 \text{ and 21% O}_2) + \text{H}_2\text{O(steam)} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2 + \text{H}_2\text{O (unreacted steam)} + \text{C (Char)} + \text{Ash} + \text{Tar} \quad [2.6]
\]

\[
\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \quad \Delta H = +401.9 \text{ kJ/mol} \quad [2.7]
\]

\[
\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} = +241.1 \text{ kJ/mol} \quad [2.8]
\]

The most important reaction takes place in the reduction zone of a gasifier between the different solid reactants is given by the following endothermic chemical equations. The gas forming reaction that takes place in the reduction zone of the gasifier is as follows:

**Boudouard reaction:**

\[
\text{C} + \text{CO}_2 \rightarrow 2\text{CO} \quad \Delta H = +164.9 \text{ kJ/mol} \quad [2.9]
\]

**Water-gas reaction:**

\[
\text{H}_2\text{O (steam)} + \text{C} \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H = +122.6 \text{ kJ/mol} \quad [2.10]
\]

**Water shift reaction (“water-gas equilibrium” \(K_{we}\)):**

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H = -42.9 \text{ kJ/mol} \quad [2.11]
\]

**Methane production reaction:**

\[
\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4 \quad \Delta H = +75 \text{ kJ/mol} \quad [2.12]
\]

\[
\text{C} + \text{O}_2 + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H = +205.9 \text{kJ/mol} \quad [2.13]
\]
Figure 2.5 presents a flow chat of the gasification process from the pre-treatment stage of the biomass to the generation of electricity and heat from the process.

Figure 2-5: The gasification process flow chart [Kirkels and Verborg, 2011]
2.10 COAL

Coal is mainly formed as the result of slow metamorphosis of biomass over a long period of time. The degree of that metamorphosis is among the criteria used to determine coal rank. It is also classified according to the ratio of volatile to fixed carbon and the its heating value as well as the relative content of elemental carbon [Jayah et al., 2011]. South African coals are classified and ranges from high to low grade coal. High grade coal is washed and exported while low grade coal is screened and used locally for electricity generation and fine chemical production including oil. It has been reported that coal extraction implies non-renewable energy reserves depletion [Mangena and Brent, 2006].

Coals are organic sedimentary rocks derived from plant remains. The properties of coal reflect the nature of original plant materials (species and relative proportions of wood, buck and leaves). Coalification process: peat, lignite, sub-bituminous, bituminous and anthracite. The rate of coalification is influenced by the combined effects of increased temperature and pressure over an extended period. The organic components of plant material are principally cellulose and lignin. Coal is actually derived from lignin. Cellulose biochemically degrades to CO$_2$ and H$_2$O during accumulation. Petrographically, coal contains microscopically identifiable components (macros). Lithotypes are classified into three macerals groups namely vitrinite (from wood), exinite (from pollen and plant waxes) and inertinite. Vitrinite is present in all coal, hence used as a measure of coal ranking e.g. reflectance measurements which increases with coal ranking from 0.3 % Peat (brown coal) to 2.5% in anthracite. For petrographic analysis of reflectance in coal is according to order: Exinite < vitrinite < inertinite [British Geological Survey, 1989].
2.10.1 THE PROPERTIES OF COAL

Coal is a naturally occurring combustible material consisting primarily of the element carbon, but with low percentage of solid, liquid and gaseous hydrocarbon and other materials such as nitrogen and sulfur. Coal is usually classified into the sub-groups known as anthracite (highest rank), bituminous, sub-bituminous, lignite (lowest rank) and peat. The physical, chemical and other properties vary considerable from sample to sample. Lignite has been widely used as electricity generation and heat, besides producing various refined chemicals. Structural characterization of lignite coal presented major challenges because of extreme complexity and heterogeneity of low rank coal [Meuzelaar et al., 1996]. The properties of coals as they occur today, reflects the nature and the original plant materials (species and relative proportion of wood, bark, leaves) and the conditions prevailing during, and subsequent to, accumulation period. The coalification process is believed to progress through the sequence: peat, lignite (brown coal), sub-bituminous, bituminous, to anthracite. The rate of coalification or increase in rank is influenced by the combined effects of increased temperature and pressures over an extended period, and build-up of overlying, low conductivity and mineral (organic) sediments. Cellulose and lignin are organic components of plant material [Durie, 1982]. A description of the different types of coal are provided in the following sub-sections.

2.10.1.1 LIGNITE

Lignite is the first product of coalification and is intermediate between peat and subbituminous coal according to the coal classification used in the United States and Canada. In many countries lignite is considered to be a brown coal. Lignite contains about 60 to 70 percent carbon (on a dry, ash-free basis) and has a calorific value near 17 megajoules per
kilogram (7,000 British thermal units per pound). It has been estimated that nearly half of the world’s total proven coal reserves are made up of lignite and subbituminous coal, but lignite has not been exploited to any great extent, because it is inferior to higher-rank coals (e.g., bituminous coal) in calorific value, ease of handling, and storage stability. In areas where other fuels are scarce, the production of brown coal far exceeds that of bituminous coal [Britannica Inc., 2014]. It has been reported that lignite coal (lowest rank) as much as it is used for electricity generation, it is also providing a variable target for CO$_2$ sequestration and potential for methane production from it is questionable [Botnen et al., 2009]. Lignite was reported to release proportionately more CO$_2$ emission than other fossil energy carriers, and coal will meet the requirements for sustainable climate protection [Thielemann et al., 2007].

2.10.1.2 SUB-BITUMINOUS

Sub-bituminous coal is a type of coal whose properties range from those of lignite to those of bituminous coal and are used primarily as fuel for steam-electric power generation. It may be dull, dark brown to black, soft and crumbly at the lower end of the range, to bright jet-black, hard, and relatively strong at the upper end. They contain 15-30% inherent moisture by weight and are non-coking (undergo little swelling upon heating) [Babcock & Wilcox Company, 2014]. Sub-bituminous coals may be dull, dark brown to black, soft and crumbly at the lower end of the range, to bright jet-black, hard, and relatively strong at the upper end. They contain 15-30% inherent moisture by weight and are non-coking (undergo little swelling upon heating) and have heat content that range from 8300 to 11,500 BTu/lb or 19,306 to 26,749 kJ/kg [Babcock & Wilcox Company, 2014]. 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. The heat content of sub-bituminous coals range from 8300 to 11,500 BTu/lb or 19,306
to 26,749 kJ/kg. 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.

2.10.1.3 BITUMINOUS

Bituminous coal is a relatively soft coal containing a tarlike substance called bitumen. It is of higher quality than lignite coal but of poorer quality than anthracite coal. Bituminous coal is an organic sedimentary rock formed by diagenetic and submetamorphic compression of peat bog material. Bituminous coal has been compressed and heated so that its primary constituents are macerals vitrinite, exinite, and so on. The carbon content of bituminous coal is around 60-80%; the rest is composed of water, air, hydrogen, and sulfur, which have not been driven off from the macerals and its heat content of ranges from 24 to 35 MJ/kg on a moist, mineral-matter-free basis [Princeton, 2014].

Bituminous coal is usually black, sometimes dark brown, often with well-defined bands of bright and dull material. Bituminous coal seams are stratigraphically identified by the distinctive sequence of bright and dark bands and are classified accordingly as either "dull, bright-banded" or "bright, dull-banded" and so on. The four most abundant minerals found in bituminous coals are quartz, kaolinite, illite and pyrite. Size and textural are important considerations as to whether coal cleaning can remove most sensitive trace elements [Palmer and Lyons, 1996].

2.10.1.4 ANTHRACITE

Anthracite is a hard natural coal of high luster differing from bituminous coal in containing less volatile matter and in burning very cleanly (called also hard coal). It contains higher
quantities of fixed carbon than any other form of coal and the lowest quantity of volatile (quickly evaporating) material, giving it the greatest heat value. Anthracites are black and have a brilliant, almost metallic lustre. Hard and brittle, they can be polished and used for decorative purposes. They are difficult to ignite but burn with a pale-blue flame and require little attention to sustain combustion. In the past they were used for domestic heating, but today they have given way to other sources of energy (e.g., natural gas and electricity) [Babcock & Wilcox Company, 2014].

2.11 AVAILABILITY AND USE OF COAL IN SOUTH AFRICA

In South Africa, coal is largely found in 19 identified major coal-fields. These coal-fields are located mainly in KwaZulu-Natal, Mpumalanga, Limpopo and the Free State. Lesser quantities of coal are found in Gauteng, North, Western and Eastern Cape. In Mpumalanga province, coal mining fields are based in Witbank, Middleburg, Ermelo and Standerton, Secunda while in Free State / Gauteng; it is Sasolburg, Vereeniging and North-Western KwaZulu-Natal [Jeffrey, 2005]. The most coal reserves are found in Mpumalanga. The South African utility company (Eskom) derives most of its electricity from coal. Electricity power stations are stationed mostly in Mpumalanga and Northern Cape provinces near coal mining areas. Generated power supply electricity not only to South Africa, but also beyond its borders to neighbouring countries such as Zimbabwe, Mozambique, Zambia and Tanzania (Eskom, 2007).
2.12 ADVANTAGES AND DISADVANTAGES OF USING COAL AS A FUEL

Coal as a fuel source carries both advantages and disadvantages. It can be found in many places worldwide, and there is plenty in South Africa. It can be easily transported to the power stations. It is a relatively cheap energy source. Associated disadvantages include but not limited to creating mines through digging the ground, which can be dangerous, coal transportation (logistics) by trains or trucks to the power station causes pollution. Burning coal produces pollution gases such as sulfur dioxide which makes acid rain, burnt coal releases the most greenhouse gases which may add to global warming, it is non-renewable source and will run out in about 100 years, coal miners can be affected by black lung diseases or pneumoconiosis and also emphysema if they breath in the too much coal dust [Babcock & Wilcox Company, 2014].

2.13 COAL GASIFICATION

Coal gasification technology turns coal and coke feedstocks into a synthetic gas (syngas), a mixture of hydrogen and carbon monoxide that burns as cleanly as natural gas. Syngas can then be used to produce a wide range of high-value products such as electricity, fertilizers, transport fuels and chemicals. Compared to conventional coal-fired power plants, those producing electricity using coal gasification process emit less CO₂ and pollutants. Moreover, the CO₂ from gasification process can be more easily captured from smokestacks-potentially for storage underground. Syngas is synthesized by mixing pulverized coal with oxygen and steam at a higher temperature between 1 400–1600 °C. Compressed nitrogen is used to
transport the dense stream of coal into the gasifier. This approach is more efficient than the slurry of coal and water used with other techniques. The process produces a number of by-products which are sold for use in other industries: fly ash is used in the cement industry; Sulphur is used to make fertilizer, explosives and for chemical applications; and slag is used in building materials and road fill [Parker, 2006]. Figure 2.6 shows a summarized schematic diagram of coal gasification.

![Diagram of coal gasification](image)

Figure 2-6: Basic schematic for coal gasification [Duret et al., 2005].
2.14 GASIFICATION OF BIOMASS AND COAL

The thermodynamic efficiency of gasifiers and gasification systems is affected by the fuel composition. Kyoto protocol emphasized the need to combat carbon dioxide emission. Using biomass (organic feedstock) as fuel is considered as neutral because produced carbon dioxide is consumed during photosynthesis. It has been reported that as much as it solves CO\textsubscript{2} emissions, but it has a lower efficiency in comparison to fossil fuel (coal) [Prins et al., 2007]. The difference in coal and biomass has been noted to lie on their organic matter – woody biomass contains around 50\% weight percentage carbon and 45 percent oxygen while coal has been reported to contain 60 – 85\% weight percentage carbon and 5 – 20\% oxygen [Prins et al., 2007]. Because of biomass high oxygen content, less oxygen is needed for gasification, but it has a low calorific value thus not beneficial for gasification. Coal has been reported to have higher calorific values and gives highest efficiency besides its environmental problems.

2.14.1 CO-GASIFICATION OF COAL AND BIOMASS

Co - gasification process involves mixing together coal and biomass and converting the mixture into the gaseous product stream (synthetic gas), which can be used to produce electricity, hydrogen, chemicals and liquid transportation fuels. Blending of coal and biomass in the co-gasification process decreases the environmental impact because biomass are carbon neutral, if carbon sequestration technology is applied, one actually arrives at a process that is carbon negative, as carbon is consumed. The main advantage of using coal is the steady supply of coal supplies a baseline that can be supplemented by biomass whenever available. Energy crop (Wheat straw and switchgrass) grows quickly.
There are technologies to gasify coal and to gasify biomass, but there are uncertainties on how to mix them. The questions raised include: how does the quality of feedstock affect the quality of product? What are the optimum percentage of various blends of coal and biomass? Geographical implication coal and biomass easily also addressed. For any emerging technology, one of the drivers of commercialization is economics. As energy demand increases, alternative approaches such as co-gasification becomes more attractive. It is drawing lots of attention [NETL, 2008]. Co-gasification of waste/biomass and coal technology offers several benefits such as combining the use of reliable coal supply with waste/biomass thus qualifying for renewable obligation and climate change benefits, allows the economies of scale from larger plant than could be supplied just with waste biomass, capable of achieving high environmental standards on all fuel sources, flexible in choice of gas to electricity technology reciprocating engine, gas turbine, boiler and in future fuel cell, potential for petrochemical feedstock besides electricity, potential for sitting at collieries. Gas cleaning challenges are different from coal and biomass. Sulfur is a major concern for coal gasification, but chlorine compounds are more important for waste and biomass gasification [DTI, 2002].

Co-gasification of coal and biomass can be considered as a potential for gasification and further syngas production and methanol synthesis with excess produced gas, an alternative liquid fuel which can be directly used for fuel cells. It allows economy of production, operational stability, optimal thermal efficiency and decreases impact on the environment. Integrated coal, biomass co-gasification system combined with gas-steam cycle offers various advantages such as possible continuous operation of coal-gasification reactor at nominal rates, lowering the cost of electricity production, stabilizing of the quality of the feedstock
and gasifier operation and improvement of economic flexibility of the system (two final products) [Chmielniak, et al., 2003].

Oxygen blown co-gasification (oxy-co-gasification) gasifies coal and biomass by using oxygen and steam as a gasifying agent after nitrogen removal enables the use of renewable resource and additional CO₂ reduction to produce syngas. This technique increases the biomass contribution to electricity generation. It is mainly used in large coal-fired power plants and for production of H₂ and fine chemicals. Gasification with air is usually used in small plants of several megawatts [Valero et al., 2003]. Columbian biomass/coal blends and mixtures ratios co-gasification in the fluidized bed working at atmospheric pressure studies show that a mixture of both fuels produces songs that can be used as a chemical precursor, reduction of greenhouse emission, higher the heating value and higher efficiency It also showed additional environmental advantage such as reduction of nitrogen oxides and sulfur emission. Disadvantage of biomass in fluidized beds is the low ash melting point of sawdust resulting in loss of fluidizability, agglomeration, sintering, deposition, erosion and corrosion caused by ash [Velez et al., 2008]. Figure 2.7 shows the schematic diagram of co-gasification of coal and biomass
2.15 THE 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, the proportion of biomass in the coal-biomass blend, the properties and type of biomass used as well as the particle size of the biomass and coal, which must be uniform for optimum efficiency.
2.16 TYPES OF GASIFIERS / REACTORS

Gasifiers are available in different types and sizes. They are run on various types of feedstock including coal, wood, straw, rice husks and agricultural wastes. The maximum power output of a gasifier is 80 MW. They are classified as fixed bed (updraft, downdraft and crossdraft), moving bed (fluidized) and entrained gas flow. Since there is an interaction of air or oxygen and biomass / coal in the gasifier; they are classified according to the way oxygen or air is introduced in it [Chopra et al., 2007].

2.16.1 FIXED BED GASIFIER

2.16.1.1 UPDRAFT / COUNTER CURRENT MOVING BED GASIFIER

The updraft gasifier is the simplest with easy internal heat exchange and high charcoal burnout. It is the oldest type of gasification reactor. The reactor can operate with biomass having moisture content as high as 60% on a wet basis. The reactor was reported to yield producer gas with a calorific value of 1.80 to 3.33 MJ/kg, when oxidized with air. Oxygen as an oxidant in updraft gasification reactors produces highest calorific value gas of between 5-11 MJ/kg [Bridgewater, 1995]. The tar composition of the gas from the updraft reactor is approximately 0.0050 to 0.0150 kg/m³. It derived its name from the way in which the oxidant is fed through the reactor. The biomass fuel is loaded through the top into the reactor and moves downward through the different stages of gasification through gravitational forces, as displayed in Figure 2-8.
2.16.1.2 DOWNDRAFT GASIFIER

The downdraft gasifier is similar to the updraft, however, the difference lies in the gasification agent gas which flows in co-current configuration with the fuel (downwards, hence the name "down draft gasifier"). Heat needs to be added to the upper part of the bed, either by combusting small amounts of the fuel or from external heat sources. The produced gas leaves the gasifier at a high temperature, and most of this heat is often transferred to the gasification agent added in the top of the bed, resulting in an energy efficiency on level with the counter-current type. Since all tars must pass through a hot bed of char in this
configuration, tar levels are much lower than the updraft type [Mamphweli and Meyer, 2009].

A schematic diagram of a typical downdraft biomass gasifier system is presented in Figure 2.9.

![Downdraft gasifier diagram](image)

Figure 2.9: Downdraft / co–current gasifier [Adapted from Beeneckers, 1999]

### 2.16.1.3 CROSS-DRAFT GASIFIER

A cross-draft gasifier is adapted for the gasification of charcoal. The advantage of using charcoal instead of wood in gasification is that charcoal gives virtually no tars. Very few steps of cleaning equipment are thus needed; only particulates need to be removed. The crossdraft gasifier operates in small scale; installations are typically of less than 10 kW electricity. The technology is mainly used in developing countries. The gasifier system is simple, cheap and easy to operate. The drawback of using charcoal is that high combustion
temperature is reached (1500°C), which can lead to problems. Also, manufacturing charcoal from wood represents a large loss of energy potential and the manufacturing process itself is in many developing countries done without regards to the health of the workers [Babcock & Wilcox Company, 2014]. Figure 2.10 shows the schematic of a typical crossdraft gasifier.

![Crossdraft gasifier schematic](image)

**Figure 2-10: Crossdraft gasifier [Adapted from Mamphweli, 2009]**

Table 2-3 shows both the advantages and disadvantages of using a fixed bed gasifier.
Table 2-3: Advantages and disadvantages of fixed bed gasifier [Rajvanshi, 1986]

<table>
<thead>
<tr>
<th>Gasifier type</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Updraft</td>
<td>- Small pressure drop</td>
<td>- Great sensitivity to tar and moisture and moisture content of fuel</td>
</tr>
<tr>
<td></td>
<td>- Good thermal efficiency</td>
<td>- Relatively long time required for startup of IC engines</td>
</tr>
<tr>
<td></td>
<td>- Little tendency towards slag formation</td>
<td>- Poor reaction capability with heavy gas load</td>
</tr>
<tr>
<td>Downdraft</td>
<td>- Flexible adaptation of gas production to load</td>
<td>- Design tends to be tall</td>
</tr>
<tr>
<td></td>
<td>- Low sensitivity to charcoal dust and tar content of fuel</td>
<td>- Not feasible for very small particle size of fuel</td>
</tr>
<tr>
<td>Crossdraft</td>
<td>- Short design height</td>
<td>- Very high sensitivity to slag formation</td>
</tr>
<tr>
<td></td>
<td>- Very fast response time to load</td>
<td>- High pressure drop</td>
</tr>
<tr>
<td></td>
<td>- Flexible gas production</td>
<td></td>
</tr>
</tbody>
</table>

2.17 ENVIRONMENTAL BENEFITS OF CO-GASIFICATION

Brar et al., 2012 reported that greenhouse emissions from coal are higher than that from biomass gasification and was mainly due to high carbon content and low volatile percentage
in coal. The following equation [2.14] best describes greenhouse gas emission index (GHGI) measurement which is defined as the life cycle of greenhouse gas associated with the energy products divided by the life cycle of greenhouse emissions associated with fossil-fuel-derived products [Brar et al., 2012].

\[
\text{GHGI} = \frac{\text{Life cycle of gas emission associated with energy}}{\text{Life cycle of gas emissions associated with fossil–fuel–derived products}} \tag{2.14}
\]

The study conducted by Brat et al., 2012 for electricity generation from coal and biomass, reported GHGI from coal gasification to be 1.71 which was eventually reduced to 0.96 when a mixture of 40% biomass – 60% coal was used as feedstock, hence concluded that using biomass and coal blend was beneficial for the environment in terms of greenhouse gas emissions [Brar et al., 2012].
CHAPTER THREE: RESEARCH METHODOLOGY

3.1 INTRODUCTION

This chapter presents different methods used to generate the data required for this research. Moisture meter was used to determine moisture content of biomass and coal independently then followed by blends. The methodology employed involves CHNS analyzer for ultimate analysis measurements, thermogravimetric analysis (TGA) for fixed carbon determination, calorimeter (CAL 2K) for calorific / energy value measurements, and gasification simulation for maximum efficiency determination.

3.2 SAMPLE PREPARATION

The biomass materials used for this study, were eucalyptus wood, pine wood, corn stover, cow dung and chicken litter. They were obtained in the Eastern Cape Province of South Africa. The coal used was a low grade sub-bituminous coal with high ash composition, also obtained in the Eastern Cape Province of South Africa. Some of the biomass samples (cow dung, chicken litter and corn stover) were received with some amount of moisture (up to 40%) and were air-dried to lower their moisture content so as to make them suitable for analytical operations using the instruments required for characterization. A coning and quartering method was applied for size reduction of the samples using a Condux-Werk Wolfgang bei Hanau mill so as to obtain smaller fractions as required by the analytical instruments. The size obtained for all samples were in the range of 25μm to approximately 1mm.
3.3 MATERIAL CHARACTERIZATION

Calculating the usefulness of a fuel requires an understanding of its properties and composition [Anukam et al., 2014]. The first step taken to determine the suitability of biomass and coal for co-gasification purposes is to characterize the samples in terms of composition. The composition and properties of the various biomass and coal were characterized in terms of proximate (which gave properties such as moisture, volatile matter and ash contents of the samples as well as fixed carbon) and ultimate analysis (which provided elemental composition of the samples). Because one of the objectives of this research was to establish the best biomass material that would be blended with coal based on composition and energy value, proximate and ultimate analysis of the pure and blended samples as well as energy values were undertaken.

3.3.1 PROXIMATE ANALYSIS OF VARIOUS BIOMASS AND COAL

Proximate analysis involves determination of percentage by weight of fixed carbon, volatile matter, moisture and ash content. Fixed carbon acts as a main source of energy during burning. The high volatile matter content indicates easy ignition of fuel [Anukam et al., 2014].

The proximate analysis results of the various biomass and coal including their blends were obtained from a series of TGA plots which are available in appendix B. These were measured on a dry basis according to the European standards (EN 15148 for volatiles, EN 14775 for the ash content, EN 14774-3). The content of fixed carbon (char) was calculated by subtracting
from 100 the weight composition of the other three components. This analysis was undertaken in order to compare the physical properties of the various biomass samples with that of coal as well as their blends so as to enable proper selection of the biomass sample to be blended with coal for co-gasification through computer simulation.

3.3.2 ULTIMATE ANALYSIS OF VARIOUS BIOMASS AND COAL

The CHNS analyzer was used to obtain results of the ultimate analysis of the various biomass and coal as well as their blends. The amount of C, H, N, and O present in the pure and blended materials were determined. This analysis was necessary in order to compare the biomass samples and determine which would be suitable for co-gasification with coal as well as determine their potential thermal conversion. The weight percentage of oxygen was calculated by difference.

3.3.3 SEM ANALYSIS

Solid fine powdered samples of pure coal (100%), pure corn stover (100%), blends (90% coal : 10% corn stover and 10% coal : 90% corn stover) were mounted on a stub using a carbon double-sided tape. Following this, they were coated with gold-palladium using EIKO IB3 Ion Coater. The samples were then viewed with JEOL JSM 6390 LV Scanning Electron Microscope using a secondary electron detector operated at 15kV. Images were captured at different magnifications. The analysis was done by Noran System Six software.
3.3.4 CALORIFIC VALUE OF VARIOUS BIOMASS AND COAL

The energy value or calorific value of a fuel is the amount of energy in form of heat released by burning the fuel in air. It indicates the amount of energy stored in the fuel which is available for conversion to useful energy and varies considerably in biomass materials depending on certain factors such as climate, soil in which the biomass was grown as well as other conditions [Anukam et al., 2014]. An oxygen calorimeter (CAL2K model) was used to determine the energy value of the various biomass materials and coal after calibration with a 0.5 g of benzoic acid before taking measurements. The vessel for the calorimeter was pressurized to 3 000 kpa using oxygen. This experiment was repeated in triplicate and average value of the calorific value calculated and recorded. Figure 3.1 presents the oxygen bomb calorimeter used during analysis of the calorific values of the samples.

![Oxygen bomb calorimeter](image)

**Figure 3-1: Oxygen bomb calorimeter**
3.3.5 MATERIAL CHOICE

The specific biomass material that was blended with coal was meant to be chosen based on composition in terms of proximate and ultimate analysis as well as energy values. However, this was not the case for this study as corn stover was chosen because of its ready availability in the Eastern Cape Province of South Africa, and because limited data are available on the co-gasification of coal with corn stover in the literature.

The blends of corn stover with coal were prepared in the following ratios; 90% CS:10% CL, 80% CS:20% CL, 70% CS:30% CL, 60% CS:40% CL, 50% CS:50% CL, 40% CS:60% CL, 30% CS:70% CL, 20% CS:80% CL, 10% CS:90% CL.

3.3.6 THERMOGRAVIMETRIC ANALYSIS

The standard method of measuring the thermal degradation of a sample is through the thermogravimetric analyzer in which a small sample of the material to be analyzed is heated at a controlled rate in a controlled atmosphere while simultaneously recording weight, time and temperature. It provides quantitative measurements of any weight changes (loss/gain) associated with thermally induced transition as a function of temperature or time. Thermogravimetric analyses are useful in characterizing materials, thermodynamic investigation and reaction kinetics as a result of the application of heat to these materials. It is used to study the thermal behavior of a material when heat is applied to the material [Torre and Kenny, 1998]. This analysis was undertaken in order to establish the thermal behaviour of all samples analyzed.
An SDTQ 600 thermogravimetric analyzer was used to study the thermal degradation behavior of blends of corn stover/coal. A 5.08mg of each sample were heated over a temperature range of 20°C-1000°C under a nitrogen atmosphere at 20°C/min heating rate. This heating rate was selected because it is a typical gasification heating rate. Figure shows a schematic diagram of the thermogravimetric analyzer.

Figure 3-2 Schematic diagram of a thermo gravimetric analyzer [Mackenzie, 1979].

3.3.6.1 DERIVATIVE THERMOGRAVIMETRIC ANALYSIS

Derivative thermogravimetric analysis (DTG) is used to estimate the degree of thermal degradation of a sample. It plots change in mass with temperature, \( \frac{dm}{dt} \), and resolves changes more clearly.
3.3.7 COMPUTER SIMULATION OF THE CO-GASIFICATION PROCESS OF VARIOUS BLENDS OF CORN STOVER/COAL

A mathematical model developed by Chen et al., 1986 and modified by Jayah et al., 2003 was used to characterize the co-gasification performance of a typical downdraft gasifier system and the validated model was used to simulate the co-gasification process of the blend ratios of corn stover/coal for maximum efficiency. The software programme was designed specifically for the simulation of downdraft gasifiers. The ultimate analysis and the calorific value results of coal/corn stover blends were used during computer simulation of the co-gasification process. The efficiency of a gasification system is dependent on the composition and properties of the feedstock to be gasified as well as on the gasifier operating parameters/condition [Kumar et al., 2009]. The operating parameters/conditions of a downdraft gasifier considered during simulation are presented in Table 3.1.

Table 3.1: Normal operating parameters of a downdraft gasifier [Jayah et al., 2003]

<table>
<thead>
<tr>
<th>Fuel properties</th>
<th>Value</th>
<th>Gasifier operating conditions</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (%)</td>
<td>43.5</td>
<td>Throat diameter (cm)</td>
<td>94.0</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>6.5</td>
<td>Throat angle (°)</td>
<td>90.0</td>
</tr>
<tr>
<td>Oxygen (%)</td>
<td>48.5</td>
<td>Insulation thickness (cm)</td>
<td>0</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>1.50</td>
<td>Thermal conductivity (W/cm K)</td>
<td>0.87</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>22.0</td>
<td>Temperature of input air (K)</td>
<td>293</td>
</tr>
<tr>
<td>Bulk density (kg/m³)</td>
<td>0.25</td>
<td>Air input (kg/hr)</td>
<td>44.5</td>
</tr>
<tr>
<td>Diameter of particle (cm)</td>
<td>1.0</td>
<td>Heat loss (%)</td>
<td>12.8</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>6.50</td>
<td>Feed input (kg/hr)</td>
<td>40</td>
</tr>
</tbody>
</table>

The computer programme used was a model developed specifically for downdraft gasifiers. It consists of two sub-models, namely flaming pyrolysis and gasification zone sub-model. A
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 [Jayah, 2002]. The principle of mass and energy balance was also applied. Gas profiles were obtained during simulation of the co-gasification process and were used to calculate the gas heating value from the percentage composition of the combustible gases in the syngas as follows [Mamphweli, 2009]:

\[
HV_{gas} = \left( \frac{CO_{vol} \times HVCO + H_{2vol} \times HVH_2 + CH_{4vol} \times HVCH_4}{100\%} \right)
\]  \[3.1\]

where \(HV_{gas}\) is the gas heating value in MJ/kg, \(CO_{vol}\) is the volume concentration of carbon monoxide gas in percentage, \(HVCO\) is the heating value of carbon monoxide gas (usually 12.64 MJ/kg from standard gas tables) [Bjerketvedt et al., 1997], \(H_{2vol}\) is the volume concentration of hydrogen gas in percentage, \(HVH_2\) is the heating value of hydrogen gas (10.1 MJ/kg by standard) [Fossum and Beyer, 1998], \(CH_{4vol}\) is the volume concentration of methane gas in percentage, \(HVCH_4\) is the heating value of methane gas (38 MJ/kg from standard gas tables) [Bjerketvedt et al., 1997].

### 3.3.7.1 Flaming pyrolysis zone sub-model:

In the flaming pyrolysis zone, the general equation of reaction of the material can be expressed by Equation 3.2:

\[
CH_aO_b + wH_2O + m(0.21O_2 + 0.79N_2) \\
\rightarrow x_{char}Char + x_{tar}Tar + x_1CO + x_2H_2 + x_3CO_2 + x_5CH_4 \\
+ x_6N_2
\]  \[3.2\]
where char was taken as carbon and ultimate analysis of tar as CH1.03O0.03 [Adams, 1980]. From equations 3.3 and 3.4 we can obtain the equilibrium equation and the corresponding equilibrium constant respectively.

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \]  \hspace{1cm} [3.3]

\[ K_3 = \frac{x_3x_2}{x_1x_4} \]  \hspace{1cm} [3.4]

The correlation between the temperature and equilibrium constants for the above is given by equation 3.5 [Gumz, 1950]:

\[
\log(K_3) = -36.72508 + \frac{3994.704}{T} - 4.46241 \times 10^{-3}T + 6.71814 \times 10^{-7}T^2 + 12.2228\log(T) \]  \hspace{1cm} [3.5]

where T is the temperature (K).

By mass balance the following equations 3.6 – 3.9 can be obtained:

- **Carbon:** \[ 1 = x_{char} + x_{tar} + x_1 + x_3 + x_5 \]  \hspace{1cm} [3.6]
- **Hydrogen:** \[ a + 2w = 1.03x_{tar} + 2x_2 + x_1 + 2x_4 + 4x_5 \]  \hspace{1cm} [3.7]
- **Oxygen:** \[ b + w + 0.42m = 0.03x_{tar} + x_1 + 2x_3 + x_4 \]  \hspace{1cm} [3.8]
- **Nitrogen:** \[ 0.79m = x_6 \]  \hspace{1cm} [3.9]

The energy balance in flaming pyrolysis zone is given by equation 3.10:

\[ H_{c, wood} = H_c Char + H_c Tar + H_c Gas + H_c Char + H_s Tar + H_s Gas + \text{Heatloss} \]  \hspace{1cm} [3.10]
The number of moles of water \((w)\), including fuel moisture, air moisture, and steam addition, can be calculated by the following equation [Chen, 1986]:

\[
w = (12 \times 1 + 1 \times a + 16 \times b) \times mc_{db}kg
\]  

[3.11]

Moisture in fuel = dry matter in fuel \times moisture content on dry basis

The values of a and b have been given. Heat loss and \(m\) (number of moles of oxygen input) are obtained from the experiment, \(x_5, x_{\text{char}}\) and \(x_{\text{tar}}\) 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 calorific value (MJ/kg) of coal/corn stover blends, char and tar are calculated from the equation as follows [Guar and Reed, 1998]:

\[
H_{cWood} = 0.3491f_C + 0.1783f_H - 0.1034f_O
\]  

[3.12]

where \(N_2\) and ash content are neglected.

\[
H_{cChar} = 0.3491 \times f_{c,\text{char}}
\]  

[3.13]

\[
H_{cTar} = 0.3491 \times f_{c,\text{tar}} + 0.1783f_{H,tar} - 0.1034f_{O,tar}
\]  

[3.14]

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

\[
H_{cGas} = 241000x_1 + 283000x_2 - 802300x_5
\]  

[3.15]

\[
H_{sChar} = 12.15x_{\text{char}} \times (T - 300)
\]  

[3.16]

\[
H_{sTar} = 21.95x_{\text{tar}} \times (T - 300)
\]  

[3.17]

\[
H_{sGas} = x_1H_{CO} + x_2H_{H2} + x_3H_{CO2} + x_4H_{CO2} + x_4H_{H2O} + x_5H_{CH4} + x_6H_{N2}
\]  

[3.18]
3.3.7.2 Sub-model of gasification zone: The gasification zone is modelled 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 travelled by the particle. 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 modelling the gasification zone [Jayah, 2002].

The co-gasification efficiency was determined after computer simulation by the following equation:

\[ \eta = \left[ \left( \frac{HV_{gas} \times 2}{HV_{fuel}} \right) \times 100 \right] \]  

[3.19]

where \( \eta \) is the efficiency of the gasifier, \( HV_{gas} \) the gas heating value and \( HV_{fuel} \) the heating value of the fuel (corn stover/coal blends).
CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 INTRODUCTION

The results obtained using the methods discussed in chapter three are presented and discussed in relation to existing theory and the objectives of this research in this chapter. The results were also used to answer the research questions presented in chapter one, justifying the need for the data presented and the methods employed in this research.

4.2 PROXIMATE ANALYSIS OF PURE AND BLENDED SAMPLES OF CORN STOVER AND COAL

Table 4.1 shows the proximate analysis results of the pure and blended samples of corn stover and coal. These were obtained from the TGA plot in Figure 4.5 in section 4.5.3. This analysis was carried out in order to compare the physical properties of corn stover with that of coal as well as their blends, and to establish the thermal behavior as well as the co-gasification temperature of the samples under study. The weight composition of fixed carbon was obtained by difference in both the pure and blended samples.
Table 4-1: Proximate analysis of pure and blended samples of corn stover and coal

<table>
<thead>
<tr>
<th></th>
<th>PURE SAMPLES</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>COAL</td>
<td>CORN STOVER</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MC (%)</td>
<td>VM (%)</td>
<td>FC (%)</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>25</td>
<td>24</td>
</tr>
</tbody>
</table>

|                  | BLENDED SAMPLES                       |                  |                  |
|                  | COAL/CORN STOVER (wt.%)               |                  |                  |
|                  | RATIO                                 | MC (%)  | VM (%) | FC (%) | AS (%) |
|                  | 90:10                                 | 2.5       | 68     | 22     | 7.5    |
|                  | 80:20                                 | 2.6       | 54     | 21     | 22.4   |
|                  | 70:30                                 | 3.1       | 23     | 49     | 24.9   |
|                  | 60:40                                 | 3.4       | 56     | 20     | 20.6   |
|                  | 50:50                                 | 4.2       | 59     | 21     | 15.8   |
|                  | 40:60                                 | 5.4       | 61     | 20     | 13.6   |
|                  | 30:70                                 | 5.9       | 42     | 21     | 31.1   |
|                  | 20:80                                 | 6.5       | 48     | 20     | 25.5   |
|                  | 10:90                                 | 7.6       | 45.1   | 22     | 25.3   |

Note: MC = Moisture content, VM = Volatile matter, FC = Fixed carbon, AS = Ash.

The values obtained for both pure and blended samples in Table 4.1 are within acceptable ranges found in the literature. However, comparing the properties of the pure samples with those of the blended samples, it could be easily noticed that a typical South African sub-bituminous coal used for this study has high amount of ash in comparison to the corn stover with a relatively low ash composition. The properties of the blended samples vary according
to the ratio of corn stover/coal in the blends. Ash content of coal varies over a wide range and this variation occurs not only in coals from different geographical areas or from different seams in the same region, but also from different parts of the same mine [Inside Power Station, 2011]. These variations result primarily from a wide range of conditions that introduces foreign materials during or following the formation of coal. The reason for the high amount of ash in the pure coal used for this study, as noted from Table 4.1 is most likely due to the influence of extraneous mineral matter introduced during mining operations.

The difference in the pure and blended samples is also obvious in Table 4.1 as the blends with high percentage of coal exhibited high ash content. Ash composition of the blends of corn stover/coal are also quite high except for the 90:10 (CL:CS) ratio with an ash composition of approximately 8%. This relatively high amount of ash is due to the composition of both feedstock (coal and corn stover) which is dependent on various factors such as source and type of biomass and coal used as well as variation in ash fraction, growth processes, including the ability of plant species to take up/extract selectively, specific compounds from water, soil and air, transporting and depositing them within the plant tissues (in the case of biomass), and mining operations for coal. High amount of ash is undesirable as it could cause agglomeration, slagging and fouling as well as deposition and corrosion during co-gasification of coal/corn stover blend [Gustafsson, 2011]. However, combustion temperature significantly affects the total yield of ash as its yield is determined at a relatively high temperature (between 100 – 1300°C) lowering the amount of ash produced during co-gasification [Vassilev et al., 2010]. Therefore, ash composition in any feedstock must be below 5% for slagging problems to be avoided and for the smooth running of the gasifier [Anukam et al., 2014].
The difference in volatile matter content between coal and corn stover can also be observed, which can be linked to difference in properties between the two feedstocks. Fuels with high volatile matter content is always better for gasification because they tend to vapourize before combustion compared to fuels with low volatile matter content which burns primarily as glowing char and this affects the performance of the combustion chamber of the gasifier which is usually taken into account when designing gasification systems [Ciolkosz, 2010]. The ease of ignition during gasification is determined by the volatile matter content of the fuel and typical biomass material and coal have volatile matter content in the range 60 – 90% and 20 – 35% respectively [Ganesh, 2006].

Another important fuel property worthy of description when pre-treatment options are not available or desirable is the moisture content of the fuel. Moisture in the feedstock lowers the temperature inside the combustion unit and will lead to an increased fuel throughput, thereby increasing the volume of flue gas released [Khan et al., 2009]. Moisture content of pure coal is relatively low as can be seen in Table 4.1 while it varies in the biomass materials. It also varies in the blends which are most likely due to the difference in properties and source of the corn stover. This was due to the fact that the samples were dried before analysis. The fixed carbon of coal is higher (24%) than that of corn stover which is as a consequence of the difference in physical properties between corn stover and coal. In contrast, the fixed carbon content of the blends showed a slight variation which is due to the ratio of volatiles in the pure coal. Fixed carbon is calculated as a function of moisture, volatile matter and ash content, the uncertainties of these properties affects the uncertainty in the concentration of fixed carbon [Anukam et al., 2014]. The fixed carbon content of the sample (blends of corn stover/coal) were also in narrow ranges which is due to the amount of volatile matter and moisture as well as ash driven off in the sample during thermal analysis.
4.3 ULTIMATE ANALYSIS OF PURE AND BLENDED SAMPLES OF CORN STOVER AND COAL

Table 4.2 shows the ultimate analysis data obtained using a CHNS analyzer on pure and blended materials. Oxygen composition was obtained by difference. This data was necessary in order to establish the variation in the elemental composition of corn stover, coal, and their blends so as to determine which mixing ratio would be suitable for co-gasification purposes as well as establish their potential thermal utilization.
Table 4.2: Ultimate analysis of pure and blended samples of corn stover and coal

<table>
<thead>
<tr>
<th></th>
<th>PURE SAMPLES</th>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COAL</td>
<td>CORN STOVER</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>O</td>
<td>N</td>
<td>C</td>
<td>H</td>
<td>O</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>(%)</td>
<td>69.5</td>
<td>1.7</td>
<td>26.9</td>
<td>1.7</td>
<td>39.6</td>
<td>6.7</td>
<td>45.5</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

BLENDED SAMPLES

<table>
<thead>
<tr>
<th>COAL/CORN STOVER (wt.%)</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>90:10</td>
<td>63.6</td>
<td>4.0</td>
<td>30.9</td>
<td>1.6</td>
</tr>
<tr>
<td>80:20</td>
<td>61.3</td>
<td>4.1</td>
<td>32.9</td>
<td>1.6</td>
</tr>
<tr>
<td>70:30</td>
<td>60.7</td>
<td>4.5</td>
<td>33.0</td>
<td>1.7</td>
</tr>
<tr>
<td>60:40</td>
<td>57.4</td>
<td>4.9</td>
<td>36.0</td>
<td>1.7</td>
</tr>
<tr>
<td>50:50</td>
<td>54.6</td>
<td>5.1</td>
<td>38.7</td>
<td>1.6</td>
</tr>
<tr>
<td>40:60</td>
<td>51.6</td>
<td>5.4</td>
<td>41.3</td>
<td>1.7</td>
</tr>
<tr>
<td>30:70</td>
<td>48.3</td>
<td>5.8</td>
<td>44.1</td>
<td>1.8</td>
</tr>
<tr>
<td>20:80</td>
<td>45.2</td>
<td>5.8</td>
<td>47.5</td>
<td>1.5</td>
</tr>
<tr>
<td>10:90</td>
<td>43.5</td>
<td>6.5</td>
<td>48.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Note: C = Carbon, H = Hydrogen, O = Oxygen, N = Nitrogen.

The elemental analysis of coal and corn stover including their blends showed that the main chemical constituents of the samples are carbon, hydrogen and oxygen, which is due mainly to the organic nature of both feedstocks. Table 4.2 shows that pure coal has higher carbon content with percentage composition of approximately 70% (which implies that it is the primary constituent in coal), in comparison to the pure corn stover with carbon content of less than 50%. However, the oxygen composition of pure corn stover is quite higher (45.5%)
compared to that of pure coal (27%). This difference in oxygen composition is due to the carbohydrate nature of corn stover. Hydrogen in the pure corn stover was also found to be higher than in the pure coal, which can be attributed to the difference in chemical properties between corn stover and coal. The carbon content in all of the blends is quite lower than that of the pure coal with carbon content of 69.5%. This is due to the blend ratio as the blends with a higher ratio of coal has higher carbon content. There is an insignificant decrease in the composition of carbon and oxygen as the ratio of corn stover increases in the blends. Carbon and hydrogen in the blends are oxidized during co-gasification by the exothermic reactions forming carbon dioxide and water. The carbon and hydrogen content has a positive contribution to the calorific value of the fuel and the carbon dioxide formed is emitted as a major product of complete combustion because incomplete combustion in the oxidation zone of the gasifier can lead to emissions of unburnt carbon based pollutants such as hydrocarbons, polycyclic aromatic hydrocarbons, tar and soot [Anukam et al., 2014].

The composition of oxygen in the blends also varies. This variation is equally due to the ratio of biomass in the blends. Oxygen will reduce the energy density of the fuel [Kumar et al., 2009]. However, the presence of oxygen is important to start the syngas formation process as it reacts with carbon and hydrogen in the feedstock to form carbon dioxide and water.

Nitrogen composition varies both in the pure and blended samples, however, the variation was found to be insignificant. Nitrogen in the fuel is almost entirely converted into gaseous nitrogen and nitric oxides (NOx, [NO, NO₂]) during co-gasification. Recent studies have shown that one of the main environmental effects of combustion of coal and biomass is caused by the emission of NOx [Nussbaumer, 2002]. NOx can be formed through reaction pathways such as reaction of nitrogen with oxygen radicals at high temperatures (above
1300°C) and the amount increases with increasing temperature. It could also be formed from airborne nitrogen at yet again, temperatures above 1300°C but under low oxygen conditions in the presence of hydrocarbons [Miller and Bowman, 1989, Fenimore, 1971]. Furthermore and most important mechanism in gasification systems is the formation of NOx from the oxidation of fuel nitrogen during a series of elementary reaction steps and emission increases with increasing fuel nitrogen content [Leckner and Karlsson, 1993]. However, the major influencing parameters for NOx formation include air supply, combustion zone geometry and temperature, as well as type of gasification technology used [van Loo and Koppejan, 2002].

Emission related problems for solid fuels exceeding emission limits can be expected at fuel nitrogen concentrations above 0.6% and the technological possibilities of emission reduction include primary measures such as air staging in the combustion chamber which results in a 30 to 50% reduction in NOx emission, and a secondary measure which includes selective catalytic reduction and selective non-catalytic reduction [Obernberger, 2003]. In both techniques, ammonia (NH3) or urea (CO(NH2)2) is injected to reduce NOx to N2 with or without a catalyst. Nitrogen composition in the blends are quite minimal and poses no environmental concern during co-gasification. The chemical composition of a fuel has manifold impact on their thermal utilization [Obernberger et al., 2006].

The results of the ultimate analysis and the calorific value of coal and corn stover blends were used in the calculation of the efficiency of the co-gasification process through computer simulation. A detailed description of the computer simulation program and process have been presented in chapter 3.
4.4 CALORIMETRIC VALUE OF PURE AND BLENDED SAMPLES OF CORN STOVER AND COAL

The calorific values of the pure and blended samples are presented in Table 4.3. These were presented in order to compare the energy values of the pure and blended samples so as to determine the impact of blending the two feedstocks on their calorific values. The calorific values gave a clear indication of the energy contained in the samples and were obtained after analysis by the oxygen bomb calorimeter. Increasing the biomass content during co-gasification enhances calorific value due to higher composition of hydrocarbons in biomass [Valero and Uson, 2006] and [Fermoso et al., 2009].
Table 4-3: Calorific values of pure and blended samples of corn stover and coal

<table>
<thead>
<tr>
<th>CALORIFIC VALUES OF PURE SAMPLES (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COAL</td>
</tr>
<tr>
<td>22.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CALORIFIC VALUES COAL/CORN STOVER (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RATIO</td>
</tr>
<tr>
<td>90:10</td>
</tr>
<tr>
<td>80:20</td>
</tr>
<tr>
<td>70:30</td>
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<td>60:40</td>
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<td>50:50</td>
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<td>40:60</td>
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<tr>
<td>30:70</td>
</tr>
<tr>
<td>20:80</td>
</tr>
<tr>
<td>10:90</td>
</tr>
</tbody>
</table>

There is a significant difference between the calorific value of corn stover and coal. The pure coal sample has a much higher calorific value (22.8 MJ/kg) than that of corn stover. The difference in calorific values of the two feedstocks is attributed to the ash content as well as the quantity of carbon and oxygen in each of the material. A 1% increase in carbon concentration will elevate the calorific value by approximately 0.39 MJ/kg and coals generally have calorific values greater than biomass because of lower degree of oxidation [Jenkins et al., 1989]. In contrast, the calorific values of the blends vary in accordance with the ratio of coal to biomass in the blends. It increases with increasing ratio of biomass in the
blends. This is due to the high rate of reactivity for corn stover, which acts as a catalyst for coal combustion.

The following sections will describe the morphology and thermal behavior as well as the computer simulation of the co-gasification process of the various blend ratios of corn stover with coal.

4.5 MORPHOLOGICAL CHARACTERIZATION OF CORN STOVER/COAL AND THEIR BLENDS

Morphological characterization of the sample of pure corn stover and coal, including their blends (90% CS:10% CL and 90% CL:10% CS) were undertaken with the use of a scanning electron microscope described in chapter 3. This was undertaken to better understand the structural features/ composition of the samples. Figure 4.1 presents the SEM images of the pure samples (pure corn stover and coal).

![Figure 4-1: SEM images of pure samples, (a) 100% corn stover and (b) 100% coal](image)
There are no changes in the physical structures of both samples which suggests that there was no chemical pre-treatment process undertaken on the samples prior to analysis. However, there is a significant difference between the morphology of the two samples which is as a result of differences in properties. The structure of pure corn stover shows evidence of plant cell wall vascular bundles and a highly fibrillar structure while that of pure coal sample is more compact, which results in a higher bulk density. The bulk density of a fuel affects its residence time in the reactor during gasification as lower bulk density may result in lower co-gasification efficiency since it gives rise to poor mixing characteristics and a nonuniform temperature distribution, both of which will create unfavorable operating conditions of the thermochemical conversion systems [Rozainee et al., 2008]. However, the SEM image of corn stover shows that the particles are coated with natural binders, which are pressed out of the biomass cells during milling, while for coal a bulk microstructure could be noticed from the image. The microstructure is composed of homogenously distributed network of small crystallites which shows the presence of minerals.

The SEM images of the blends were analyzed to understand the binding mechanisms of corn stover and coal. According to Rumpf (1962), bonding between particles can take place through a solid bridge or through inter-particle attraction forces when there is no solid bridge. Solid bridges are developed due to partial melting of components, crystallization of soluble substances, chemical reaction, hardening of binders, adsorption layers due to highly viscous binders (adhesion and cohesion forces due to the binder layer between particles), and mechanical interlocking of particles. When there is no solid bridge between particles, but the particles are brought together, short-range attraction forces such as molecular (valence forces, for instance, due to free chemical bonds; hydrogen bridges; and van der Waals' forces),
electrostatic, and magnetic forces can cause the particles to adhere to each other [Rumpf, 1962]. The SEM images of the blends of corn stover and coal are presented in Figure 4.3.

Figure 4-2: SEM images of blends, (a) 90% corn stover:10% coal and (b) 10% coal:90% corn stover

Morphological changes are quite evident in the physical structures of both images which is due mainly to blending. Luminous and non luminous features could be noticed in both images. These features indicate the presence of minerals distributed in the organic matrix. The bright luminosity is due to the presence of aluminium. However, there are higher concentrations of luminosity in the 10% coal/90% corn stover blend which is due to higher concentration of coal in the blend.

4.6 THERMAL INVESTIGATION OF COAL/CORN STOVER BLENDS

The rate of degradation of a sample during thermogravimetric analysis is an indication of the thermal behavior of the sample under gasification [Anukam et al., 2014]. Therefore, TGA
have been used to establish the thermal behavior as well as the co-gasification temperature of coal and corn stover blends. Figure 4.2 shows the weight loss of coal/corn stover blends obtained using a thermogravimetric analyzer, carried out under a nitrogen atmosphere at 10, 15 and 20°C/min heating rates. The maximum temperature reached was 900°C.

![Figure 4-3: TGA curves of pure corn stover and coal as well as their blends](image)

It can be observed from Figure 4.5 that initial mass loss occurred at 105°C temperature for all samples. This initial mass loss is due to the evaporation of moisture from the samples. Rapid weight loss due to devolatilization in the 100% corn stover started at 400°C which is considerably lower than the temperature corresponding to the start of the devolatilization of 100% coal at 530°C. At all mix ratios, the curves corresponding to the blends maintained essentially the same shape and position and displayed three stage of weight losses with the last stage of devolatilization occurring at a much higher temperature (600-800°C) due to char
oxidation except for the 70% CS:30% CL blend which is characterized by four weight loss stages due to much higher volatile matter content of corn stover in the blend, with last stage of weight loss occurring at 715°C. The devolatilization behavior of the blends as revealed by TGA analysis implies that during co-gasification, the maximum expected temperature for complete devolatilization of all materials would occur at about 900°C with rapid weight loss occurring between 300-550°C for all blends.

4.6.1 DTG EVALUATION OF COAL/CORN STOVER BLENDS

This sub-section deals with the derivatives of coal/corn stover blends after being subjected to heat for a prolong time. The DTG plot of coal/corn stover blends is presented in Figure 4.4. It was obtained from the TGA plot in Figure 4.3 and was used to estimate the rate at which thermal degradation of the blends took place over a wide temperature range (900°C).
It could be noticed from Figure 4.4 that the samples displayed one peak at temperatures less than 108°C which represented the removal of moisture from the samples. Above this temperatures, varied peaks were observed for corn stover, coal and their blends. The thermal evolution profile of all blends displayed another major peak over a wide temperature distribution ~350 - 800°C. These peaks represent the release of carbon containing volatiles from coal. The maximum peak temperature for the pure coal is approximately 660°C. It is worth noting that the maximum weight loss rate of the pure corn stover sample is much lower than that of the pure coal. This can be attributed to the fact that corn stover contains much higher content of volatile matter than the coal.

The thermal evolution profile of corn stover can be divided into three stages apart from its dehydration which corresponds to the removal of cellulose, hemicellulose and lignin.
components of corn stover. However, as it can be observed from Figure 4.4 and as mentioned earlier, the thermal decomposition profile for corn stover falls in a much narrower temperature range than that for coal, ~220-650°C. This, as mentioned earlier, is mainly due to the high volatile matter and lower fixed carbon contents of corn stover as compared to that of coal. This difference is also attributed to the strength of the molecular structure of the fuels. The immobile phase present in the coal structure comprises dense polycyclic aromatic hydrocarbons linked together by aromatic rings with very high bond energy of about 1000 kJ/mol [Cai et al., 2008].

In contrast, the polymers of hemicellulose, cellulose, and lignin which constitute the macromolecular structure of biomass and other woody materials are linked together by relatively weak bonds with a bond energy of about 380–420 kJ/mol [Vuthaluru, 2004]. These bonds are less resistant to heat at low temperatures. As a consequence, a much higher mass loss rate results in biomass samples as compared with coal. As observed, the DTG profile of corn stover results in a split peak in the temperature range of ~220–350°C. As for the blends, the DTG evolution profiles showed two distinct peaks in the temperature range of approximately 130-800°C. The first peak occurs at a maximum peak temperature of approximately 320-350°C representing the devolatilization of corn stover while the second peak occurs at a maximum peak temperature of 400–800°C representing the devolatilization of the sub-bituminous coal used for this study.

It could also be observed that the maximum weight loss rate (%/min) for the corn stover devolatilization profile increased with increasing concentration of corn stover in the blends and vice versa for the coal devolatilization profile, without an apparent change in the shape and position of the peaks when compared to those of the pure samples. This may be attributed
to the fact that the release of volatiles containing oxygenated components during the devolatilization of corn stover, generally does not affect the devolatilization of coal at higher temperatures [Aboyade et al., 2013].

4.7 COMPUTER SIMULATION OF THE CO-GASIFICATION PROCESS OF VARIOUS BLENDS OF CORN STOVER AND COAL

Gasification efficiency is an expression of the energy content of gaseous products to energy content of biomass, coal or a mixture of them as solid fuel [Anukam et al., 2014]. The computer simulation programme described in section 3.3.7 in chapter 3 was used to undertake the simulation of the co-gasification process of all blends of corn stover/coal. The parameters used for simulation have been presented in Table 3.1 also in chapter 3. The simulation process established the blend of corn stover/coal that resulted in maximum efficiency. Figure 4.5 shows the efficiency plot of the co-gasification process of all blends of corn stover/coal obtained after computer simulation.
Changing the contents and types of biomass and/or coal in co-gasification has significant effects on different output parameters including the efficiency of the co-gasification process [Fermoso et al., 2009]. Various researchers have reported an increase in the efficiency of a co-gasification process by increasing the ratio of biomass in the blend. As evident from Figure 4.5, although there is no significant differences in the efficiency of some of the blends, while in some other blends a significant difference could be noticed. The blend 90%CS:10%CL resulted in maximum efficiency of approximately 58%. This optimum efficiency was due to a number of factors, one of which was the calorific value of the blend.
(90% corn stover/10% coal), which was reported as higher than all other blends of corn stover/coal (Table 4.3, section 4.4). High calorific value of a fuel mixture results in increased co-gasification efficiency [Fermoso et al., 2009]. The calorific value of all blends were used in calculating the efficiency of the co-gasification process after computer simulation. The gasifier operating parameters/conditions presented in Table 1 were also other factors responsible for the optimum co-gasification efficiency shown by the blend (90% corn stover/10% coal), and the ratio of corn stover in the blend. Raising the ratio of biomass in a co-gasification process increases the efficiency of the process [Lapuerta et al., 2008].

4.8 COMPARISON WITH EXPERIMENTAL DATA

A comparison between the simulated process studied and experimental data from the literature was undertaken for this study and results presented in Table 4.4.
Table 4-4: A comparison of the simulated results from this study with experimental data from the literature

<table>
<thead>
<tr>
<th>Blend ratio (%)</th>
<th>Materials blended</th>
<th>Gasification efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90:10</td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>80:20</td>
<td></td>
<td>53.5</td>
</tr>
<tr>
<td>70:30</td>
<td></td>
<td>54.4</td>
</tr>
<tr>
<td>60:40</td>
<td></td>
<td>52.6</td>
</tr>
<tr>
<td>50:50</td>
<td>Corn stover : Coal</td>
<td>51.3</td>
</tr>
<tr>
<td>40:60</td>
<td></td>
<td>50.8</td>
</tr>
<tr>
<td>30:70</td>
<td></td>
<td>49.3</td>
</tr>
<tr>
<td>20:80</td>
<td></td>
<td>46.1</td>
</tr>
<tr>
<td>10:90</td>
<td></td>
<td>44.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Blend ratio (%)</th>
<th>Materials blended</th>
<th>Gasification efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90:10</td>
<td>Wood : Coal [Aigner et al., 2011]</td>
<td>50 – 95</td>
</tr>
<tr>
<td>80:20</td>
<td>Wood : Coal [Aigner et al., 2011]</td>
<td>43</td>
</tr>
</tbody>
</table>
| 70:30           | Pine chips : Coal [Li et al., 2010]   | Improved H₂ eff. From 17% to 22%
| 60:40           | Mulia coal: Japanese cedar [Kumabe et al., 2007] | 47.9
|                 | Coal : Pine chips [Seo et al., 2010]  | Improved efficiency
| 50:50           | Woody biomass:Coal [Kumabe et al., 2007] | 65 – 85
|                 | Indonesian Tinto coal : Sawdust [Seo et al., 2010] | 45
|                 | Coal : pine chips [Pan et al., 2000]   | Improved efficiency
| 30:70           | Bagasse : Coal [Long and Wang, 2011]  | 55.03
| 20:80           | Pine chips : Coal [Li et al., 2010]   | Continuous and stable operation/Improved efficiency
| 10:90           | Coal : Pine sawdust [Fermoso et al., 2009] | 82.3
|                 | Coal : Almond shell [Fermoso et al., 2009] | 77.7
|                 | Coal : Olive stones [Fermoso et al., 2009] | 81.6

It can be clearly observed from Table 4.4 that there is only about 5 to 8% variation between reported and simulated results. Therefore, it is fair to say that the mathematical model developed by Chen et al., 1986 can be used for further analysis with acceptable accuracy. The
validated model was used to study the effect of process efficiency. The simulation results concur with the experimental data found in the literature and are useful in predicting experimental observations reasonably well based on process efficiency.
CHAPTER FIVE: SUMMARY, CONCLUSIONS AND
RECOMMENDATIONS

5.1 SUMMARY OF RESEARCH FINDINGS

This study investigated corn stover and coal for the purpose of co-gasification so as to establish the best mixing ratio that would be suitable for co-gasification based on composition and energy content as well as using computer simulation. The composition of all samples used were determined in terms of proximate and ultimate analysis as well as energy value. These analyses were undertaken so as to compare the physical and chemical properties as well as the energy content of the corn stover used with that of coal and their blends.

The results of these analyses showed that the values obtained were within acceptable ranges found in the literature. However, the results established the differences in composition between corn stover and coal as well as the their blends. The result also showed that a typical South African sub-bituminous coal has high amount of ash in comparison with the corn stover. Similar results were found with other properties of the two feedstocks, while the properties of the blended samples varied slightly.

The high ash content of the coal used was attributed to the influence of extraneous mineral matter introduced during mining operations where the coal was obtained. The difference in the pure and blended samples was also noticed from as the blends with high quantities of coal exhibited high ash contents. Volatile matter content increased with increase quantities of corn stover in the blends. The fixed carbon content of corn stover was found to be lower than that
of coal. This was due to the difference in property between coal and biomass. In contrast, the
fixed carbon content of the blends showed slight variation which was due to the ratio of
volatiles, moisture as well as ash contents of the pure coal.

It was also found that the pure coal sample used for this study had higher carbon content
(approximately 70%), in comparison with the pure corn stover with percentage composition
less than 50%. This establishes the fact that carbon is the primary constituent in coal. Oxygen
composition in corn stover was found to be higher in concentration than that for coal. This
difference was attributed to the carbohydrate nature of corn stover. The difference in
hydrogen composition between corn stover and coal was also noted and was attributed to
differences in chemical properties between both feedstocks. The carbon content of all blends
were quite lower than that of the pure coal which was due to blend ratio as the blends with
higher quantities of coal showed higher carbon content. A variation in oxygen and nitrogen
composition for all blends was also observed, which was also due to the ratio of biomass in
the blends.

The pure coal sample showed a much higher calorific value (22.8 MJ/kg) than the corn
stover. The difference in calorific value was attributed to the concentration of carbon and
oxygen in the samples. The composition of various blends of corn stover/coal was undertaken
in terms of proximate and ultimate analysis as well as energy value which established the
blend of corn stover/coal that was suitable for co-gasification and that resulted in optimum
process efficiency during co-gasification simulation. The thermal stability of the various
blends of corn stover/coal was established. It was found that the maximum temperature
reached for the devolatilization of all blends of corn stover/coal was approximately 900°C at
20°C/min heating rate. It was also found that at all mix ratios, the curves corresponding to the
blends maintained essentially the same shape and position and displayed three stages of weight loss with the last stage of devolatilization occurring at a much higher temperature (600-800°C) due to char oxidation, except for the 70% CS:30% CL blend which was characterized by four weight loss stages due to much higher volatile matter content of corn stover in the blend. The last stage of weight loss occurred at 715°C. However, an initial mass loss occurred at 105°C temperature for all samples of various blends of corn stover/coal.

It was also noted that the maximum weight loss rate of the pure corn stover sample was much lower than that of the pure coal. However, the thermal decomposition profile for corn stover fell in a much narrower temperature range than that for coal, ~220-650°C. Above this temperatures, varied peaks were observed for corn stover, coal and their blends which was mainly due to the high volatile matter and lower fixed carbon contents of corn stover as compared to that of coal. The thermal evolution profile of corn stover can be divided into three stages apart from its dehydration which corresponded to the removal of cellulose, hemicellulose and lignin components of corn stover. This was attributed to the fact that corn stover contains much higher content of volatile matter than the coal.

The SEM images of the blends provided an understanding of the binding mechanisms of corn stover and coal with morphological changes evident in the physical structures of both images which was attributed mainly to blending. However, the images confirmed that corn stover and coal, including their blends are carbonaceous materials suitable for co-gasification in a downdraft gasifier properly designed to accommodate the properties of blends of corn stover and coal.

The simulation results of the co-gasification process showed that the efficiency of the co-gasification process increased with increasing ratio of biomass in the blend and the
90%CS:10%CL blend resulted in maximum efficiency of approximately 58%. A comparison of the computer simulation results presented and experimental data from the literature showed that the simulation results can serve as a useful tool in predicting experimental observations reasonably well based on process efficiency.

5.2 SUMMARY OF CONTRIBUTIONS

A lot of information is available on the co-gasification of other biomass materials with coal than it is for corn stover with coal. This is basically because trials with these feedstocks met with challenges related to availability, hence the reduced interest its co-gasification with coal. This research has, however, added information on the co-gasification of corn stover with coal as well as the effect of blending corn stover and coal on the chemical composition of the materials.

5.3 CONCLUSIONS

The properties and suitability of corn stover and coal have been investigated to establish the best mixing ratio that results in enhanced conversion efficiency. However, all results showed that the suitability of biomass and coal for co-gasification purposes depends on a number of factors which includes the properties and composition of both feedstock which must be kept within range for optimum efficiency, the ratio of blending and the operating conditions of the gasifier. The results further showed that the type and composition of the samples as well as the ratio of the blends affect the efficiency of the co-gasification process.
It was also noted from the results that the properties of corn stover and coal should be kept in range for optimum co-gasification efficiency. The thermogravimetric analysis undertaken also revealed the co-gasification temperature of various blends of corn stover/coal and further established that the blends with higher ratio of coal degraded at a much wider temperature range due to lower volatile matter content of coal, as compared to the blends with lower ratios of corn stover. The study also revealed that co-gasification efficiency increased as the ratio of corn stover in the blends increased due to the high reactivity of corn stover as a result of high oxygen content. The variation of the co-gasification efficiency was insignificant, only within 1-2% difference. However, for the blend 10% corn stover:90% coal (10% CS:90% CL), it was noted that as the content of coal increased in the blend, CO production reduced during simulation thereby leading to a reduction in the co-gasification efficiency. Based on these results, there is evidence to suggest that gasifying corn stover with sub-bituminous coal will raise the efficiency of the co-gasification process. However, the most favourable blend in terms of efficiency is the 90% corn stover/10% coal (90%CS:10%CL) whose efficiency reached a maximum of approximately 58% due to a number of factors one of which is the ratio of corn stover in the blend and the calorific value of the blend as well as the operating conditions/parameters of the gasifier. Furthermore, a comparison of the simulated data from this study and experimental data from the literature showed similar results in terms of efficiency, implying that a laboratory scale or a large scale downdraft gasification system for the purpose of co-gasification of corn stover and coal can be designed using simulation results.
5.4 RECOMMENDATION FOR FUTURE RESEARCH

Despite much research in this field, co-gasification of coal with corn stover has not yet been fully explored. The tar production from this process needs further investigation as well as variation of the operating conditions of the gasifier so as to examine their effect on the efficiency of the co-gasification process. The pre-processing of the corn stover before blending and co-gasification with coal is also recommended to lower its moisture content and increase its bulk density for gravity feed in the gasifier.
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APPENDIX A: RESEARCH OUTPUTS ASSOCIATED WITH THIS STUDY

The research outputs associated with this work are as follows:

A1: JOURNAL PUBLICATION

A1.1 Submitted paper


A2: CONFERENCE PROCEEDINGS

A2.1 South African Institute of Physics Conference

APPENDIX B: MEASUREMENTS USED IN THIS STUDY

**TGA plot of pure (100%) materials**

**DTG of pure (100%) materials**