A metallurgical coke replacement derived from torrefied wood chips pre-treated by wet oxidation

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Abstract

The global population is ever increasing resulting in an ever-increasing energy demand and reliance of fossil fuels which has increased over the past few decades. The production of coke relies on the availability, cost and the quality of coking coals. Environmental pressure together with depleting coking coal resources has forced the metallurgical industry to search for alternative methods/resources to produce coke to be used as a reductant. Studies have shown biomass to be an attractive alternative to coking coal when producing metallurgical coke, especially woody biomass.

In this study, the use of thermally treated wet oxidized biomass as feedstock for the production of a metallurgical coke substitute was investigated. The soft wood chips sample was collected from Sappi Ngodwana (Nelspruit) and washed and dried to remove extraneous debris before further utilisation. The biomass sample was subjected to severe torrefaction at 280 °C under an inert atmosphere (nitrogen). This was done as a pre-treatment method to improve the energy density of the biomass. The torrefied biomass was then subjected to wet oxidation at 80 °C for a residence time of 30 minutes. The wet oxidized biomass was pelletized into 0.5 g 10 mm pellets and subjected to thermal treatment at 900 °C at a heating rate of 10 °C/min for a residence time of 2 hours under N_2 at atmospheric pressure in order to obtain a metallurgical coke substitute.

Characterisation of the raw biomass, torrefied biomass, wet oxidized biomass, thermally treated torrefied biomass, thermally treated wet oxidized biomass was conducted using: Free swelling index (FSI), Fourier-transform infrared spectroscopy (FTIR), ultimate and proximate analysis, gross calorific value (CV), compositional analysis (ADF, ADL & NDF), compressive strength, surface area (BET), coke reactivity index (CRI) and the coke strength after reaction (CSR). These obtained values were then compared to those of metallurgical coke used in the industry (ArcelorMittal). In addition to these characterisations, an economic evaluation has also been conducted.

The results concluded that the final reactivity of the prepared coke substitute was significantly higher than that of the metallurgical coke, *i.e.* the thermally treated wet oxidized torrefied biomass having a reactivity towards CO_2 of 132.4 $\times 10^4$ min^{-1} and 21.2 $\times 10^4$ min^{-1} of coke, respectively. This result is confirmed by the BET analysis which showed the thermally treated wet oxidized torrefied biomass has a significantly larger surface area than the metallurgical coke at 327.1 m^2/g and 8.8 m^2/g, respectively. Degradation of coke can be prevented by using a coke with a higher reactivity forcing the gasification reactions to be limited to the surface layer of the coke structure and thus leaving the stability of the coke intact. The coke substitute had an ash yield of 4.3 wt.% compared with 16.1 wt. % for metallurgical coke, which is advantageous as it will increase the productivity of the blast furnace. Observations indicated that when the ash yield increases by 1 wt. %, the metal production reduces by 2 to 3 wt. %. When taking the low ash yield of the substitute coke into account, the productivity of the blast furnace was four times higher than when using coke. The sulphur content of the coke substitute was <0.1 wt.% compared with 0.7 wt. % for the metallurgical coke. This is advantageous due to an increase in sulphur content leading to a decrease in blast furnace reactivity.

The economic evaluation showed that when 50 % of the coke is replaced with biomass, there is a 6.8 % change in the production cost of one ton of liquid iron; 50 % is also considered to be the most economical option. A sensitivity analysis revealed that when using 7.7 % biomass and 92.3 % coke the plant will break even, and when using 88.2 % coke, the plant will start to make a profit. The most economical option explored in this study was to replace the coke with 50 % biomass.

Keywords: coke production, woody biomass, economic evaluation, reactivity, wet oxidation, biomass torrefaction, coke production.

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List of Abbreviations

a.d.	Air-dried
ADF	Acid detergent fibre
ADL	Acid detergent lignin
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
CO_2	Carbon dioxide
CRI	Coke reactivity index
CSN	Crucible swelling number
CSR	Coke strength after reaction
CV	Calorific value
d.a.f.	Dry-ash-free basis
Db	Dry-based
FC	Fixed carbon
FSI	Free swelling index
FTIR	Fourier-transform infrared spectroscopy
GHG	Greenhouse gasses
HGI	Hardgrove grindability index
HTL	Hydrothermal liquefaction
IEA	International energy agency
IMDC	Inertinite maceral derived components
kg	Kilogram
kN	Kilo Newton
kpa	Kilopascal
m^2	Meters squared

min	Minutes
MJ	Megajoule
mm	Millimetre
Mpa	Megapascal
N	Newton
N_2	Nitrogen
NDF	Neutral detergent fibre
NSC	Nikkel steel corporation
PCI	Pulverised coal injection
PSD	Particle size distribution
RMDC	Reactive maceral derived components
TGA	Thermogravimetric analyser
VM	Volatile matter
wt.%	Weight percentage
XRF	X-Ray flourescence

Nomenclature

m_0	Initial char mass
m_t	Char mass at time t
m_f	Final mass after gasification
r	Reactivity at 50%
R_i	Initial reactivity
R_f	Final reactivity
N	Number of data points
τ_{50}	Time required for 50% conversion
X	Fractional conversion
ΔX	Change in fractional conversion
Δt	Change in time
P	Pressure
F	Force
A	Area

1. Chapter 1 Introduction

1.1 Background and motivation

The global population is ever increasing and individuals' living standards are rising as shown by the escalating worldwide energy demand, which has intensified over the last several decades. (Chen, et al., 2015). In the pursuit to meet the worlds growing energy demand, the use of fossil fuels such as coal has increased (Gil *et al.*, 2015). Coal is South Africa's most widely used fossil fuel for energy production and is ranked sixth in the world's top consumers of coal (Zhang, et al., 2000). The use of coal results in diminishing fossil fuel reserves, increased pollution and high greenhouse gas (GHG) emissions (Chen, et al., 2015). Coal conversion industries also release vast amounts of CO_2 to the atmosphere; one of these industries responsible for large CO_2 emissions is the steel making industry (Fick, et al., 2014). Traditionally, the steelmaking industry uses coke made from coking coal as a feedstock to their blast furnaces. In 2010, the steel industry contributed 6.7% of total global emissions of $CO_{2,}$ with metallurgical coke responsible for 93% of all steel industry GHG emissions (Weldegiorgis & Franks, 2014). In an effort to make these industries improve their carbon management, the CO_2 allowances should significantly be reduced from the year 2013 to 2020 (Fick, *et al.*, 2014). In 2015, South Africa was ranked the 23rd largest crude steel producing country in the world and produces approximately 45% of the total crude steel production on the African continent (Ratshomo & Nembahe, 2017). In 2019 alone, South Africa consumed 1886 thousand metric tons of metallurgical coke for various applications (Knoema, 2020).

South Africa is one of the world's most carbon intensive economies. The South African government has set a target to reduce the GHG emission without crippling the economy. One of the ways by which the government want to achieve this is by introducing carbon tax (Alton, et al., 2014). The carbon tax in South Africa is set to be R120 per tonne of $CO_{2,}$ but a reduced tax ranging from R6 to R48 per tonne of CO_2 is implemented to provide current emitters time to transition into a phase of lower emissions. This carbon tax will increase annually by inflation plus 2 percent until 2020 (SARS , 2019).

Climate change is the main driving force for new technologies and low emission energy sources (Fruehan, 2005). To address this, various efforts in developing renewable energy and alternative fuels have been carried out and substantial progress has been made. Unfortunately, due to poor technology reliability and limited resources, their applications are still limited (Chen, et al., 2015). In the quest for an alternative source, biomass is considered as one of the most promising resources which meets the standards required to be a substitute fossil fuel for reducing steel industry emissions (Saidur, et al., 2011). Biomass has great potential as a low-carbon energy source for large scale energy production due to the abundance of biomass on the earth’s surface. Thus far, bioenergy is the largest renewable energy source which accounts for 10% of primary energy demand in the world according to the International Energy Agency (IEA) (2011).

Biomass as a renewable energy resource is considered a suitable feedstock due to its CO_2 neutrality, low NO_X and SO_2 emissions and its autonomy which will contribute to reducing the dependence on fossil fuels as energy source (García, et al., 2012). A decisive advantage of biomass is that various processes in the iron-making route could easily accept biomass as an alternative with very few modifications (Fick, et al., 2014). However, biomass does possess a few drawbacks stemming from its characteristics. These include its high moisture content, low calorific value (CV) , hygroscopic nature and low bulk density, which results in a low conversion efficiency paired with difficulties in its collection, grinding, storage and transportation (Sami, et al., 2001). To address the mentioned disadvantages a number of pre-treatment methods have been developed (Chen, et al., 2015). According to Bridgeman et al (2010), one of the more promising pre-treatment methods for reducing some of these deficiencies is torrefaction since it is known to improve the solid fuel properties of the biomass.

Torrefaction is generally characterised as a thermal treatment under mild conditions, *i.e.*, temperature between 200-300 °C and a reaction time between 30 and 180 minutes at atmospheric pressure (Fisher *et al.*, 2012; Shang *et al.*, 2012; Nunes *et al.*, 2014). Torrefaction is thus a mild pyrolysis process which removes moisture and some of the volatile content and leaves a dry, partially carbonised solid (Bridgeman, et al., 2010). This process increases the energy density in the fuel on a mass basis, and after pelletisation on a volume basis as well. Torrefied biomass pellets have an energy density that nears that of coal (Bergman, 2005). This, combined with chemical changes in the solid, will also reduce the microbial activity which creates advantages for storage (Trifonova, et al., 2009). The physical changes in the biomass increases its brittle nature and reduces the tenacity of the polymeric fibres present in woody and herbaceous biomass, which suggests that the ease of grindability of the torrefied product also increases (Bridgeman, et al., 2010).

Biomass is thus a precursor to producing biochar via torrefaction, however this biochar does not meet all the necessary requirements for coke production (Díez, et al., 2002). In order to enhance the properties of the biochar to meet these certain requirements, the biochar can be pre-treated by a process called wet oxidation. Wet oxidation oxidatively depolymerizes the biochar through the treatment with hydrogen peroxide (H_2O_2) aqueous solution at temperatures ranging from 40 – 60 °C (Miura, et al., 1996). There are a number of pre-treatment methods available. For example: depolymerisation by oxidative degradation reactions and low temperature oxidation with O_2 (Ashida, et al., 2019).

In a study conducted by Das et al (2002), it was concluded that by mixing biomass with coking coal, a suitable coke could be produced. The coking coal used had a high ash yield (32 %) and the biomass used had a low ash yield (5-7 %). This suggests that there are advantages to using biomass as an alternative fuel source due to the low ash yield. Observations indicate that, when the ash yield increases by 1 wt. % metal production reduces by 2 to 3 wt. % (Díez, *et al.*, 2002).

1.2 Problem statement

The metallurgical industry generates a large amount of CO_2 due to the use of fossil fuels as a fuel or as a reductant. One of these reductants is metallurgical coke which is used in the production of pig iron. For years it has been proposed that the fossil fuel reductant be replaced by a more environmentally friendly reductant (Montiano, et al., 2014). The production of metallurgical coke from biomass can be advantageous due to biomass's CO_2 neutrality. This will result in a significant reduction in CO_2 emissions (Adrados, et al., 2015). South Africa has an abundance of biomass waste available which can be used to produce biochar and then a metallurgical coke substitute via wet oxidation pre-treatment, pelletisation and thermal treatment. The substitute coke derived from the depolymerisation of torrefied biomass will not only reduce the CO_2 emissions, but also produce less slag due to the lower ash yield and thus is expected to have economic advantageous as well.

1.3 Aims & objectives

This study seeks to compare the performance characteristics (CO_2 reactivity, mechanical strength, economics) of a laboratory prepared metallurgical coke substitute derived from the depolymerisation of torrefied woodchips having a low ash yield (<4% ash) with a commercial coke (<15% ash yield) derived from washed coking coal (<1.4 g/cm^3) from the Waterberg Coalfield.

This will be achieved by addressing the following objectives:

- Determine the torrefaction conditions for the preparation of feedstock and characterise.

- Perform wet oxidation on the torrefied biochar and determine the effect on swelling properties.
- Produce a pelletised and thermally treated substitute coke and compare coke strength and reactivity with metallurgical grade coke.
- Evaluate the economics of the coke substitute process and compare with that of a metallurgical grade coke.

1.4 Study outline

The dissertation is organised into 5 chapters.

In Chapter 1 the study is introduced which contains a brief background and motivation, stating the aim and objectives and providing a study outline.

A comprehensive literature review is given in Chapter 2 which discusses coke, how coke is produced, the characterization of coke and some general uses of coke. Biomass as renewable energy source is also discussed in detail providing previous case studies where biomass was used as a substitute for coking coal, and finally the chapter will be summarized.

The chemical and physical characterization of woodchips will be given in Chapter 3. Here the different characterization methods applied will be discussed in detail. All of the materials used will also be discussed with a description of the experimental setup and methods followed given.

The biochar produced from the torrefied woodchips will be characterised and the optimal H_2O_2 concentration for the wet oxidation experiments will be determined. The mass loss, reactivity, Coke reactivity Index and Coke strength after reaction index of the thermally treated biochar will be investigated and the results and discussion of these findings will form chapter 4, together with a comprehensive economic analysis.

Chapter 5 will provide the conclusions obtained from the results of this study. From the reached conclusions, recommendations for future work in the area of metallurgical coke substitutes will be drawn.

1.5 Scope of study

The scope of the study is shown in Figure 1-1. This will be used as the general outline of the study represented in this thesis.

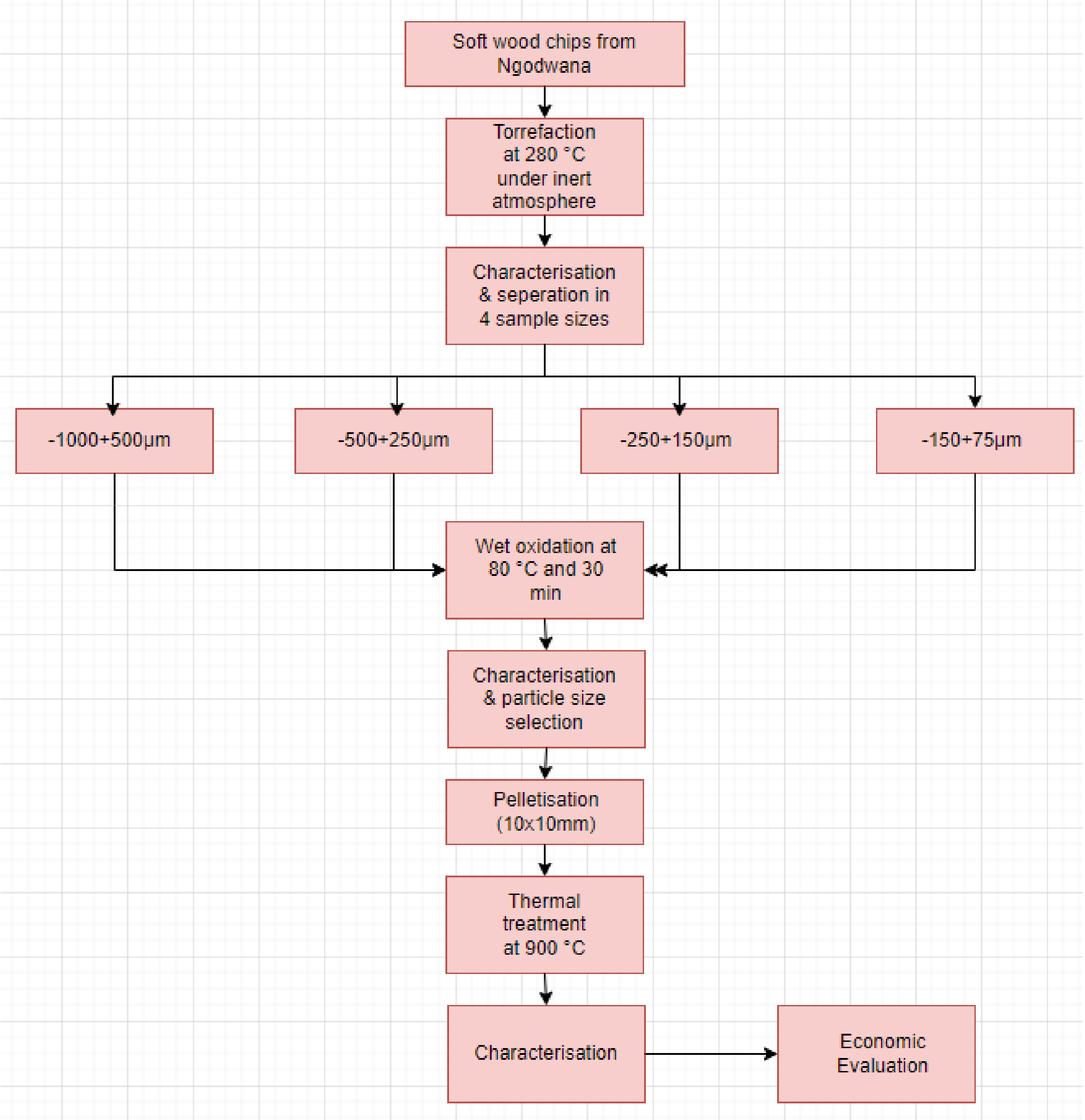

Figure 1-1: Flow chart of the scope of the study

2. Literature review

2.1 Introduction

An overview of coke and some of the variants thereof, how coke is produced, uses of coke and the reactions thereof in a blast furnace together with coke characterisation are given in this chapter. Biomass as an alternative energy source and previous studies which are of value to this dissertation are also reviewed and discussed.

2.2 Coke and its variants

Throughout literature the word “coke” appears in many contexts and can be easily used incorrectly. The variants of coke can be classified based upon the source of the feedstocks that are used to produce these cokes; *i.e.*, coke, petroleum coke and metallurgical coke (Schobert, 2013). Coke is designated as a solid carbonaceous material which is formed from a fluid phase or that passes through a fluid phase during its production (Schobert, 2013). Petroleum coke is a term used to describe carbonaceous solids produced by severe thermal processing of fractions of petroleum (Schobert, 2013). According to Diéz et al (2002) metallurgical coke is described as a macroporous carbon material that possesses a high strength produced by carbonization of coals of a specific rank or of coal blends at temperatures of up to 1100 °C.

2.3 Production of coke

The global metallurgical coke market is one of the biggest markets and is expected to reach a value of $ 239.34 billion by 2026. In 2015, South Africa was ranked the 23rd largest crude steel producing country in the world and produces approximately 45% of the total crude steel production of the African continent (Ratshomo & Nembahe, 2017). In 2019 alone, South Africa consumed 1886 metric tons of metallurgical coke for various applications (Knoema, 2020).

Metallurgical coke is manufactured by using coal as feedstock (Schobert, 2013). Good coking coals (referred to as prime coking coals), are characterised by a number of parameters and these need to be between fixed limits to qualify as a prime coking coal in order to produce a high-quality coke. These parameters are ash yield, volatile matter and sulphur contents, maceral composition, plastic properties and coking pressure (Barriocanal, et al., 2003). One of the reasons why the coke making industry uses coal blends rather than single prime coking coals is that prime coking coals are expensive and scarce (Barriocanal, et al., 2003).

To produce metallurgical coke, the carbonisation of coal blends is carried out in slot type ovens grouped in batteries (Loison, et al., 1989). The coals used to produce coke are bituminous coals whilst a small amount of inerts, such as coke fines, petroleum coke or anthracite can be introduced into the coal blend (Hays, et al., 1976). In general, coking coals subjected to a slow heating rate of 2-3 °C/min, in the absence of air, will soften and become plastic and after further heating re-solidify (Hays, et al., 1976).

The carbonisation of coal to produce coke is divided into three different stages namely: pre-plastic stage, plastic stage and the post-plastic stage (Díaz-Faes, et al., 2007). Up to 350 °C is considered the pre-plastic stage were the transformation of water, carbon dioxide and some light hydrocarbons occurs. The plastic stage occurs between 350-500 °C and this is where extensive molecular disruption and a considerable transformation of volatile matter takes place (Díaz-Faes, et al., 2007). In the afore-mentioned temperature range, coking coals present thermoplastic behaviour which is referred to as thermoplasticity. During the pyrolytic decomposition, the thermoplasticity is evident and seen as a result of several elementary phenomena that occur at once (Loison, et al., 2014). Depolymerization occurs within the thermoplastic temperature range and gives rise to molecular fragments which are stabilized by transferrable hydrogen (Lee, et al., 2020). Due to the instability of some of these molecular fragments they are released as tars. An increase in the fluidity of coal is a result of some molecular fragments which do not volatilize but become solvents. This is an intermediate phase which is referred to as the metaplast, which contributes to the plastic properties of coal (Lee, et al., 2020). Bubbles are formed within the coal particles during the plastic state which leads to physical changes in the coal such as swelling and porosity changes (Gray, 1988). In the post-plastic stage, hydrogen is eliminated by means of condensation, resulting in the formation of a more ordered structure (Díaz-Faes, et al., 2007).

Commercial coke making processes can be classified into two categories, *i.e.*, by-product coke making and non-recovery coke making (Schobert, 2013). By-product coke making operation consists of the following steps: Selected coals from mines are blended, pulverized and oiled to ensure bulk density control. The coal blend is then charged into the slot ovens wherein each oven shares a common heating flue with the adjacent oven.

Figure 2-1: Coke side of a by-product coke oven battery taken from Valia, (2005).

This is where the carbonisation of coal occurs, whereafter the off-gas is collected and sent to the by-product plant where a variety of by-products are recovered, hence the name by-product coke making (Valia, 2005). Figure 2-1 depicts a typical by-product coke oven battery.

In non-recovery coke plants, the carbonisation of coal occurs within large chamber ovens with a beehive structure as shown in Figure 2-2. The heat necessary for the carbonisation process to take place is supplied by radiant heat transfer from the top and by means of conduction through the sole floor from the bottom. There are several holes located above the charge level and in both pusher and coke side doors of the oven where primary air for combustion is supplied. Partially combusted gases exit through the down comer passages in the oven wall and enters the sole flue which then heats the sole of the oven. All the combusted gases collect in a common tunnel and exit via a stack. There are no by-products recovered and hence the name “non-recovery coke making” (Valia, 2005).

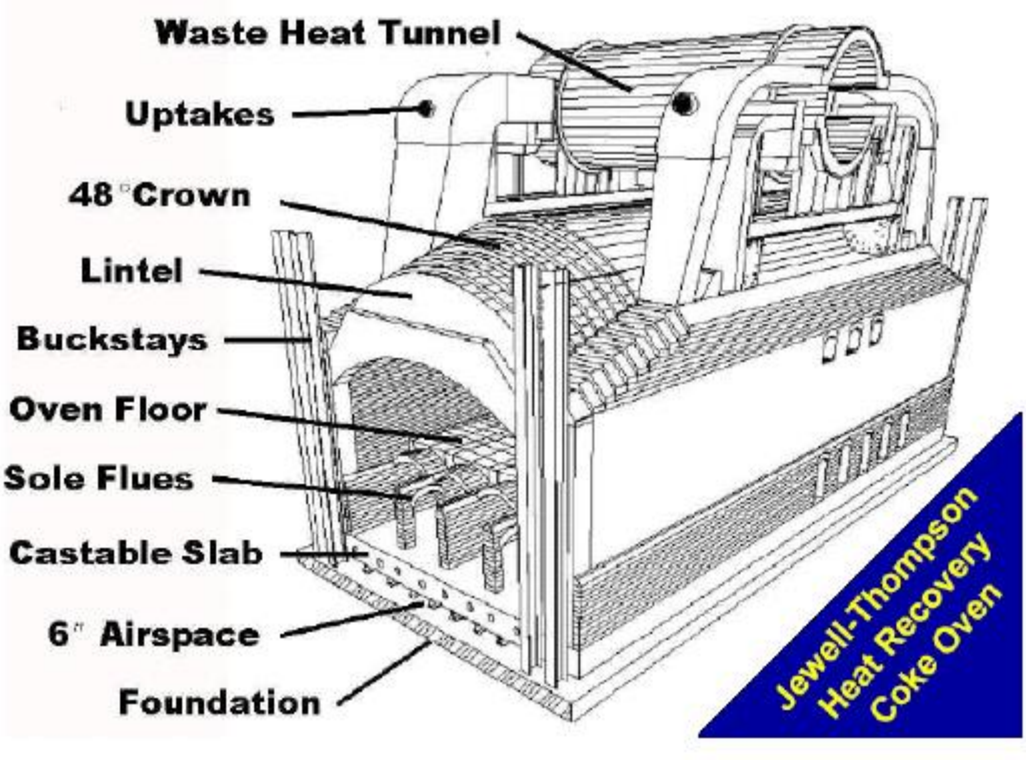

Figure 2-2: Beehive coke oven used in non-recovery coke making adapted from Valia (2005).

2.4 Uses of coke

Coke produced (90%) from different coking coal blends are used to maintain the process of pig iron production in blast furnaces (Díez, et al., 2002). According to Hilding *et al.* (2005), blast furnace smelting is the most dominant process of ironmaking worldwide and coke is the most important and expensive raw material used in blast furnaces and has a strong influence on the hot metal quality and the process efficiency. Coke is fed into the blast furnace together with iron ore where it has four major roles within the blast furnace. These roles are: (1) as a fuel that provides heat for the endothermic requirements, (2) as a chemical reducing agent, (3) as a permeable support which provides a permeable matrix necessary for slag and metal to pass down into the hearth and for hot gases to pass upwards into the stack, and (4) a source of carbon for carburizing hot metal (Li, *et al.*, 2014; Wang *et al.*, 2016). In order to reduce the coke consumption of blast furnaces thereby reducing the CO_2 emissions, the first two roles of the four can be substituted by oil, gas, plastics and coal. These substitutes are injected at the tuyers for generating energy and as a carbon source (Díaz-Faes, *et al.*, 2007; Shen, *et al.*, 2012). Figure 2-3 shows a schematic representation of an iron blast furnace used in the production of pig iron with metallurgical coke as a reductant.

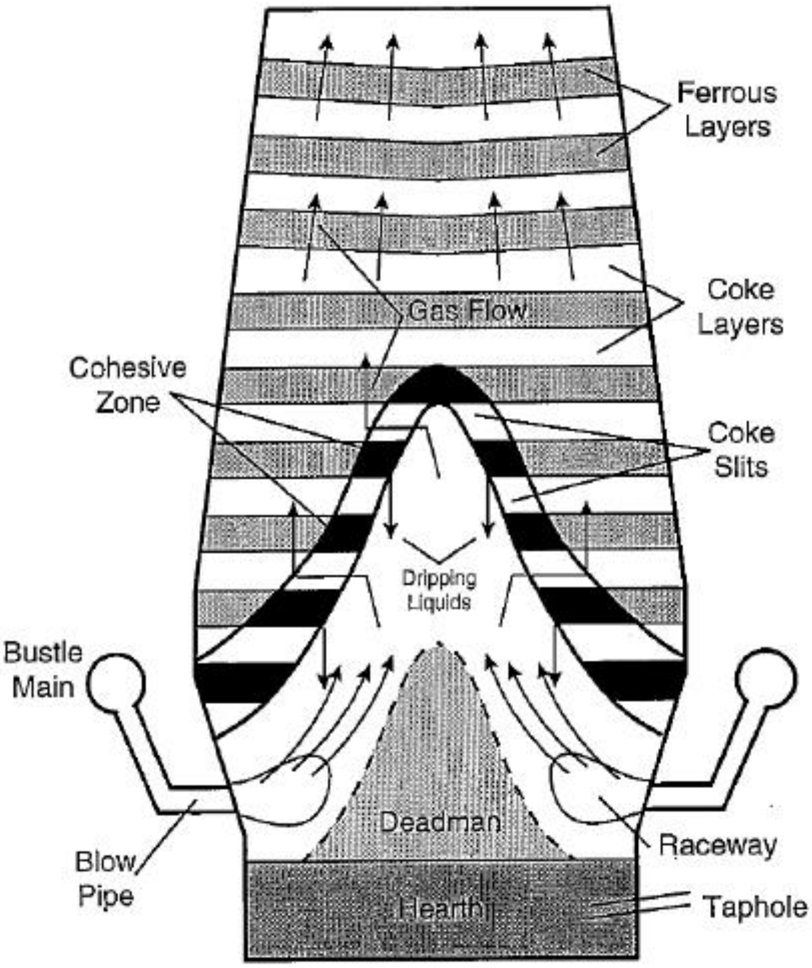

Figure 2-3: Schematic representation of an iron blast furnace (Iwamasa et al., 1997).

Iron ore (hematite), which consists of sintered ore and pellets, together with coke in alternating layers are fed into the top of the blast furnace (Mio, et al., 2007). Gas at a high temperature

(900-1100 °C) is introduced through the tuyers and as the coke descends in the blast furnace it undergoes gasification and reactions with wustite (FeO). Due to this counter-current mode of operation, coke is subjected to degradation as it descends the blast furnace (Wang, et al., 2016). According to Ishii (2000), the degradation of coke can be prevented by using a coke with a higher reactivity forcing the gasification reactions to be limited to the surface layer of the coke structure and thus leaving the stability of the coke intact. This shows the importance of the coke reactivity which was reported by Diez *et al.* (2002). As the reactivity of coke increases, the faster the coke will combust and gasify (Ishii, 2000).

Over the past few decades, the ironmaking industry pushed to increase the size and throughput of blast furnace performance while simultaneously decreasing the amount of coke used. This is done by pulverized coal injection (PCI) where high levels of carbon are injected via the tuyers. In these instances, the role of coke as a permeable support increases in importance and thus advocating for further improvements in coke quality (Díez, et al., 2002). A decrease in coking rate, creates a decrease in the coke layer thickness with an increase in the residence time of coke in the blast furnace (Diez *et al.*, 2002, Ishii, 2000). Negro *et al.* (1996) conducted a study on the degradation of coke in a blast furnace and reported a 30% increase in the residence time of coke in the blast furnace with variations in coal feed rate from 100 to 200 kg/t. According to Adrados *et al.* (2015), PCI is advantageous due to the decrease in the usage of metallurgical coke and the abundance of hydrogen produced which improves the reduction of iron thus improving the quality of iron produced.

There are several chemical reactions which takes place within the blast furnace. Equations (1) to (4) show the main reactions which takes place within the blast furnace (Yang, et al., 2010).

$$C + O_2 \rightarrow CO_2 \tag{1}$$

$$CO_2 + C \rightarrow 2CO \tag{2}$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \tag{3}$$

$$CaO + SiO_2 \rightarrow CaSiO_3 \tag{4}$$

Equation (1) shows the coke that burns in the presence of oxygen to produce carbon dioxide and heat which is an exothermic reaction. Limestone ($CaCO_3$) is also introduced as a fluxing agent, which is used to remove impurities from the iron. The limestone is calcined in order to produce carbon dioxide and calcium oxide (CaO). The carbon dioxide then reacts with carbon to produce carbon monoxide via Equation (2). Equation (3) shows how the hematite ore (Fe_2O_3) is reduced to produce pig iron or molten iron, which will be collected at the bottom of the furnace. The introduced calcined limestone reacts with impurities which forms slag, this is represented by Equation (4). The slag floats on top of the pig iron and can be removed by tapping (Seetharaman, 2014).

As previously mentioned, coke in combination with iron ore and flux travels in a counter current flow with reactant gas within the blast furnace (Mio, et al., 2007). Pulverized coal (- 75 µm > 80%) is also injected into the blast furnace via the tuyers. The blast furnace gas is recovered at the top of the blast furnace which is used as an energy source (Nomura & Lecther, 2020). The coke used to load the blast furnace is typically in the range of 50 mm which also helps to ensure high efficiency in the blast furnace (Díez, et al., 2002). Typically, the residence time for iron ore to leave the blast furnace is about 6 – 8 hours (Nomura & Lecther, 2020).

2.5 Coke characterisation

Coke is produced at an industrial scale from coking coal of different blends and geographical origin; it would be beneficial for producers to be able to predict the properties of the raw materials used to avoid expensive large-scale testing (Díaz-Faes, et al., 2007). There are a number of models being used to predict the coke quality in the coke industry with each model considering different properties of the feed materials. Each company employs different models adapted to its operational characteristics which will change as a function of the coals available on the market (Álvarez, et al., 2007). Díaz-Faes *et al.* (2007) researched the possiblity of using TGA parameters to predict coke quality. It was reported that it is possible to introduce TGA parameters into models designed for coke quality predictions. Álvarez *et al.* (2007) stated that there is no universally applicabile prediction formula which can predict the quality of coke and that most research focused on coal of the same geographic origin. This is advantageous due to the properties of coals that constitute a blend can be used to predict the coke quality. According to Diez *et al.* (2002), future research in coke optimisation is needed to increase the critical quality parameters of coke in order to reach higher productivities.

A realistic prediction of the likely performance of coke within a blast furnace operating with or without injection technology should always include the properties of coke that reflects the coke resistance to degradation under the chemical and thermal environment of the blast furnace (Díez, et al., 2002). According to Díez et al (2002) the properties for providing guidelines for coke use, relate to lump size, shape and size uniformity, mechanical strength, chemical composition and thermal and chemical stabilities. In order for blast furnace coke to be successful, there needs to be a compromise between its structure and properties. To ensure a high-quality blast furnace coke, the coke should be moderately large with a narrow size distribution and a high mechanical strength. The high mechanical strength will withstand the weakening reactions with CO_2 and alkali, abrasion as well as the thermal shock within the blast furnace. Due to a number of unknown factors, it is near impossible to universally apply quality indices common to all blast furnaces (Díez, et al., 2002). The most commonly used index to measure coke quality is the mechanical strength after coke has reacted with CO_2, also called the coke strength after reaction index (CSR index) (Díaz-Faes, et al., 2007). Mechanical tests, which are used to measure resistance to size degradation, include dynamic loading in the form of shatter tests (ASTM D3038) or the revolving drum test such as ASTM Tumbler (ASTM D3402). In Europe, the MICUM and IRSID (ISO 556 and ISO 1881) tests are dominant (Díez, et al., 2002).The CSR index depends on a number of factors such as coal rank, thermoplastic properties, ash and maceral composition which are mainly related to the characteristics of the raw material (Díaz-Faes, et al., 2007). Properties such as ash yield and sulphur content are important because as they increase, the coke productivity in the blast furnace deceases. The ash in coke is the non-productive part of coke which influences the slag volume and composition. Experience shows that when the ash yield increases by 1 wt. %, metal production reduces by 2 to 3 wt. % (Díez, et al., 2002).

Another test which is used to indicate the coke performance in the blast furnace is the coke reactivity index (CRI Index). The CRI index accounts for the physical properties which includes the cold mechanical strength, the resistance to degradation and fragmentation by fissuring, cohesion and abrasion (Álvarez, et al., 2007). The Nippon Steel Corporation (NSC) showed that there is a need for a new quality parameter of coke based on the reactivity towards CO_2 at a high temperature and the resistance to size degradation of the partially gasified coke (Ida, et al., 1971). The new test developed is a combination of the CRI index and the CSR index and is widely accepted by the steel industry (Álvarez, et al., 2007). The NSC test has recently been adopted as an ASTM standard procedure (ASTM D 5341 – 93a) and is being prepared by the International Organization for Standardization (Díez, et al., 2002). Recent studies still use the previously mentioned method as an ASTM approved method (Díaz-Faes, et al., 2007).

Ishii (2000) reported that to increase the coke reactivity usually the coke strength is reduced. A good quality coke has a high CSR index paired with a low CRI value resulting in the coke reacting faster than it can degrade. A good (high) CSR index value is considered to be above 60 % with an acceptable or good (low) CRI value to be between 20 - 30 % (Díez, et al., 2002). A high CSR value, above 60 %, prevents coke from breaking down, improves the permeability of both gas and liquid whilst increasing the productivity as well as decreasing the specific coke consumption (Hilding, et al., 2005). If the CSR values are below 60 % the coke is not acceptable, which will result in higher pressure losses and reduced furnace permeability. Studies have been done by various researchers regarding the relationship between the CRI and CSR indices and a high correlation was found from the NSC method as well as the Spanish National Coal Institute reactivity test (INCAR: ECE) method (Díez, *et al.*, 2002;

Menendez, *et al.*, 1999). A poor-quality coke shows a high reactivity together with a high degradability. Coke possessing a high degradability has an altered coke consumption in the blast furnace due to an inadequate gas flow to maintain the needed integrity (Rodero, et al., 2015). A poor-quality coke is seen as a coke which does not meet the chemical and physical requirements of blast furnace coke. A high degradability results in an inefficient blast furnace due to the permeability being reduced and the tuyers being blocked by the residues (Díez, et al., 2002). In order to maintain an adequate permeability, a large mean size with a narrow size distribution is used. The mean optimum size of this size distribution is in the range of 50 – 55 mm (Díez, et al., 2002). At low temperatures, the coke degradation is influenced by the coke reactivity, but at high temperatures the coke degradation is influenced by the cracking of the coke (Hilding, et al., 2005). Figure 2-4 shows the factors influencing the CSR Index of coke with CO_2 at 1100 °C. Various authors have shown the relevance of the CSR within blast furnace operation to maintain the permeability at constant and optimum values (Nakamura, *et al.*, 1999; Hatano, *et al.*, 1990).

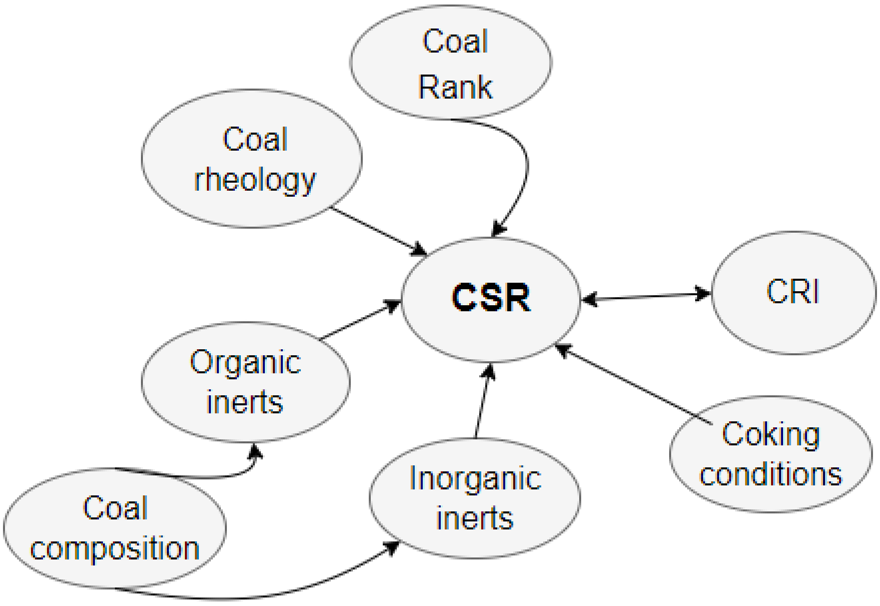

Figure 2-4:Main factors influencing CSR Index of coke with carbon dioxide at 1100 °C adapted from Diez et al (2002).

Impurities within the coke have a negative effect on the performance of coke in the blast furnace and thus they need to be kept as low as possible. Such impurities are moisture, volatile matter, ash, sulphur, phosphorous and alkali contents. These impurities decrease the cokes’ role as a fuel in terms of amounts of carbon available for direct and indirect reduction roles and its role as permeable support (Díez, et al., 2002). Both high and variable moisture content affect the coke rate as well as the balances within the blast furnace. Whilst high volatile matter contents cause more operational problems when it comes to cleaning of the blast furnace gas. Coke moisture content ranges from 1 wt.% to a maximum of 6 wt.% with the most common values being between the range of 3 – 4 wt.% (Leonard, et al., 1996). Impurities like sulphur and ash are of important because as they increase, the coke productivity within the blast furnace decreases. Ash yield is a non-productive part of coke which influences slag volume and composition (Leonard, et al., 1996). Table 2-1 shows the European range for chemical properties of blast furnace coke.

Table 2-1: Required chemical properties of blast furnace coke adapted from Leonard et al (1996).

Chemical Property	**European range**
Moisture (wt.%)	1-6
Volatile matter (wt.% db)	<1.0
Ash (wt.% db)	8-12
Sulphur (wt.% db)	0.5-0.9
Phosphorous (wt.% db)	0.02-0.06
Alkalies (wt.% db)	<0.3
Db = dry-based	

The physical properties of coke are important and are linked to the need to support the ferrous burden and to provide a permeable matrix where the reducing gases can flow and the molten material can percolate in the lower region of the blast furnace (Díez, et al., 2002). These physical properties are coupled to its size and the coke resistance to breakage and abrasion. Screening processes control coke size to ensure a large mean size coupled with a narrow size distribution (50 – 55 mm). Table 2-2 shows the required physical properties of blast furnace coke currently in operation. M_{40} and M_{10} show the acceptable abrasion indices for coke. This ensures that an adequate permeability is maintained. Tests such as dynamic loading or revolving drum tests are used to measure the resistance to size degradation (Díez, et al., 2002).

Table 2-2: Required physical properties of blast furnace coke adapted from Diez et al (2002).

Physical property	European range
Mean size (mm)	47 - 70
M_{40}	53 – 55
M_{20}	>77.5
CSR value	>60
CRI value	20 - 30

Other characterisation techniques to determine the quality of coke include proximate and ultimate analysis, free swelling index and agglutination indices (caking index) (Maree, et al., 2020). Petrography is a tool that is used to characterize and quantify coke microtexture (Lomas, et al., 2017). As early as 1980, automated petrography has been used to characterize coke microtexture. Microstructure together with microtexture of coke are complex and a consequence of its inherent heterogenous nature. The microtexture consists of different carbon forms present in coke (Lomas, et al., 2017). They are classified into reactive maceral derived components (RMDC) and inertinite maceral derived components (IMDC) which are all depended on whether the carbon came from material that fused during coking or material which did not. IMDC and RMDC differ in their degree of optical anisotropy, with IMDC showing low anisotropy (Gray, 1991). In the characterising and quantifying of coke microtexture, petrography is an important tool. As early as the 1980's, automated coke petrography has been used to characterise coke microtexture (Greeff & Smith, 1987). Studies have also shown recent advances in the algorithm used to classify these different forms of carbon based on their bireflectance and mean maximum reflectance of coke (Danloy, et al., 2009). Lomas *et al.* (2017) stated that there was no link between the coke microtexture and coke performance in the blast furnace, thus providing an opportunity for new research.

2.6 Biomass as an alternative energy source

The challenge of global warming needs to be addressed on an urgent basis in order to avoid cataclysmic consequences for the world as a whole. This issue raised renewed interest into biomass as an alternative energy source which could play a significant role in the global energy demand. Biomass is known to have been used to produce biofuels such as bioethanol, methanol, biomethane, biodiesel; even electricity, and has been used for heating purposes (Basu, et al., 2011). Overall, different biomass samples have different chemical and structural characteristics resulting in different fuel applications (Rosillo-Calle, 2016).

Biomass is receiving increasing attention due to tecofriendly characteristics it possesses. Biomass does emit CO_2 which is comparable with the levels emitted by coal, but due to its CO_2 neutrality it is advantageous over coal (Painuly, 2001). Energy produced by biomass can make a large contribution to the world's energy demand, but due to large geographical differences, the global natural energy sources are very unequally distributed. This can be mitigated by means of an international bioenergy trade (Rosillo-Calle, 2016). According to Hall and Rao (1999), the total earth annual biomass production is estimated to be around 220 billion oven dry tonnes. The current biomass energy is estimated to vary from 10 to 14% of the world primary energy (Hall & Rao, 1999). Most renewable sources depend to some extent on the use of other, non-renewable sources like the use of diesel to transport biomass (Timmons & Mejia, 2010).

In Section 2.4, PCI and some of its advantages thereof are described. Bio-PCI or Bio-pulverized carbon injection concords completely with traditional PCI as a particle size of 75 µm is used, but instead of coal fines, biochar is injected through the tuyers (Feliciano-Bruzual, 2014). The biochar used in Bio-PCI contains substantially less sulphur and phosphorus than coke which results in a higher quality of pig iron with a higher (32 – 45%) market value. Biochar has a lower ash yield than coke thus generating up to 50% less slag in the blast furnace (Feliciano-Bruzual, 2014). Biochar is highly porous and given its high specific area, the combustion rates in the blast furnace can be improved by biochar (Ueda, et al., 2009). With these advantages, biochar also has some practical limitations. These includes the low crushing strength of biochar which does not allow complete substitution of coke in large blast furnaces (>600 m^3). The low bulk density of biochar negatively affects the pneumatic conveying at high rates of injection (Mathieson, et al., 2011).

2.6.1 Wood Chips as bioenergy source

Processes like wood-based construction, yields a lot of waste wood and thinned wood that cannot be successfully recycled. This creates an opportunity for these materials to be used as an alternative energy source (Matsumura, et al., 2008). Woody biomass also referred to as solid biomass, is used in an abundance of applications ranging from small traditional to modern, both small and large scale, applications. The concern with solid biomass is far less alarming than that of liquid biofuels. This is mostly the result of solid biomass being widely available and comprises a wide range of feedstock which includes large amounts of residues and wastes which are currently mostly being unutilized (Rosillo-Calle, 2016).

The utilization of woody biomasses allows for the use of existing plant infrastructure and low temperature exhaust heat which is attractive for the steel industry (Matsumura, et al., 2008). Iron production is a complex process and the biomass introduced should have precise chemical and physical requirements (Fick, et al., 2014). Amongst these processes is the coke making process which not only allows for the processing of carbonized products but also gas and hydrocarbon oil derived from woody biomass with existing infrastructure (Matsumura, et al., 2008). Due to the biomass's variety and composition which depends on origin, a series of operating problems occurs during conversion processes. As a result, it is necessary to continuously improve the properties of biomass, *i.e.*, hydrophilic nature, low heating value and high energy required during grinding to improve its efficiency during utilisation (Magdziarz, et al., 2017).

2.7 Thermal conversion processes

In order to obtain various types of energy from fuels like biomass and coal they have to undergo a series of thermal conversion processes (Mafu, et al., 2017). Solid fuels are mainly converted by three thermal conversion processes namely: (1) Pyrolysis, (2) Gasification and (3) Combustion (Mafu, et al., 2016). Overall, combustion can be replaced by torrefaction (reference?) as it is more relevant to this study. Torrefaction is seen as a pre-treatment method used to improve the properties of biomass to improve the efficiency during conversion processes.

2.7.1 Torrefaction

According to Magdziarz et al (2017), in order to improve the properties of biomass to increase the efficiency when utilised, biomass should undergo a pre-treatment method known as torrefaction. Some of the properties that biomass possesses are inconvenient, particularly the high oxygen content, low calorific value, hydrophilic nature and the high moisture content (Stelt, et al., 2011). Results from recent research suggests that after undergoing torrefaction, these disadvantageous properties are improved to a great extent (Gouws, et al., 2020). Torrefaction has also been called mild pyrolysis since torrefaction is conducted at conditions similar to those of pyrolysis but at a lower temperature of 200 – 300 °C and under inert conditions (Felfri, et al., 2005). The process of torrefaction yields benefits which include: (1) a higher energy density or heating value, (2) lower atomic oxygen to carbon and hydrogen to carbon ratios together with lower moisture content, (3) higher water-resistivity and hydrophobicity, (4) improved grindability and reactivity, and (5) yields more uniform properties of biomass (Chen, et al., 2015). Figure 2-5 shows the property variation of biomass undergoing torrefaction.

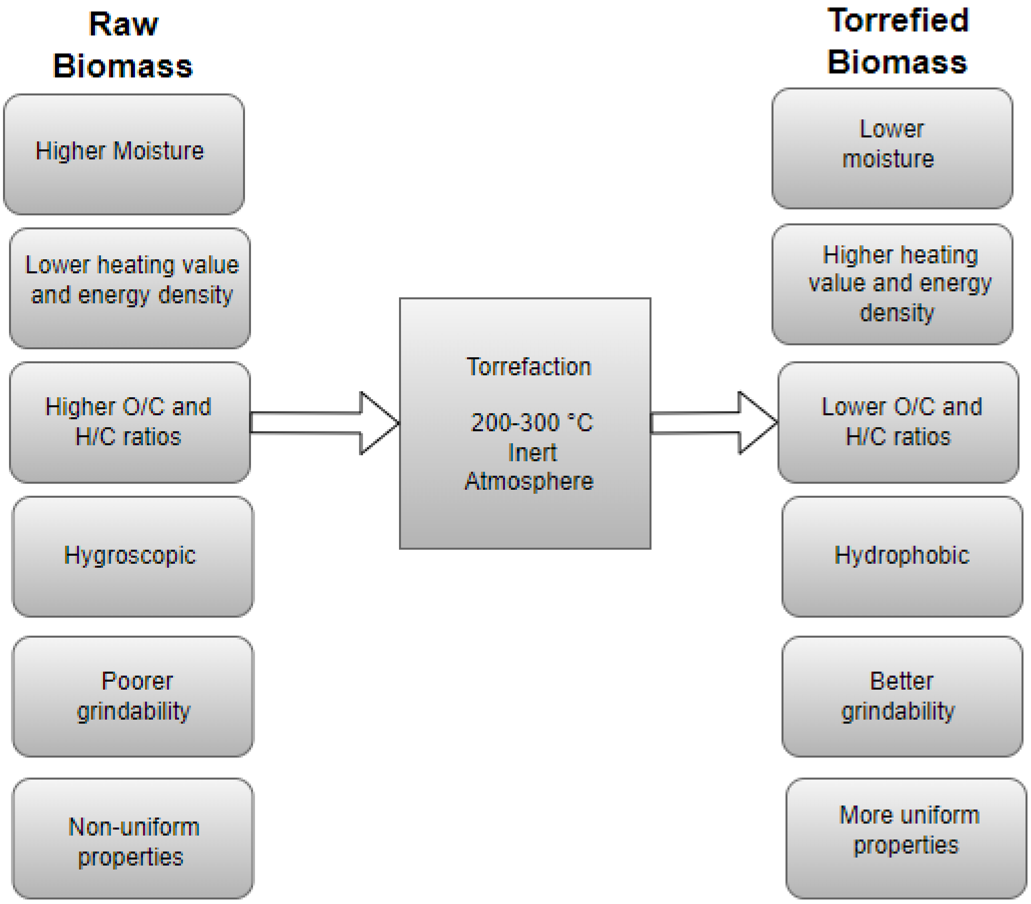

Figure 2-5: Schematic showing the property variation of biomass when undergoing torrefaction adapted from Chen et al (2015).

Moisture content plays an important role in biomass as a high moisture content in the biomass fuel leads to high energy loss in the course of burning. If the biomass is to be used as a feedstock, it is desirable to lower the moisture content thereof (Chen, et al., 2015). In order to increase the energy efficiency paired with improving the energy product quality and reduce the emissions of thermochemical processes, the reduction of the moisture content plays a significant role (Fagernas, et al., 2010). Research suggests that torrefaction changes the hygroscopic nature of biomass to hydrophobic, resulting in a significant decrease of the saturated moisture content in biomass (Chen, et al., 2015). Sadaka & Negi (2009) found that the moisture content in wheat straw, rice straw and cotton gin waste was reduced by 70%, 49% and 49 wt.% respectively after torrefaction. Apart from moisture content, torrefaction also changes properties such as volatile matter (VM), fixed carbon (FC) and ash yield. Table 2-3 shows these properties of treated and untreated biomass and coal. The volatile matter that decreases as the biomass undergoes torrefaction is as a result of dehydrogenation. The FC content of biomass increases as the VM content decreases (Chen, et al., 2015).

Table 2-3: Properties of untreated and torrefied biomass and coal adapted from Chen et al (2015).

Material	Volatile Matter (wt.%)	Fixed carbon (wt.%)	Higher heating value (MJ kg^{-1})
Raw biomass	67 - 88	0.5 - 20	15 - 20
Torrefied biomass	34 - 85	13 - 45	16 - 29
Coal	0.5 - 50	46 - 92	25 - 35

Torrefaction can be further classified into light, mild and severe torrefaction with corresponding temperatures of 200 – 235 °C, 235 – 275 °C and 275 – 300 °C respectively (Chen & Kuo, 2011). When biomass is subjected to light torrefaction, the moisture and low molecular weight volatiles contained within the biomass are released. Among hemicellulose, cellulose and lignin, the most active in biomass is hemicellulose. Hemicellulose is thermally degraded to a certain extent as a result of light torrefaction, whereas the other two, cellulose and lignin, are only slightly or hardly affected (Rousset, et al., 2011). This results in only a slight improvement of the biomass properties (Chen, et al., 2015).

This is in contrast with mild torrefaction; whereby the biomass is subjected to mild torrefaction with hemicellulose decomposition and volatile liberation. Hemicelluloses are greatly depleted and cellulose is also consumed to a certain extent (Chen, et al., 2015). Severe torrefaction of biomass results in the complete depletion of hemicellulose and cellulose is oxidized to a great extent. Hemicellulose and cellulose are the two main constituents in biomass. Lignin is the most recalcitrant constituent to thermally degrade and thus its consumption within the torrefaction temperature range is very low (Chen, et al., 2015). Thus, the significant removal of hemicellulose and cellulose from biomass through severe torrefaction results in the weight and energy yield of biomass being substantially lowered although the energy density is greatly intensified (Chen & Kuo, 2011).

When assessing the performance of torrefaction, time or duration is an important factor. The torrefaction process can be carried out between several minutes to several hours (Wannapeera & Fungtammasan, 2011). Felfri *et al.* (2005) found that rapid thermal degradation of biomass occurs at a torrefaction time of less than one hour and becomes slow beyond one hour. Thus, torrefaction time is generally controlled within one hour (Felfri, et al., 2005).

2.7.2 Pyrolysis

The pyrolysis of biomass is reported as the thermal decomposition of the biomass organic matrix in a non-oxidising atmosphere which results in the formation of bio-oil, solid biochar and non-condensable gaseous products (Kan, et al., 2016). Pyrolysis generally has three main stages: (1) initial evaporation of free moisture or drying, (2) primary pyrolysis, and (3) secondary pyrolysis (Mulligan, et al., 2010). The drying stage occurs at temperatures lower than 150 °C, resulting in the evaporation of moisture together with the degradation of light molecular weight hydrocarbons (Kan, et al., 2016). The primary pyrolysis stage produces volatiles as chemical bonds of lignocellulosic components are degraded into gases, condensable components and char (Yang, et al., 2006). Secondary pyrolysis may take place after or simultaneously with primary pyrolysis. In the instance where secondary pyrolysis occurs after primary pyrolysis, the char produced from primary pyrolysis may be converted through cracking reactions and vapours may be polymerized into secondary char (Mafu, et al., 2017).

Based on the heating rate and residence time, biomass pyrolysis can be divided into three main types namely: slow pyrolysis also called conventional pyrolysis, fast pyrolysis and flash pyrolysis (Demirbas & Balat, 2007). Slow pyrolysis makes use of long residence times, lasting hours to days, and at temperatures ranging between 300 – 700 °C, and a wide range of particle sizes can be used. In order to maximise the solid yield through re-polymerization reactions, the thermal decomposition of biomass needs to proceed under a very low heating rate with sufficient residence time (Demirbas & Arin, 2002). Fast pyrolysis makes use of high heating rates in the range of 10 – 200 °C, paired with short residence times in the range of 0.5 – 10 seconds, but typically under 2 seconds. Fast pyrolysis has a high bio-oil yield which can be as high as 50 – 70 wt.%. Flash pyrolysis makes use of higher heating rates in the range of 10^3 – 10^4 °C/s and a shorter residence time of <0.5 seconds, which results in the formation of high bio-oil percentages in the range of 75 – 80 wt.% (Demirbas & Arin, 2002).

Parameters that should be taken into consideration when conducting pyrolysis includes feedstock type selection, reaction conditions and miscellaneous variables such as the addition of a catalyst (Kan, et al., 2016). During the process of pyrolysis, a number of reactions take place in series or parallel which involves dehydration, depolymerisation, isomerization, decarboxylation and charring (Lange, 2007). Dehydrogenation, depolymerization and fragmentation are the main competitive reactions dominant at different temperatures (Kan, et al., 2016).

2.7.3 Gasification

Gasification is an important process in the thermo-chemical conversion of biomass. Biomass is converted in the presence of a gasifying agent into a multifunctional gaseous mixture, called syngas. Syngas can be used for the production of energy, chemicals (ammonia) and biofuels. After biomass conversion, a solid residue called char, is produced (Molino, et al., 2018). This conversion of biomass into useful products used in fuel production plays an important role in reducing the fossil fuel dependency and also lowers the CO_2, NO_x and SO_x emissions (Rosillo-Calle, 2016).

Gasification takes place within a gasification unit or a gasifier. The main operating parameters of a gasifier are design, temperature, flow rates of biomass and gasifying agents, catalyst and the biomass type and properties (Kumar, et al., 2009). For optimal gasification to occur, the biomass undergoes pre-treatment like torrefaction to change the properties of the biomass as shown in Figure 2-5. Gasification takes place between 600 – 1000 °C with heat being supplied either directly or indirectly. Typical gasifying agents used are air, steam, nitrogen, carbon dioxide, oxygen or a combination of both. The presence of the gasifying agent allows the large polymeric molecules of biomass to decompose into lighter molecules and then, eventually into syngas, ash, tar and char (Mansaray & Ghaly, 1997). The tar and char are a results of incomplete conversion of the biomass (Kumar, et al., 2009).

Biomass has a high gasification reactivity when comparing it to that of coal. Nevertheless, there are still notable differences in gasification characteristics within the biomass classes (Kirubakaran, et al., 2009). Studies have shown that the pyrolysis conditions also have an impact on the gasification reactivities. Higher gasification reactivities are generally paired with chars produced when using a higher heating rate than those produced from slow pyrolysis (Cetin, et al., 2004). According to Kirubakaran et al (2009), due to the fact that biomass can be assumed to be highly porous, it represents the opportunity for the reactant gas to diffuse into the gasification reaction sites and thus delivering a higher gasification reactivity.

Equation (5) shows the overall reaction in an air and steam gasifier. This reaction proceeds with multiple pathways. Equations (6) – (12) are some of the most common reactions that occur during gasification. In a nitrogen atmosphere, weight loss generally occurs in three stages: (1) dehydration (< 125 °C), (2) active pyrolysis (125 – 500 °C) and (3) passive pyrolysis (> 500 °C). The first stage reflects the loss of water whereafter, active pyrolysis results in the loss of hemicellulose, cellulose and a part of lignin. Lastly, passive pyrolysis causes a slow and continuous loss of residual lignin. All three stages' temperature ranges are dependent on the rate of heat transfer, the biomass composition and the degree of the oxidizing environment (Kumar, et al., 2009).

$$CH_xO_y + O_2 + H_2O \rightarrow CH_4 + CO + CO_2 + H_2 + H_2O + C\ (char) + tar \quad (5)$$

$$2C + O_2 \rightarrow 2CO \quad (6)$$

$$C + O_2 \rightarrow CO_2 \quad (7)$$

$$C + 2H_2 \rightarrow CH_4 \quad (8)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (9)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (10)$$

$$C + H_2O \rightarrow CO + H_2 \quad (11)$$

$$C + CO_2 \rightarrow 2CO \quad (12)$$

2.8 Previous research conducted on biomass as a substitute

Table 2-4 summarises several studies that have been conducted that focused either on the improvement of biomass proprieties being used as a feedstock or biomass being used as a substitute to lower the emissions of the pig iron production whilst varying the type of biomass used.

Table 2-4: Previous studies conducted on biomass varying biomass type and the focus of the research

Author	Biomass Type	Main Focus
Shang et al (2015)	Wheat straw	Grindability of biomass
Gouws et al (2020)	Wood chips	Co-pyrolysis
Gil et al (2015)	Pine, black poplar and chestnut woodchips	Grindability and combustion behaviour / emissions
Maree et al (2020)	Spent coffee grounds (SCG)	Waste management
Srivastava et al (2013)	Fine wood	Waste management
Zandi et al (2010**)**	Sunflower husk pellets, olive residues and bagasse pellets	Renewable energy
Fick et al (2014)	Wood and crop residues	Waste management

Shang et al (2012) studied the mechanical and chemical behavioural changes of biomass (wheat straw) after torrefaction. The study reported that after torrefaction at 200 °C, the hardgrove grindability index (HGI) value of the torrefied biomass showed almost no improvement, implying that torrefaction at 200 °C did not improve the grindability of the samples. This is in contrast with torrefaction temperatures of 230 – 300 °C where the HGI value increased significantly. Shang *et al.* (2012) reported a close relationship between the grindability and the tensile strength after torrefaction; whereby the grindability increased while the tensile strength decreased. Shang *et al.* (2012) stated that the main reason for the improvement in grindability is as a result of the degradation of hemicellulose. When assessing the relationship between energy loss and weight loss, it was reported that the percentage of energy loss increased more rapidly than the weight loss when torrefaction conditions become more severe. Shang *et al.* (2012) also reported that this is a result of the degradation of lignin and cellulose that occurs at 270 – 300 °C. In order to preserve energy in the torrefied biomass, lower torrefaction temperature paired with a shorter residence time is preferred.

Gouws *et al.* (2020) investigated the co-pyrolysis of coal and raw/torrefied biomass and its effects on the chemistry, kinetics and the implementation thereof. This investigation showed that in order to produce a torrefied material with required properties, operating temperatures between 225 – 325 °C were optimal. This will result in sufficient degradation of hemicellulose. There is a difference in the physical and chemical properties of raw and torrefied biomass which suggests that the extent of heat and mass transfer limitations during co-pyrolysis is reduced. Gouws *et al.* (2020) reported that although the biomass has less H-donors, the increased activity of the surface sites, leads to the increased catalytic effect during co-pyrolysis.

Gil *et al.* (2015) studied the combustion behaviour and grindability of torrefied biomass blends. In this study a particle size distribution (PSD) was used to assess the grindability of biomass after pulverisation. Gil *et al.* (2014) reported that all untreated biomass samples were difficult to pulverize, whist pre-treatment via torrefaction successfully increased the grindability of the samples. From the torrefaction parameters, temperature was the most important, whilst residence time also had a significant influence on the grindability. Gil *et al.* (2015) used a chestnut biomass sample for the combustion behaviour research (co-firing with coal) as it was the easiest sample to grind after the sample was torrefied at 280 °C at a residence time of 22 minutes. Burnout values of close to a 100 % were obtained after coal combustion and co-combustion of coal and torrefied biomass blends. Gil *et al.* (2014) stated that this is as a result of the inherently high reactivity of bituminous coal. Lower emissions of NO_x and SO_x were also reported during the co-combustion of coal and biomass compared to coal. The NO_x emissions lowered from 500 mg/Nm^3 to 180 mg/Nm^3 at a fuel ratio of 20 % biomass. The SO_x was reported lower but not as significant as the NO_x, changing from 840 mg/Nm^3 to 480 mg/Nm^3 at a biomass coal blend of 30 %.

Maree *et al.* (2020) studied the chemical and physical characterization of spent coffee ground derived biochar which was pre-treated by wet oxidation in order to produce a coke substitute. The biochar used in this study was produced using hydro thermal liquefaction (HTL), whereafter the biochar was treated using a wet oxidation step. Whilst using three different H_2O_2 concentrations, Maree *et al.* (2020) found that a 30 vol % addition was the preferred concentration where the FSI values of the biochar increased when applying long time durations (6 – 24 hours) at room temperature. Alternatively, it was found that short time durations (0.5 hours) are also a viable option, but then the treatment should occur at elevated temperatures of 80 °C where the FSI values were increased to 2 and 1.5 respectively. It was found that the pre-treated biochar met most of the metallurgical industry specifications of the necessary coke properties like moisture content, sulphur content, fixed carbon content and gross calorific value. Finally, Maree *et al.* (2020) concluded that it is possible to produce a coke substitute through wet oxidation which adheres to most of the industry requirements and that the coke substitute produced has the potential to be used as a fine reductant (PCI) in blast furnaces during the production of pig iron.

Srivastava *et al.* (2013) conducted a study on producing pig iron by utilizing biomass as a reducing agent. In the aforementioned study, self-reducing iron oxide pellets together with biomass pellets were made and fired at different temperatures and residence times. This study found that it is possible to produce pig iron pellets when using biomass as a reducing agent. Srivastava *et al.* (2013) also found that the total iron loss in slag from initial pellets was below 1 % which means that the reduction of iron was completed. Srivastava *et al.* (2013) reported that when the iron loss in slag decreases the operating temperature and residence time increases. From the experiments, the iron nuggets produced contained 97 % iron, even when fired at 1425 °C for only 20 minutes. It was also reported that the combustion of biomass resulted in less CO_2 emitted (58 %) than for the combustion of coal. This means that biomass as a reducing agent will be more environmentally friendly compared to coal. Biomass is considered sustainable, renewable and not derived from fossil fuels and Srivastava *et al.* (2013) found that biomass can also be used alone as a reducing agent. The study reported that biomass produced a better-quality pig iron at lower operating temperatures compared to coal.

Zandi *et al.* (2010) investigated the possibility of using biomass for iron ore sintering. This investigation entailed using different biomass materials as a supplementary fuel in the iron ore sintering process. In this study, one type of biomass was identified which could be satisfactory to be used in the sintering process, *i.e.* the residues from food processing. Zandi *et al.* (2010) compared coke breeze with 75 % coke breeze and 25 % biomass fuel on a constant carbon content basis and reported that the peak temperature is lower with the biomass/coke breeze blend and thus substituting on a carbon basis will not be sufficient to achieve sintering. Zandi *et al.* (2010) reported that the biomass composition greatly influences the combustion characteristics in the sinter bed. A tendency with the biomass experiments was reported where the temperature rose earlier than for coke breeze. Zandi *et al.* (2010) recommended that a particle size of smaller than 1 mm should be used for the studied biomass when co-firing with coke breeze for sintering. The residence time was also reported to be shorter whilst using the biomass blend. Using the biomass blend resulted in a lower SO_x emission whilst the NO_x emissions remained largely unaffected. The lower SO_x emissions are as a result of the lower sulphur content in the biomass compared to coke breeze. The NO_x emissions observed were only based on one fuel test and more research needs to be done to confirm this finding.

Previous research conducted by Fick *et al.* (2014) (desktop study) attempted to effectively use biomass for pig iron production. In this study the researchers replaced 20 % of the fossil fuels used for pig iron production with renewable biomass. Both torrefaction and carbonization were successful in producing solid char with properties similar to that of fossil coal. Fick *et al.* (2014) reported that the produced torrefied biomass could be used as a pulverized powder injected through the tuyeres. However, the carbonized biomass was reported to be used as lumps loaded at the top of the blast furnace and as mid-size fines (1-10 mm) in the sintering process. Fick *et al.* (2014) also conducted a screening GHG footprint assessment which showed that using torrefied and pulverized biomass in the blast furnace would be an environmentally friendly route. The GHG screening footprint also reported a 14.7 % CO_2 equivalent reduction followed by pulverized biomass char injection and charcoal lumps loaded at the top of the blast furnace, with 14.5 and 14.4 % CO_2 equivalent reduction, respectively. Replacing all the anthracite with biomass resulted in a 6.7 % CO_2 equivalent reduction. Fick *et al.* (2014) also reported that the bio-oil formed can be used in soil amendment to ensure an optimum CO_2 equivalent reduction.

2.9 Summary

The steel industry uses coke as a reductant in order to produce pig iron which is then sold at a profit. The coke used in the blast furnaces can be classified according to the feedstock used to produce this coke. Carbonisation of coking coal blends is carried out in slot type furnaces grouped in batteries in order to produce metallurgical coke for blast furnace use. The steel industry is under pressure to reduce its CO_2 emissions, which arise from the use of coal as a feedstock.

Numerous previous studies have focused on reducing the use of fossil fuels in the metallurgical industry by partially replacing fossil fuels with biomass. These studies have shown success when partially replacing the coke with coke derived from biomass or biochar. New technologies such as Bio-PCI have shown potential when used correctly to effectively reduce emissions in a cost-effective manner. Biomass needs to be pre-treated to improve some of the properties in order to effectively use it as a substitute material. Torrefaction is one of these pre-treatment methods which shows great advantages. If biomass or biochar can successfully be incorporated in the metallurgical industry, the emissions will sufficiently decline in the coming years.

Maree *et al.* (2020) studied the possibility of spent coffee grounds, prepared through hydro thermal liquefaction, being used as an alternative energy source. The spent coffee ground was pre-treated using torrefaction and wet oxidation. The wet oxidation was done at three different volume percentages of hydrogen peroxide. In this study, the wood chips will also be pre-treated using torrefaction (280 °C) and wet oxidation (80 °C and 30 vol % and 30 minutes) whereafter the biochar will be pelletized and thermally treated at 900 °C in order to prepare a metallurgical coke substitute. Maree *et al.* (2020) found that the biochar which was treated at 30 vol % at a treatment time of 24 hours showed the most promising characteristics when compared to blast furnace coke.

Fick *et al.* (2012) conducted a study on using biomass for pig iron production. In the economical assessment conducted it was reported that when substituting 20 % of biomass for coke resulted in a reduction of 15 % of the greenhouse gas emissions. Fick *et al.* (2012) conducted a desktop study. The economic evaluation in this study, will be based on experimental work done. In this study a similar economic evaluation will be conducted where different scenarios will be considered. After that a sensitivity analysis will conclude when the plant will break even and at what point a profit will be made.

3. Materials and Experimental method

3.1 Introduction

In this chapter, the materials which were used in the experiments and experimental procedures followed to successfully complete this study are explained. In Section 3.2, all of the relevant information regarding the materials and equipment used in this investigation are discussed. The experimental procedures used are discussed in Section 3.3 and the analytical methods used are listed in Section 3.4. For all the test conducted, a confidence level of 95 % was used.

3.2 Materials and equipment

3.2.1 Wood chips

The wood chips were obtained from a Sappi plant located in Ngodwana, 30 kilometres outside of Nelspruit in South Africa. The wood chips were classified as soft wood from pine trees. These wood chips underwent a number of preparation steps whereafter they were used to prepare a metallurgical coke substitute. 200 kg (+10 mm) of sample was received and used for experimentation. These woodchips were used as feedstock for a torrefaction process to produce biochar.

3.2.2 Gas

For torrefaction, nitrogen gas was used to flush the system to ensure that the experiments were conducted under inert conditions. A nitrogen cylinder, supplied by African Oxygen (Afrox) (Pty) Ltd, South Africa, was connected to a pilot scale continuous rotary kiln reactor via a gas line. The nitrogen flow was regulated using a flow meter to achieve a flow rate of 4 ℓ/min. Due to the continuous nature of the system, the nitrogen gas was supplied continuously. The gas was supplied in 11 kg cylindrical bottles.

3.2.3 Hydrogen peroxide (H_2O_2)

For the wet oxidation experiments, Hydrogen peroxide (H_2O_2) was obtained from Ace chemicals, South Africa. One concentration of hydrogen peroxide was used, namely: 30 vol % which was supplied in a glass container.

3.2.4 Scale

The wood chips were weighed using a high accuracy Mechatronic QAL-DCS4050 floor scale with a maximum capacity of 300 kg and an accuracy of 10 grams. The scale uses a 220VAC and has a built-in battery which can be recharged delivering up to 70 hours of battery life.

3.3 Experimental method

3.3.1 Sample preparation

The sample that was received from Sappi had to undergo a few preliminary preparation steps in order to prepare it as a substitute in coke production. The first step was to wash the sample to prepare it for the torrefaction process; this was needed in order to remove any extraneous debris so as to not compromise the ash yield of the wood chips. The wood chip sample, 15 – 20 kg per batch, was placed in two 100 ℓ drums which was then filled three quarters of the way with tap water. The sample and water were continuously mixed for 15 minutes to ensure the entire sample in the barrel was thoroughly rinsed, whereafter the mixed sample was left to soak for 30 minutes. After the washing process, the sample (floating) was separated from the water by means of a 1mm sieve whereafter it was spread out on a tarpaulin and left to dry for 72 – 96 hours. After air drying, the sample was placed in bags, weighed and ready for the next step. The dried sample was then subjected to the torrefaction process described below.

3.3.2 Torrefaction

In order to torrefy the large amount of sample, a pilot scale continuous rotary kiln reactor with a diameter of 0.3 m and a length of 2 m was used to produce the torrefied biomass. The torrefaction processing was done at Thermo Power furnaces South Africa located in Pretoria. The sample of biomass was fed at a rate of 20 kg/h at a residence time of 1 hour. To ensure an inert atmosphere within the reactor, nitrogen at a flow rate of 4 ℓ/min was supplied to the reactor. The optimal torrefaction temperature for soft woodchips was obtained from open literature as 280 °C. The above-mentioned torrefaction method is the same method as applied by Gouws *et al.* (2020) to torrefy the biomass used in their study.

3.3.3 Wet oxidation

The wet oxidation experiments were conducted by combining 5 grams of torrefied biomass with 50 ml of 30 % (vol %) H_2O_2. The slurry was then placed in a water bath which was kept at 80 °C using a heating plate. The glassware containing the sample was connected to a reflux condenser to prevent the evaporation of H_2O_2 due to prolonged treatment times. The torrefied biomass was wet oxidized for a total time of 30 minutes whereafter it was washed with deionised water, filtered and left to dry at 80 °C overnight. The method described is the same method as used in a study done by Maree *et al.* (2020). The conditions used were taken from Maree *et al.* (2020) as 80 °C for a treatment time of 30 minutes as these were found to be the optimal conditions.

In order to find the optimal particle size to use in the wet oxidation experiments, four different particle sizes were used namely -1mm +500 µm, -500 µm +250 µm, -250 µm +150 µm and -150 µm +75 µm. Conditions were kept the same for all four particle sizes. The Free Swelling Index (FSI) of each particle size was determined so as to choose an optimal particle size to be used for the rest of the study. This decision was made based on the FSI value together with literature (Farrokha, et al., 2020).

3.3.4 Pelletisation of biochar

The torrefied biochar which was wet oxidized, was crushed to a 100% passing a size of 75 μm and then pelletised by using a LRXplus strength tester, operating with a 5 kN load cell. The wet oxidised torrefied biochar was placed in a Specac PT 10 mm die set and compressed at a rate of 15 mm/min until a 1.5 kN load was achieved. This load was then kept on the die for 30 seconds to ensure that the sample was compressed sufficiently. Industrial coke was obtained and then machined to the same dimensions as the pelletised torrefied biochar which has been treated via wet oxidation. The pelletisation process did not make use of any form of chemical binder; 8 % water was added to the 0.5 g sample that was being pelletised in order for the sample to produce a pellet (10 x 10 mm).

3.3.5 Thermal treatment of pellets

After completion of the wet oxidation and pelletisation of torrefied biomass, the samples were subjected to thermal treatment in order to produce a coke substitute. The pellets (40 pellets at ca 0.5 g per pellet) were loaded into the tube furnace whereafter the system was flushed with nitrogen at a flow rate of 100 ml/min, to ensure an inert atmosphere. The furnace was heated at a heating rate of 10°C/min to a temperature of 900 °C. The pellets were kept isothermally at this temperature for 2 hours. The pellets were kept in the furnace until they reached room temperature whereafter they were removed. An electric tube furnace from Lenton Elite thermal systems with a programmable controller was used.

3.3.6 Characterisation

The characterisation of the samples before and after wet oxidation was done to determine the effectiveness of the pre-treatment method on the physical and chemical properties of the biochar. Characterisation of the samples after thermal treatment was also done to determine the chemical and physical properties of the produced coke substitute. To obtain the chemical and elemental composition, proximate and ultimate analysis were performed. The calorific values (CV) were determined to indicate whether the produced coke substitute has a suitable heating value. The Free swelling index (FSI) was used to determine the effect of the wet oxidation process on the plasticity of the biochar (Loison, et al., 1989). The CSR and the CSI was determined and compared to that of commercial grade metallurgical coke. The CSR was used to determine the coke quality and the CRI was used to give an indication of the physical properties such as cold mechanical strength. Table 3-1 shows the analysis method as well as the institution used for this method and what standard was used by the institution.

Table 3-1: Institution where analysis will be conducted.

Analysis	Institution	Standard
Brunauer-Emmett-Teller (BET)	NWU Coal chemistry labs	ASTM D1993
X-ray Fluorescence (XRF)	NWU Coal chemistry lab	ASTM D6247
Proximate analysis	Bureau Veritas	ISO 17246:2010
Ultimate analysis	Bureau Veritas	ISO 17246:2013
Fourier-transform infrared spectroscopy (FTIR)	NWU Coal chemistry labs	ASTM E168
Calorific value (CV)	NWU Coal chemistry labs	ISO 1928:2009
Free-swelling index (FSI)	NWU Coal chemistry labs	ASTM D720-91
Coke hot strength (CSR)	NWU Coal chemistry labs	ASTM D5341
Coke reactivity index (CRI)	NWU Coal chemistry labs	ASTM D5341M
Acid Detergent Fibre (ADF)	ARC-Analytical	ASM 060
Neutral Detergent Fibre (NDF)	ARC-Analytical	ASM 060
Acid Detergent Lignin (ADL)	ARC-Analytical	ASM 060

3.3.5.1 Brunauer-Emmett-Teller (BET) Analysis

As particles decrease in size, the ratio of the surface area to the overall volume of the particle increases. The generally accepted means of characterizing surface area is commonly referred to as “BET” surface analysis (Brame & Griggs, 2016). In 1938, the BET theory was developed by Stephan Brunauer, Paul Emmet and Edward Teller. The BET theory was an extension of the Langmuir theory which was developed by Irving Langmuir in 1916 (Hwang & Barron, 2011).

Nitrogen is mostly used in BET surface analysis due to its availability in high purity and its strong interactions with most solids. The surface of the sample is cooled using liquid nitrogen in order to obtain detectable amounts of adsorption. This is as a result of the weak interactions between gaseous and solid phases (Hwang & Barron, 2011). Afterwards known amounts of nitrogen are introduced stepwise into the sample cell. A relative pressure which is lower than atmospheric pressure is achieved by creating a partial vacuum. After saturation pressure, minimal adsorption occurs regardless of any pressure increase. Pressure changes due to the adsorption process is measured by means of highly accurate pressure transducers. After adsorption layer formation, the sample is removed from the nitrogen atmosphere and heated in order to release the adsorbed nitrogen from the surface and quantified. The data is then displayed in the form of a BET isotherm (Hwang & Barron, 2011).

The surface area and porosity properties of the sample were evaluated using a Micrometrics 3-Flex multi-port surface area and porosity analyser, using CO_2 as adsorbate. The N_2 absorption was also determined using the abovementioned equipment. Sample preparation was done by vacuum drying the samples in an oven at 90 °C for 3 hours. Whereafter representative aliquots of sample (0.5g) was loaded into the sample tubes and coupled with the multi-activity ports of the equipment. The analysis temperature (300 °C) was maintained using the Micrometrics Pro ISO Controller. The absorption data was captured automatically from the equipment and analysed on the Micrometrics Microactive v5.02 platforms, using various absorption isotherms.

3.3.5.2 X-ray fluorescence

XRF is a non-destructive, fast and accurate method that can be used on a variety of materials and sample sizes (Bouwer, 2010). With XRF, very accurate results are possible when there are good standard specimens available, but also where there are no specific standards available (Shackley, 2011). XRF analysis are cost-effective and requires only a minimum sample preparation (Bouwer, 2010).

In XRF, the sample is irradiated by x-rays produced by means of an X-ray tub or alternatively a synchrotron or a radioactive material. When the sample is irradiated by X-rays, the different elements present will emit X-ray fluorescence radiation with discrete energies characteristic for those elements (Bouwer, 2010). Each energy is different and each energy is equivalent to a different colour. XRF has a qualitative and quantitative analysis step. The qualitative analysis step is where the different energies emitted by the sample, is measured in order to determine which elements are present. The quantitative step is where the intensities of the emitted energies are measured allowing the determination of the amount of each element present (Bouwer, 2010).

An XRF spectrometer (PANalytical Axios Max) was used to determine the elemental compositions. For quantification, the intensity of characteristic lines of the element to be analysed was measured. Coal ash contains typically Fe, Al, Mg, Mn, V, Ti, Si, Ca, Na, K, P, S and Cr, which are reported as oxides by default (Fe_2O_3, Al_2O_3, MgO, MnO, V_2O_3, TiO_2, SiO_2, CaO, Na_2O, K_2O, P_2O_5, SO_4 and Cr_2O_3).

For XRF analysis, each coarse solid sample (coke and biomass particles) was initially ground to 100% passing 75 µm. The powdered sample was then calcined at 1000°C in air for 3 hours in order to remove all organic compounds and water originally contained in the sample. The calcined sample was then converted into a solid solution by fusion with lithium tetraborate: lithium metaborate (67:33) (Norrish and Hutton, 1969).

The prepared solid solution and standard (WROXI from PANalytical) were placed in the sample holders. The sample holder was then placed in the sample compartment of PANalytical Axios MAX XRF instrument. The intensity of a characteristic line of an element to be determined was measured and concentration of the element in the sample was calculated from the intensity measured.

3.3.5.3 Proximate analysis

Proximate analysis is formally determined by a series of ASTM test methods and is a determination of the moisture, volatile matter, fixed carbon (by difference) and ash yield of coal/biomass. These quantities are determined by measuring the mass loss when the sample undergoes heating at 900 °C under a nitrogen atmosphere and then held at 900 °C while the atmosphere is switched to air (Donahue & Rais, 2021). When considering biomass thermal conversion, one of the most important characterisation techniques is the proximate analysis (García, et al., 2013). Properties such as the fixed carbon, volatile matter and moisture content affect the combustion behaviour of biomass.

The moisture content is determined by the mass loss that the sample undergoes after it has been heated to 110 °C in a nitrogen atmosphere. The volatile matter of the sample corresponds to the volatile matter released between 110-900 °C under nitrogen due to thermal decomposition (Donahue & Rais, 2021). After combustion occurs, fixed carbon is the solid combustible material which remains after the loss of moisture and volatile matter without accounting for ash. The combustion reaction occurs at 900 °C (Donahue & Rais, 2021). The ash is what remains after the moisture and volatile matter is lost and the fixed carbon has undergone combustion (Donahue & Rais, 2021).

3.3.5.4 Ultimate analysis

The ultimate analysis is used to measure the percentage of elements present in the sample which includes: hydrogen, carbon, nitrogen, sulphur and oxygen (by difference). This analysis was outsourced to Bureau of Veritas where a standard ISO method (ISO 17246:2013) was used.

3.3.5.5 Fourier-transform infrared spectroscopy (FTIR)

In order to obtain the infrared spectrum of absorption, emission and photoconductivity of liquids, solids and gases an analytical technique called Fourier-transform infrared spectroscopy is used (Shameer & Nishath, 2019). FTIR is used to identify the organic, inorganic and polymeric materials by means of utilizing infrared light to scan a sample that is presented. Changes in the material composition is indicated by changes in the characteristic pattern of absorption bands (Shameer & Nishath, 2019). FTIR is a very useful tool in identifying and characterising unknown materials, detecting contaminants in a material, finding additives and identifying decomposition and oxidation. This makes FTIR an irreplaceable tool for chemical identification (Shameer & Nishath, 2019).

Major functional groups were determined by performing FTIR analyses on the coke, biomass, and thermally treated biomass using a Shimadzu IRAffinity-1 FTIR spectrometer equipped with a DLATGS pyroelectric detector. Coke, biomass and thermally treated biomass samples were crushed and mixed with potassium bromide (KBr) in a ratio of 10 wt.% sample, 90 wt.% KBr. Mixtures were loaded into metal sample cups which were mounted on a PIKE EasiDiff attachment and loaded into the FTIR apparatus for analysis. The range measured was between 3600 – 300 cm^{-1}.

3.3.5.6 Calorific Value

The calorific value is defined as the number of calories generated when a unit amount of substance is completely oxidized and is determined using a bomb calorimeter (Acar, et al., 2012). A measured amount of sample is placed in a bomb calorimeter (IKA C5003), which is a device used to measure heat and report in MJ/kg. This analysis was outsourced to Bureau of Veritas where an ASTM method D5865-12 was used.

3.3.5.7 Free swelling index (FSI)

The Free Swelling Index is one of the most robust ASTM standard tests that can assess the coke-ability of coal particles or biomass (Golzadeh, et al., 2018). The FSI test measures the increase in volume of a powdered coal sample when it is heated to a specific temperature under certain conditions. The FSI is based on ASTM D 720 where the coking capability of coal particles can be classified into three groups namely: weak (0-2), medium (>2-4) and strong (>4-9) as a standard FSI index (Golzadeh, et al., 2018). Figure 3-1 represents the free swelling index profiles.

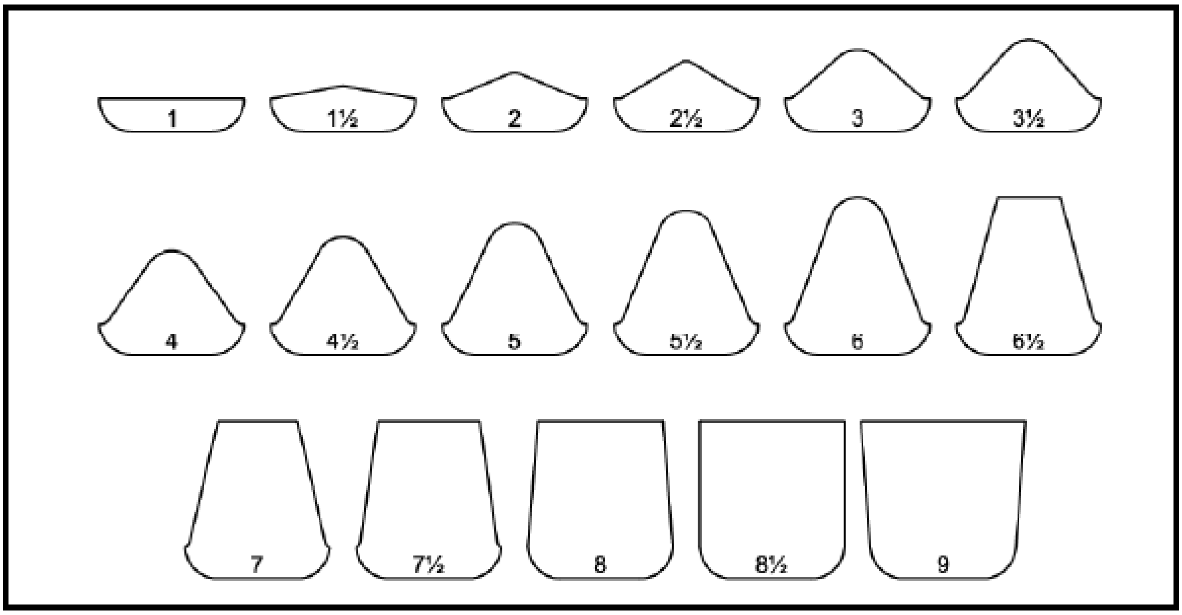

Figure 3-1: Free swelling index profiles taken from SABS (2003).

Sample (1g) was loaded into a crucible and then heated to 800 °C for 2 minutes and 30 seconds. After the samples were heated to the specific conditions, it is compared to the Free swelling index profiles shown in Figure 3-1. A higher index number is related to a higher swelling propensity, whereas the lower index numbers are related to less swelling. An index number of 1 indicates no swelling at all and refers to a coal which does not exhibit any plastic properties (Speight, 2005). The Free swelling index of coals is dependent on the fluidity of the coal together with the volatiles released during heating and the tension between the solid particles still present and the fluid particles (Speight, 2005).

3.3.5.8 Coke hot strength

Coke hot strength or mechanical strength is one of the most important qualities of blast furnace coke and is evident in all phases of the steelmaking process (Florentino-Madiedo, et al., 2020). Coke strength is generally measured by subjecting a sample of coke to standardized abuse and sizing the products on standard screens. Empirical mechanical tests, commonly used to measure resistance to size degradation, involve dynamic loading in the form of a shatter test (ASTM D3038) or by means of a revolving drum test such as the ASTM tumbler test (ASTM D3402) (Díez, et al., 2002).

According to the American Society for Testing and Materials, the coke strength after reaction is determined by subjecting the coke to a drum which is turned at 600 revolutions at 20 rev/min and then determining the percentage of +10 mm lumps of coke. The method used in this study is a method used by Botha *et al.* (2021) and Richards (1990) where a scaled down model of the tumbler test used in previous studies was used.

The scaled down tumbling test from Richards (1990) uses a variable speed motor at 80 r/min for a total of 197 revolutions. To ensure that the scaled down model is similar in terms of the mass to volume ratio as used in Richards (1990), pellets with a total weight of 17 grams (34 pellets) were tumbled. Whereafter, the fines generated were measured by sieving (6 mm) and weighing (Botha, et al., 2021). The method proposed by Botha *et al.* (2021) was used in this study, as explained above.

3.3.5.9 Coke reactivity index

The produced coke substitutes' reactivity towards CO_2 was tested using a method similar to the method used by Hilding *et al.* (2015). The reactivity experiments were conducted under isothermal conditions in a thermogravimetric analyser (TGA) (SDQT-600) as shown in Figure 3-2. The reactivity of coke is important as it is used in the blast furnace to withstand chemical and physical degradation (Díez, et al., 2002). Each sample, approximately 13 mg with a particle size of less than 300 µm, was placed in a platinum crucible whereafter it was flushed with nitrogen at a flow rate of 100 ml/min. The samples were heated to 900 °C at a heating

Figure 3-2: TGA (SDQT-600) used in the reactivity analysis.

rate of 50 °C/min. Hereafter, the reactivity was measured by introducing CO_2, at a flow rate of 10 ml/min, into the system and recording the mass loss of the samples. The samples were left isothermally in CO_2 for a minimum time of 250 minutes. The equations used to calculate the conversions, gasification rates and reactivities of the biochar derived samples were obtained from Mafu *et al.* (2018).

The fractional conversion (X) was determined using Equation (13) where the initial char mass is indicated by m_0 and the final weight after gasification is reffered to as m_f. The char at the time t is indicated by m_t. In order to the detrmine the gasification rate of biochar, Equation (14) was used.

$$X = \frac{m_0 - m_t}{m_0 - m_f} \tag{13}$$

$$r = \frac{\Delta X}{\Delta t} \tag{14}$$

Equations (15) to (17) where used to determine the average initial reactivity (R_i), the reactivity index at 50% conversion (R_{50}) and the average final reactivity (R_f).

$$R_i = \frac{\sum_{X=0\%}^{X=10\%} r}{N} \tag{15}$$

$$r = \frac{0.5}{\tau_{50}} \tag{16}$$

$$R_f = \frac{\sum_{X=70\%}^{X=90\%} r}{N} \tag{17}$$

The number of data points is indicated by N and the time required to reach 50% conversion is indicated by τ_{50}. The conversion, gasification rates and reactivities were calculated for all the thermally treated samples and pre-treated samples as well as for the commercial coke sample.

3.3.5.10 Neutral detergent fibre (NDF), Acid detergent fibre (ADF) and Acid detergent lignin (ADL)

The biomass sample was submitted to a compositional analysis in order to determine the amount of hemicellulose, cellulose, lignin and non-structural carbohydrates (wt.%). The samples were submitted to Arc-Analytical services, located in Irene, for NDF, ADF and ADL analysis. All the tests use an ASM 060 standard which is outlined in the SANAS schedule of Accreditation. The Equations used to determine the hemicellulose (wt. %), cellulose (wt. %) and lignin (wt. %) percentages were obtained from Mafu *et al.* (2016) and is shown in Equations 18-20.

$$Hemicellulose\ (wt\ \%) = NDF - ADF \tag{18}$$

$$Cellulose\ (wt\ \%) = ADF - ADL \tag{19}$$

$$Lignin\ (wt\ \%) = ADL \tag{20}$$

3.3.7 Compressive strength

The compressive strength of the thermally treated pellets together with the wet oxidised pellets were determined using a diametric compressive strength determination test on a LRXplus strength tester. The strength of each pellet was recorded in kN. The average compressive strength for 10 pellets was determined and used as the average compressive strength for that particular sample. Equation (21) was used to determine the compressive strength (kPa).

$$P(kPa) = \frac{F(N)}{A(m^2)} \times 1000 \tag{21}$$

4. Results and Discussion

In this section the results for each analysis conducted are reported and discussed as well as compared to the relevant literature. Beginning with the FSI analysis to choose a desired particle size through to a comparison between the reactivities and the coke strength after reaction. This section is concluded by a cost evaluation and sensitivity analysis of using the substitute coke compared with Industrial coke.

4.1 Free Swelling Index (FSI)

As mentioned in the previous chapter, an optimization step is needed to determine the optimal particle size of the torrefied biomass prior to wet oxidation for use in this study. In this optimization step, the crucible swelling number was used as the determining factor.

Table 4-1: Crucible swelling number for various wet oxidized biomass particle sizes.

Particle size (µm)	**Crucible swelling number**
-1000 +500	1.0
-500 +250	1.0
-250 +150	1.5
-150 +75	2.0
-75	2.0
Thermally Treated Torrefied Biomass	2.0
Thermally Treated Wet Oxidized Biomass	3.0
Coke	3.0

From Table 4-1 it can be observed that the crucible swelling number (CSN) increases as the particle size decreases. The CSN increased from 1 to 2 when the particle size decreased from -1000 +500 µm to -75 µm. This is in accordance with the findings of a study conducted by Cimadevilla *et al.* (2005) where the wet oxidation process was found to influence the plastic properties of the coal. From these results a particle size of -75 µm for the wet oxidized biomass process step was selected. This is due to the smallest particle size showing behaviour closest to that of metallurgical coke which had a CSN of 3. A higher crucible swelling number is related to a higher swelling propensity (Speight, 2005) and thus the -75 µm fraction displayed the highest coking propensity therefore being the most suitable sample size for the production of a metallurgical coke substitute. Appendix B shows a visual representation of the crucible swelling numbers of the various particle sizes used. Henceforth, when referring to wet oxidized biomass, it will be that of a -75 µm particle size.

The thermally treated samples showed an increase in the CSN (from 2 to 3) for the thermally treated torrefied biomass to the wet oxidized thermally treated biomass. When comparing these values with that of metallurgical coke, (CSN of 3), it was concluded that the wet oxidation process increases the CSN and thus is a suitable pre-treatment method (Cimadevilla, et al., 2005).

4.2 Ultimate Analysis

The ultimate analysis results of the biomass sample before torrefaction, after torrefaction and after wet oxidation together with that of Industrial coke are shown in Table 4-2 on a dry-ash-free basis. The raw biomass refers to the biomass before any pre-treatment processes. The torrefied biomass was pre-treated by means of torrefaction at 280 °C. The wet oxidized biomass relates to biomass which underwent torrefaction followed by wet oxidation.

Table 4-2: Ultimate analysis (wt. %) of Raw biomass, Torrefied biomass, Wet oxidized biomass. Thermally treated biomass and Coke.

Sample Identification	**Carbon (d.a.f.)**	**Nitrogen (d.a.f.)**	**Hydrogen (d.a.f.)**	**Sulphur (d.a.f.)**	**Oxygen (difference)**
Raw Biomass	46.9	0.01	6.0	0.1	37.6
Torrefied Biomass	55.5	0.1	5.3	0.1	29.9
Wet Oxidized Biomass	51.1	0.1	5.5	0.03	16.2
Thermally Treated Torrefied Biomass	86.9	0.2	0.5	0.1	12.4
Thermally Treated Wet Oxidized Biomass	91.6	0.2	0.6	0.1	7.5

Coke	61.9	0.9	0.1	0.7	36.5

From Table 4.2 it can be observed that the carbon content of the biomass increased from 47% to 56% as a result of the pre-treatment (torrefaction) process. This is in accordance with the findings by Ueki *et al.* (2014) which indicated an increase in the carbon content of woody biomass when carbonised at various temperature (300 - 1000°C). When comparing the raw biomass with the wet oxidized biomass, it can be seen that the carbon content increased from 47% to 51%, but decreased when compared with that of the torrefied biomass (56%). This corresponds with the findings reported by Cimadevilla *et al.* (2005) in a study done on two medium volatile bituminous coals used in the production of blast furnace coke where it was found that the oxidation of samples showed a decrease in carbon content from 89.5 wt.% to 88.0 wt.%. This reduction in carbon content was ascribed to a decrease in the volatile matter content and an incremental increase in oxygen when subjected to oxidation (Cimadevilla, et al., 2005). This is believed to be due to mild oxidation (low temperature and short oxidation time). When referring to the thermally treated samples (wet oxidized and torrefied), both showed a significant increase in the carbon content, with the thermally treated wet oxidized biomass displaying the highest carbon content (91.6 wt.%). This is in accordance with results reported by Fisher *et al.* (2012) where pyrolysis at a 1000 °C drastically increased the carbon content of torrefied biomass. The thermally treated wet oxidized biomass carbon content falls within the acceptable range for coke prescribed by Díez et al (2002). This is also in accordance with results reported by Maree *et al.* (2020) where it was reported that a decrease in volatile matter and carbon content and an increase in oxygen content were observed for samples treated by wet oxidation before thermal treatment.

The sulphur content for all the biomass samples was less than 0.5 wt. %. This is in accordance with industry standards which states that coke used should have a sulphur content of <1 wt. % (Díez, *et al.*, 2002; Leonard, *et al.*, 1996). The thermally treated samples showed no change in the sulphur content and thus meets the industry standard for coke (Díez, et al., 2002). The biomass treated by torrefaction showed a reduction in hydrogen content from 6 wt.% to 5.3 wt.%, together with a reduction in the oxygen content from 37.6 wt.% to 29.9 wt.%. The torrefied biomass displayed an increase in nitrogen content from 0.01 wt.% to 0.1 wt.%. This is in accordance with results reported by Fisher et al (2012) where severe torrefaction (280 – 300 °C) was conducted on biomass and a reduction in the hydrogen content together with an increase in the nitrogen content after torrefaction was reported. The wet oxidized biomass showed a reduction in hydrogen (6 wt.% to 5.5 wt.%) and oxygen content (37.6 wt.% to 16.2

wt.%) and an increase in nitrogen (0.01 wt.% to 0.1 wt.%). The thermally treated biomass samples showed a reduction in both the hydrogen and oxygen contents.

4.3 Proximate Analysis

The proximate analysis results of the various biomass samples before pre-treatment, after pre-treatment and after thermal treatment are shown in Table 4-3. The raw biomass is the biomass before any pre-treatment processes. The torrefied biomass was pre-treated by means of torrefaction. The wet oxidized biomass is biomass which was submitted to torrefaction together with wet oxidation. All of the results are reported on an air-dried basis (a.d).

Table 4-3: Proximate analysis (wt. %) of Raw biomass, Torrefied biomass, Wet oxidized biomass. Thermally treated biomass and Coke.

Sample Identification	**Moisture (a.d.)**	**Volatile matter (a.d.)**	**Ash (a.d.)**	**Fixed Carbon (a.d.)**
Raw Biomass	11.5	84.9	0.1	3.5
Torrefied Biomass	7.3	62.9	1.7	28.0
Wet Oxidized Biomass	0.9	70.4	1.5	27.2
Thermally Treated Torrefied Biomass	1.1	2.6	7.6	88.7
Thermally Treated Wet Oxidized Biomass	0.7	2.6	4.3	92.4
Coke	0.3	1.4	16.1	82.2

In order for coke to be used in a blast furnace, it has to adhere to certain properties which is mostly related to the proximate analysis (Díaz-Faes, *et al.*, 2007). By comparing these properties of the biomass/biochar with those of coke, it can be observed as to whether the chemical properties of the biomass processing are suitable to produce a metallurgical coke replacement. Leonard *et al.* (1996) reported that the ash yield (wt.%) of blast furnace coke should be in the range of 8-12 %. The raw biomass showed an ash yield (wt.%) of 0.1 %. This increased, from 0.1 % to 1.7 %, as the raw biomass was subjected to torrefaction. Furthermore, the ash yield (wt.%) decreased from the torrefied biomass to the wet oxidized biomass from 1.7 wt. % to 1.5 wt. % which are as a result of reactions between mineral matter present and the hydrogen peroxide (Maree, et al., 2020). Díaz-Faes *et al.* (2007) stated that the ash yield of blast furnace coke should be low since a high ash yield would result in extra energy required in order to melt the ash forming mineral matter, which will decrease the productivity in the blast furnace. The raw biomass, torrefied biomass and wet oxidized biomass all reported low ash yields and thus biomass will be beneficial in producing a metallurgical coke replacement as less energy will be required to melt the ash in the blast furnace leading to an increase in the productivity (Díaz-Faes, et al., 2007). Overall, when the ash yield increased by 1 wt. % that metal production was reduced by 2 to 3 wt. % (Díez, *et al.*, 2002). The torrefied and wet oxidized samples which were subjected to thermal treatment reported a slightly higher ash yield, but still falls within the range needed for coke production (Díaz-Faes, et al., 2007). The thermally treated torrefied biomass had an ash yield of 7.6 wt. % and the thermally treated wet oxidized biomass has an ash yield of 4.3 wt. %. These values are much lower than that of Industrial coke used in this study (16.1 wt. %). This entails that the thermally treated biomass has the potential to decrease the energy used in the blast furnace. This also indicates that when substituting the blast furnace coke with biomass the productivity of the blast furnace will be four times higher than when using coke (Díez, et al., 2002).

Díez et al (2002) reported that the coking coal used to produce blast furnace coke needs to have a moisture content in the range of 1-6 wt.% as handling of the coal becomes a problem as a result of a too high moisture content. The produced torrefied biomass has a moisture content of 7.3 wt.% which is over the desired range. The wet oxidized biomass on the other hand is within this range and is acceptable to be used as a metallurgical coke replacement with a moisture content of < 2 wt.%. As expected, the thermal treating process further lowered the moisture content of the wet oxidized sample to 0.7 wt.%. This will have a positive effect on the handling of the biomass (Leonard, et al., 1996).

The fixed carbon content (wt.%) of the biomass was increased by torrefaction from 3.5 wt.% to 28 wt.%. Similar results were reported in a study conducted by Chen *et al.* (2015) where torrefaction was employed on various biomass samples. Chen *et al.* (2015) also reported the fixed carbon content of torrefied biomass in the range of 13 – 45 wt.%. The fixed carbon content of the torrefied sample in this study is also within this range (28 %). The fixed carbon content however only slightly decreased from the torrefied biomass to the wet oxidized biomass from 28 wt. % to 27.2 wt. %. Maree *et al.* (2020) also reported a decrease in the fixed carbon content with an increase in wet oxidation time and temperature on HTL derived spent coffee ground biochar. In this study, the thermally treated samples showed a significant increase in the fixed carbon content, which was expected. The thermally treated torrefied biomass had an increase in fixed carbon content to 88.7 wt.% and the thermally treated wet oxidized biomass increased to 92.4 wt.% fixed carbon. This is confirmed by results reported in a study conducted by Fisher *et al.* (2012) where the fixed carbon content of biomass increased after charring at 1000 °C.

Díaz *et al.* (2002) reported that metallurgical coke should contain a volatile matter content of less than 1 wt.%. As expected, the raw biomass had a high volatile matter content at 84.9 wt.% which is unsuitable as a reducing agent. The volatile matter decreased when torrefied to 62.9 wt.%, whereafter it increased after wet oxidation to 70.4 wt.%. This is in accordance with results reported by Maree *et al.* (2020) where the volatile matter of biochar increased when subjected to the wet oxidation process. As expected, the thermally treated samples showed a large decrease in volatile matter content. These results are confirmed by Maree *et al.* (2020) who also reported a significant decrease in the volatile matter content when the biochar derived from spent coffee grounds was thermally treated. The thermally treated torrefied biomass volatile matter content decreased to 7.6 wt.% and the thermally treated wet oxidized biomass decreased to 4.3 wt.%. This is still slightly higher than the acceptable volatile matter content (Díez, et al., 2002). According to Valia (2005) coke is produced at a temperature of 1300 °C, but the biomass was thermally treated in this study at 900 °C. The temperature difference might be the reason for the volatile matter content of the thermally treated biomass being higher than that of metallurgical coke specification prescribed by Díez *et al.* (2002).

4.4 Gross Calorific Value

South African coals generally have a gross calorific value of approximately 30 MJ/kg (Loison, et al., 2014). Even though the general calorific value of coal is available it is not considered as a determining physical property when identifying an acceptable coking coal (Díez, et al., 2002). Table 4-4 shows the gross calorific values obtained for the raw biomass (MJ/kg), the torrefied biomass (MJ/kg), the wet oxidized biomass (MJ/Kg) and the thermally treated biomass (MJ/kg). Lioson *et al.* (2014) reported that the oxidation process does not affect the calorific value of coal, which is in agreement with these findings. The calorific value of the raw biomass was significantly improved by thermal treatment from 17.9 MJ/kg to 30.9 for the thermally treated torrefied biomass and to 32.4 MJ/kg for the thermally treated wet oxidized biomass. This is in accordance to a similar study conducted by Maree *et al.* (2020) where it was reported that the pyrolysis of biomass increased the calorific value. The thermally treated wet oxidized biomass displayed the highest calorific value (32.4 MJ/kg) and falls within the range of acceptable coal to produce coke for blast furnace use (Loison, et al., 2014). This indicates that the woody biomass might be acceptable to produce a metallurgical coke substitute.

Table 4-4: Gross Calorific values of raw biomass, torrefied biomass, wet oxidized biomass and thermally treated samples.

Sample Identification	Gross Calorific Value (MJ/kg)
Raw Biomass	17.9
Torrefied Biomass	21.8
Wet Oxidized Biomass	21.4
Thermally Treated Torrefied Biomass	30.9
Thermally Treated Wet Oxidized Biomass	32.4
Coke	25.1

4.5 Compressive Strength

The compressive strength of coke is important as it ensures gas and liquid permeability in the blast furnaces used when combusting coke. Table 4-5 shows the compressive strength (MPa) results obtained for the wet oxidized biomass, torrefied biomass, thermally treated biomass and industrial coke. It can be observed that the compressive strength of the torrefied biomass increased as it was wet oxidized from 18.1 MPa to 40.2 MPa. This is in accordance with results reported by Maree *et al.* (2020) where it was reported that the compressive strength of spent coffee grounds derived biochar from hydrothermal liquefaction increased when subjected to the wet oxidation process. This is confirmed by a study conducted by Sun *et al.* (2014) where it was reported that the wet oxidation process increased the compressive strength of biochar. The wet oxidized biomass showed a significant decrease in compressive strength after thermal treatment (92 % decrease) with the torrefied biomass also showing the same behaviour (92 % decrease). The coke sample recorded a very low compressive strength of 0.6 MPa. In a study done by Amanat *et al.* (2009), the compressive strength of metallurgical coke was reported as 22 MPa. One of the reasons for this study's coke sample having a low compressive strength might be as a result of the coke lumps being pulverized to -75 µm and then pelletised into 10 mm pellets using no binder or adhesive. In the coke strength after reaction section (section 4.10) this will be discussed in more detail.

Table 4-5: Compressive strength of various biomass, thermally treated biomass and coke sample.

Sample Identification	Compressive Strength (MPa)
Torrefied Biomass	18.1 ± 0.1
Wet Oxidized Biomass	40.2 ± 1.1
Thermally Treated Torrefied Biomass	1.3 ± 0.02
Thermally Treated Wet Oxidized Biomass	3.1 ± 0.1
Coke (lumps)	1.8 ± 0.1
Coke (pellet)	0.6 ± 0.01

4.6 FTIR

Figure 4-1 shows the Fourier-transform infrared spectroscopy results of the raw biomass, torrefied biomass, wet oxidized biomass (wet oxidized), thermally treated torrefied biomass (TT Torrefied) and the thermally treated wet oxidized biomass (TT Wet Oxidized).

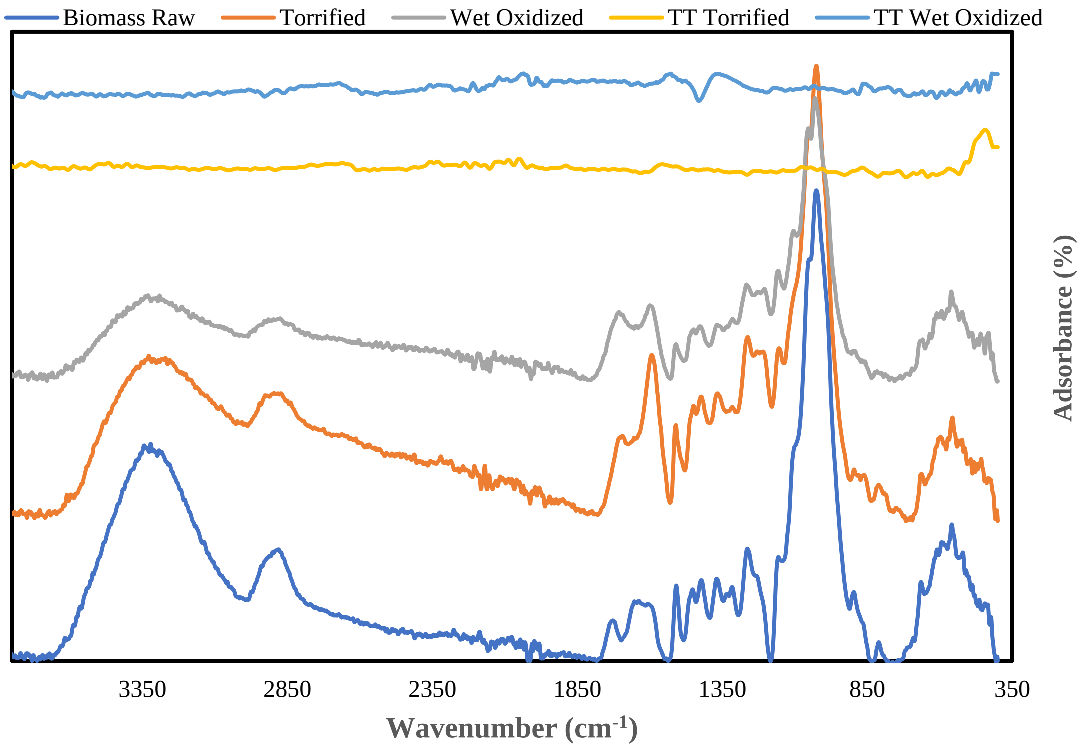

Figure 4-1: Fourier-transform infrared spectroscopy of various biomass samples.

The broad band between 2800 to 3350 cm^{-1} indicates the vibration modes attributed to the C-H functional groups (Ren, et al., 2018). These C-H functional groups are present in the raw biomass, torrefied biomass and the wet oxidized biomass, but are absent for the thermally treated samples. This is in accordance with results reported by Ren *et al.* (2018) who reported that the C-H functional groups are released during pyrolysis in typical gaseous products such as CO, CO_2 and CH_4. The stretching vibration peak of carbonyl and the bending vibration peak in the C-H plane was observed at 1800 to 1750 cm^{-1} (Ren, et al., 2018). The skeleton vibration peaks of C-O functional groups and C-C functional groups are visible in the wavenumber range of 1400 to 1300 cm^{-1} and the stretching vibration peaks of C-C can be seen at 664 to 670 cm^{-1}. Whilst the benzene ring stretching vibration peaks were present in the 600 to 1500 cm^{-1} range (Ren, et al., 2018). This is evident in the raw biomass, torrefied biomass and the wet oxidized biomass, but absent in the thermally treated samples. This is in accordance with a study done by Ren *et al.* (2018) who reported that when pyrolysis occurs the breakage of C-

H and C-O bonds appears, respectively, which corresponds with the formation of general gases.

4.7 Thermogravemetric analysis TG/DTG

The TGA and DTG analysis was done according to the method described in chapter 3. Figure 4-2 shows the results obtained for the TGA and DTG of raw biomass, torrefeid biomass and wet oxidized biomass samples.

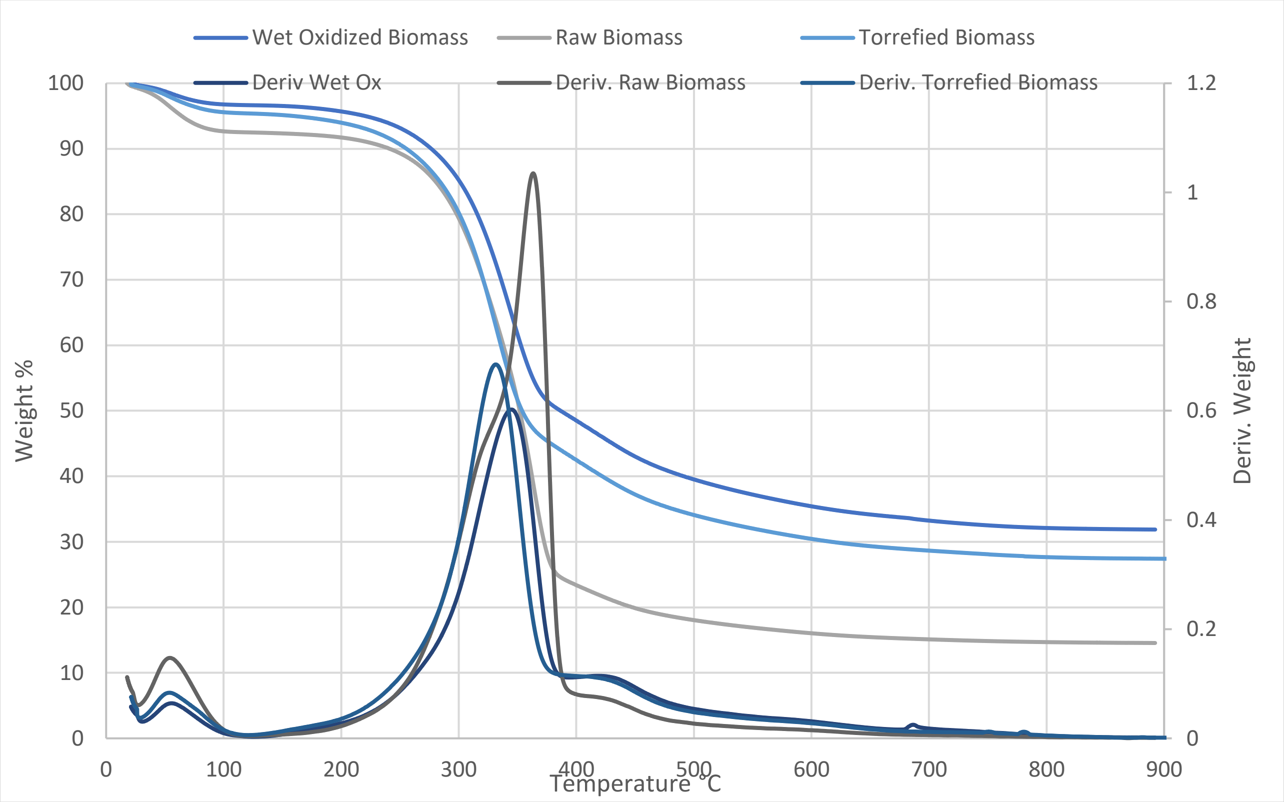

Figure 4-2: TGA and DTG of Raw biomass, torrefied biomass and wet oxidized biomass.

From the DTG results, 3 peaks were observed, with the most significant peak observed 200 – 400 °C; this peak region showed the main degradation phase, which accounts for 80% mass loss of the raw biomass, torrefied biomass, and wet oxidized biomass. All the samples showed a slight degradation peak at 53 ^{o}C; this peak region was attributed to the loss of moisture in the biomass samples. The DTG of the raw biomass sample shows a typical left shoulder in the range of 220 – 300 °C, which is commonly

attributed to the degradation of hemicellulose within the biomass. This is in accordance with results reported by Carrier *et al.* (2011). The main peak for the raw biomass is observed in the range of 330 – 380 °C, which corresponds with the degradation of cellulose, while the third peak, 380 – 600 °C, corresponds to the degradation of the lignin, (Carrier, et al., 2011). When comparing the DTG curves of the torrefied and wet oxidized biomass with that of raw biomass, clear differences in the lignocellulosic content can be observed. The DTG result of the raw biomass demonstrates a left shoulder which corresponds with the degradation of hemicellulose; this left shoulder is absent in the DTG of the torrefied and wet oxidized biomass samples, which suggest a significant reduction in the hemicellulose content in the torrefied and wet oxidized biomass. This is in accordance with findings by Chen *et al.* (2015); in their study, they reported the degradation of hemicellulose when samples are subjected to severe torrefaction. These results are in agreement with results reported in other studies (Mafu, et al., 2016). Shang *et al.* (2012) also reported a decrease in the hemicellulose content of biomass after torrefaction at 230 – 300 °C. The study as mentioned above, verifies the absence of the left shoulder for the DTG curve of the torrefied biomass, which corresponds with the degradation of hemicellulose.

The maximum mass loss of the wet oxidation treated samples was observed to be lower when compared to the torrefied and the raw biomass samples. The remaining mass percentage of the raw biomass was found to be 14.5%, while those for the torrefied biomass and wet oxidation treated samples were observed to be 27.5% and 32.0%, respectively.

4.8 Compositional analysis (ADF, ADL & NDF)

Table 4-6 shows the compositional distribution (cellulose, hemicellulose and lignin) of the raw biomass, torrefied biomass, wet oxidized biomass and their thermally treated constituents together with that of metallurgical coke.

Table 4-6: Hemicellulose, cellulose and lignin content (wt.%) of samples.

Sample Identification	**Hemicellulose**	**Cellulose**	**Lignin**
Raw Biomass	0.08	63.5	25.7
Torrefied Biomass	0	34.6	42.9
Wet Oxidized Biomass	1.24	43.4	30.4
Thermally Treated Torrefeid Biomass	7.25	0.05	92.02
Thermally Treated Wet Oxidized Biomass	3.41	0	97.12
Coke	0.25	2.84	83.45

The thermally treated wet oxidized biomass displayed the highest amount of lignin at 97 wt. % followed by the thermally treated torrefied biomass at 92 wt. %. The torrefied biomass displayed 42.9 wt. % lignin and the wet oxidized biomass showed 30.4 wt. % lignin content. The raw biomass displayed 25.7 wt. % lignin which corresponds with the range (25 - 55 wt.%) reported in literature for soft wood (Mafu, et al., 2016). The lignin content of the raw biomass increased from 25.7 wt. % to 42.9 wt. % when torrefied. The hemicellulose content of the raw biomass decreased from 0.08 wt. % to 0 wt. % after torrefaction and the cellulose content decreased from 63.5 wt. % to 34.6 wt. % (46 % reduction). These findings are in accordance with literature where Chen *et al.* (2015) reported that after severe torrefaction, that hemicellulose is almost completely depleted and cellulose is oxidized to a great extent and lignin is the recalcitrant constituent to be thermally degraded and thus its consumption through torrefaction is extremely low. The increase in the lignin content from raw biomass to torrefied biomass was reported by Park *et al.* (2013), who concluded that this is due to the rearrangement of the sample matrix into compounds or bonding structures, which are resistant to acid hydrolysis.

~~Cellulose and hemicellulose are the main constituents of biomass~~ (Chen, et al., 2015). By substantially removing cellulose and hemicellulose from the biomass, the weight and energy yield of the fuel are usually lowered although the energy density is greatly intensified (Chen, et al., 2015). This is in agreement when observing the cellulose and hemicellulose content for all samples. The thermally treated torrefied biomass showed a low hemicellulose content at 7.25 wt. % together with a low cellulose content of 0.05 wt. %. The thermally treated wet oxidized biomass also reported low hemicellulose and cellulose contents at 3.4 wt. % and 0 wt. %, respectively. This is all in accordance with literature where it is reported that substantially decreasing the cellulose and hemicellulose content significantly increases the energy density of the fuel as can be seen in Table 4-4 (Chen, et al., 2015).

4.9 BET

Table 4-7 shows the results of the CO_2 adsorption results of the surface analysis together with the N_2 adsorption analysis results for the raw biomass, torrefied biomass, the thermally treated torrefied biomass, the thermally treated wet oxidized biomass and the Industrial coke.

Table 4-7: Summary of the Surface analysis of the biomass and coke sample.

CO$_2$ adsorption data			
	D-R micropore surface area (m^2/g)	Pore Volume (cm^3/g)	Average pore diameter (Å)
Raw Biomass	48.7	0.01	4.2
Torrefied biomass	71.8	0.02	4.0
Wet Oxidized biomass	67.3	0.02	4.0
Thermally Treated Torrefied Biomass	401.9	0.21	3.7
Thermally Treated Wet Oxidized biomass	435.5	0.25	3.7
Coke	20.9	0.02	3.9
N$_2$ adsorption data			
	BET surface area (m^2/g)	Pore volume (cm^3/g)	
Raw Biomass	0.3	0.00006	
Torrefied biomass	1.3	0.0003	
Wet Oxidized biomass	1.0	0.0002	
Thermally Treated Torrefied Biomass	421.9	0.04	
Thermally Treated Wet Oxidized biomass	327.1	0.03	
Coke	8.8	0.002	

The total surface area (D-R micropore model) results range from 20.9 to 435.5 m^2/g, the pore volume ranges from 0.01 to 0.25 cm^3/g and the average pore diameter ranges from 3.7 to 4.2

Å. From the results obtained for the D-R micropore surface area conducted under CO_2 condition it was observed that the thermally treated wet oxidized biomass showed the highest surface area and decreased in the following order: thermally treated wet oxidized biomass > thermally treated torrefied biomass > torrefied biomass > wet oxidized biomass > raw biomass > coke. Theoretically, a larger surface area provides more reaction sites for a chemical reaction to occur and thus promotes gasification rates (Zhang, 2019). Ishii (2000) reported that when using a coke with a higher reactivity (higher surface area), the degradation of the coke can be prevented as the gasification reactions are limited to the surface of the coke and thus leaving the stability of the coke intact. The surface area results indicates that the thermally treated biomass samples should be a sufficient metallurgical coke substitute. The pore volume under CO_2 condition showed a decrease in the following order: thermally treated wet oxidized biomass > thermally treated torrefied biomass > wet oxidized biomass > torrefied biomass > coke > raw biomass. This is in accordance with a study done by Thanapal *et al.* (2014), where it was reported that torrefied biomass showed an improved grindability which are linked to an increase in the number of pores of the biomass. The average pore diameter was constant for all samples with only a slight decrease observed from the raw biomass to the torrefied biomass (4.2 to 4.0 Å). No change in the average pore diameter from the torrefied biomass to the wet oxidized biomass was observed. Both the thermally treated torrefied and wet oxidized biomass showed an average pore diameter of 3.7 Å. Coke showed an average pore diameter of 3.9 Å. This average pore diameter is in accordance with literature where it is reported that the average pore diameters' influence on the reactivity of the coke is overshadowed by other factors such as ash yield (Zhang, 2019).

Under the N_2 conditions, the surface area decreased in the following order: thermally treated torrefied biomass > thermally treated wet oxidized biomass >coke > torrefied biomass > wet oxidized biomass > raw biomass. The pore volume decreased in the order: thermally treated torrefied biomass > thermally treated wet oxidized biomass > coke > torrefied biomass > wet oxidized biomass > raw biomass. The reported results under N_2 conditions are in accordance with the results reported under CO_2 conditions together with that of literature (Zhang, 2019).

4.10 CSR

One of the most important indicators for assessing the quality of coke for blast furnace application is the coke strength after reaction (CSR) (MacPhee, et al., 2013). Table 4-8 shows the CSR results obtained for torrefied biomass, wet oxidized biomass, thermally treated samples and Industrial coke. All these values were determined as described in section 3.3.5.8.

Table 4-8: Coke strength after reaction for various biomass samples.

Sample Identification	CSR (%)
Torrefied Biomass	93.1 ± 0.9
Wet Oxidized Biomass	97.3 ± 0.5
Thermally Treated Torrefied Biomass	95.8 ± 0.1
Thermally Treated Wet Oxidized Biomass	97.3 ± 0.2
Coke (pellets)	0.4 ± 0.2
Coke (lumps)	92.9 ± 0.6

It can be observed that all the biomass samples reported a CSR index greater than 90% with the wet oxidized biomass and thermally treated wet oxidized biomass displaying the highest CSR index of 97.3%. These reported values are all within the required range of coke used in a blast furnace, which should have a CSR index above 60% (Díez, et al., 2002). The CSR index of the thermally treated sample shows results which are similar to values reported in literature. Schwarz *et al.* (2015) conducted a study on the usage of biomass for coke making and reported CSR values for various biomass samples in the range of 60 – 70%. However, Schwarz used a model which predicts the CSR index using the CRI index of the sample. It was also reported that some biomass samples with a higher reactivity showed a CRI value out of the desired range and the model used was unable to predict the CSR value of biomass with a high reactivity. The values reported in this study were determined by means of a miniature tumbler test (Botha, et al., 2021). The coke pellets yielded a CSR index of less than 60%, whilst the lump coke yielded values of above 60%. The lump coke's reported value is in accordance with values in literature (Díez, et al., 2002). When comparing the CSR of the coke pellets and the lump coke it is noted that the pellets have a much lower CSR at 0.4 % whilst the coke lumps have a CSR of 92.9 % which is in the desired range. In section 4.5, the compressive strength of pelletised Industrial coke was reported outside of the desired range. The CSR comparison between the coke pellets and the lumps shows that the pelletisation of the -75 µm particles has an influence on the compressive strength. This is not currently understood and further studies are needed to better understand the reason for this phenomenon. The CSR test indicated error percentages below 1 % for all samples, concluding that the tests are repeatable.

4.11 CRI

Figure 4-3 shows the mass loss curves at 900 °C in a CO_2 atmosphere for the thermally treated torrefied biomass, the thermally treated wet oxidized biomass and the Industrial coke sample. Where TT Torrefied represents the thermally treated torrefied biomass and TT Wet Oxidized represents the thermally treated wet oxidized biomass.

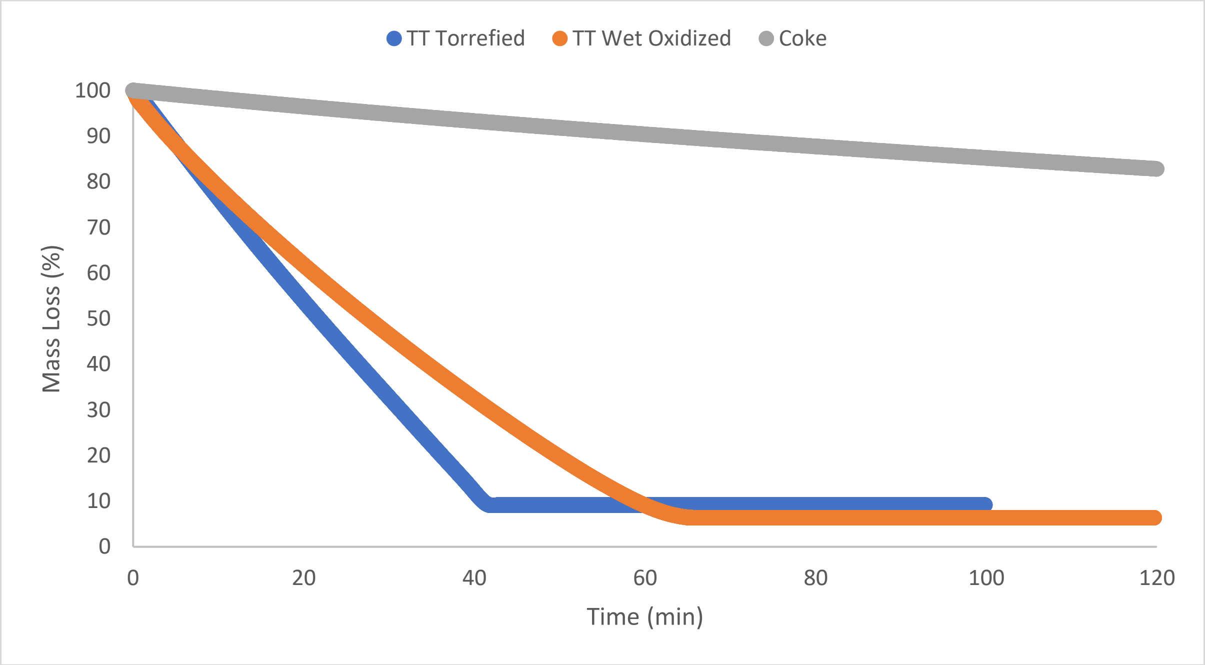

Figure 4-3: Mass loss curves at 900 °C in a CO_2 atmosphere for the coke, thermally treated torrefied biomass and the thermally treated wet oxidized biomass.

Figure 4-4 shows the fractional conversion curves at 900 °C in a CO_2 atmosphere for the thermally treated torrefied biomass, the thermally treated wet oxidized biomass and the coke sample. Where TT Torrefied represents the thermally treated torrefied biomass and TT Wet Oxidized represents the thermally treated wet oxidized biomass.

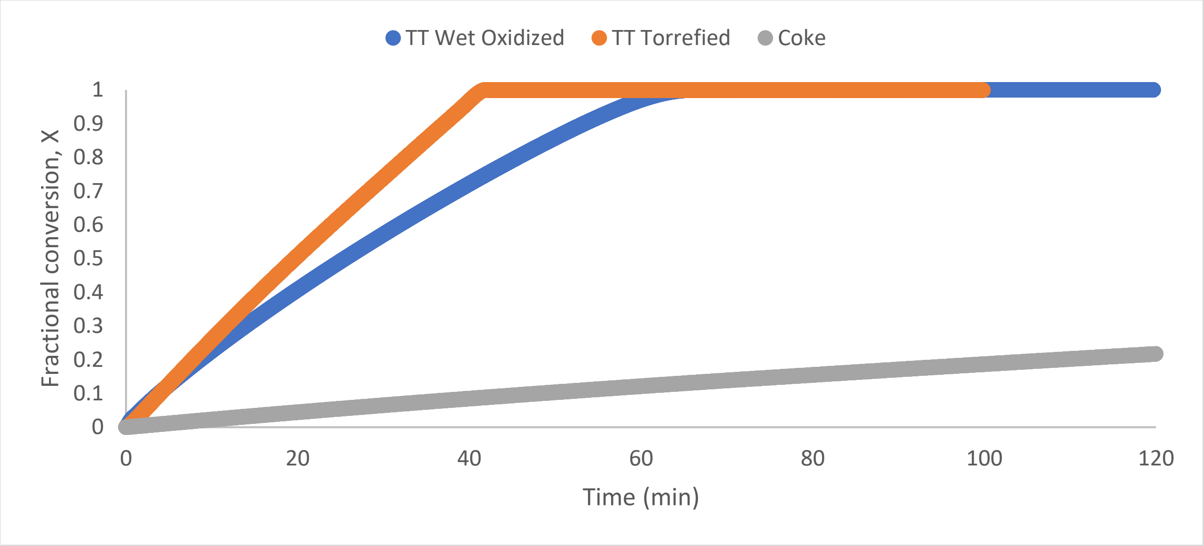

Figure 4-4:Fractional conversion curves at 900 °C in CO_2 atmosphere for the thermally treated torrefied biomass, the thermally treated wet oxidized biomass and the coke sample.

From Figure 4-4 it can be observed that both the thermally treated biomass samples showed a significantly faster conversion rate than that of the coke sample. When comparing the conversion rate of the two thermally treated biomass samples it is noted that the thermally treated torrefied biomass showed a faster conversion rate than that of the thermally treated wet oxidized biomass; *i.e.*, the torrefied sample reaches 100 % conversion after 42 minutes and the wet oxidized sample achieves the same conversion after 65 minutes. This result is in accordance with a study done by Wang *et al.* (2016) where it was reported that biomass (soft wood) had a significantly faster conversion rate than metallurgical coke. Maree *et al.* (2020) reported similar results where spent coffee grounds showed a faster conversion rate than coke.

Table 4-9 shows the reactivity towards CO_2 for the thermally treated torrefied biomass, the thermally treated wet oxidized biomass and the coke sample. The reactivities were obtained as described in section 3.3.5.9.

Table 4-9: Reactivity towards CO_2 for the thermally treated torrefied biomass, the thermally treated wet oxidized biomass and the coke sample.

Sample Identification	**Reactivity (min^{-1}) ($x10^4$)**		
	$R_{i,ave}$	R_{50}	$R_{f,ave}$
Thermally treated torrefied biomass	100.8	254.2	227.1
Thermally treated wet oxidized biomass	107.1	196.1	132.4

Coke	8.4	14.5	21.2

It can be observed from Table 4-9 that the final reactivities of the samples decreased in the order: thermally treated torrefied biomass > thermally treated wet oxidized biomass > coke. The thermally treated torrefied biomass reported a reactivity of 227.1 x 10^4 min^{-1} and the thermally treated wet oxidized biomass showed a reactivity of 132.4 x 10^4 min^{-1} and finally, the coke yielded a reactivity of 21.2 x 10^4 min^{-1}. In literature, it is stated that it is important for coke to have a low reactivity towards CO_2 (Díez, et al., 2002). Thus, a substitute coke replacement derived from biomass should have a reactivity similar to that reported for coke, which is in the range of 20 – 30 x 10^4 min^{-1} (Díez, et al., 2002). When comparing the biomass reactivity with that of coke it is observed that the biomass has a higher reactivity towards CO_2 than coke. This is in accordance with a study done by Wang *et al.* (2016a) where it was reported that biomass (soft wood) showed a significantly larger reactivity towards CO_2 than coke. This is due to the chemical and physical properties of biomass such as pore volume, surface area, ash yield and crystalline structure. Coke particles have a compact structure and intact surface, whereas biomass has a completely different microstructure (Wang, et al., 2016). From the BET results reported in Section 4.9, it was noted that biomass derived coke has greater micro and meso porosity when compared to Industrial coke. In addition, biomass particles retain the porous fibre structures from their parental biomass (Wang, et al., 2016). The larger surface area of biomass reported in section 4.9 also contributes to the larger reactivity of biomass which is in accordance with literature (Wang, et al., 2016). Typical CRI values for bituminous coal are reported as 30 -60 wt. % (Pusz & Buszko, 2012).

Considering the relationship between CRI and CSR, Lyalyuk *et al.* (2010) conducted a study on the effects of coke reactivity on the parameters of blast furnace operation. It was reported that as the CRI (wt. %) value of the blast furnace coke increases the CSR (wt. %) decreases in a linear fashion. It was also reported that this differs as a result of the geological orientation of the coal. When looking at the CRI and CSR values of the biomass used in this study, it was concluded that as the CRI values decrease from the thermally treated torrefied biomass to that of thermally treated wet oxidized biomass as the CSR values showed a slight increase. This is in accordance with the results reported by Lyalyuk *et al.* (2010).

4.12 Cost Evaluation

In order to compare the economic viability of various scenarios, four key parameters have been considered namely, the price of pre-treated biomass delivered, the price of the delivered coke, the replacement ratio of biomass and the cost of CO_2 (carbon tax) (Fick, et al., 2014).

The first three parameters are readily available in literature. Table 4-10 shows the value for each parameter together with a reference. All the values in Table 4-10 have been adjusted with an inflation percentage of 4.50 % for each year needed tuntil 2021.

Table 4-10: Parameters used in the cost evaluation.

Parameter	Value	Reference
Price of pre-treated biomass delivered	8471.50 R/t	(Fick, et al., 2014)
Price of delivered coke	7787.7 to 8861.8 R/t	(Fick, et al., 2014)
Replacement Ratio	50 % 30 % 10 %	-
Cost of CO_2	R48 /t R68 /t R120 /t	(Alton, et al., 2014)

Fick *et al.* (2014) only used one pre-treatment method namely torrefaction. In order to ascertain the price from literature more applicable to this study, an additional cost of 20 % was added to the reported cost from Fick *et al.* (2014). This was done to compensate for the wet oxidation process that was included in this study. The price of coke fluctuates due to the market stability (Fick, et al., 2014). It was decided that a comparison is needed for the three different replacement ratios in order to show which scenario will be the most economical. It is important to note that a replacement ratio of 30% indicates that 30% coke and 70% biomass derived substitute coke will be used. Carbon tax is an ever-increasing cost, but it was decided to use the carbon tax that is currently (2021) applicable to South Africa (Alton, et al., 2014). The carbon tax has three separate values indicated as each one of these has a specific replacement ratio that will be paired with it, in chronological order. The R48/t is paired with the 50% replacement ratio and so forth.

In order to complete the cost evaluation, a few assumptions had to be made. The assumptions made for the cost evaluation was as follows:

- In order to estimate the amount of CO_2 emitted, the carbon balance will only be done over the iron plant. This section includes only the blast furnace and sintering plant (Fick, et al., 2014).
- Production of biogenic CO_2 was not included in the calculations (Fick, et al., 2014).
- Used a fixed carbon tax for the plant considering three different scenarios linked to the replacement ratios.
- Assume that the price for pre-treated biomass already has a transportation fee included (Fick, et al., 2014).
- Assume three replacement ratios that will be used, namely 50%, 30% and 10%.
- Only calculating the cost of the blast furnace operation for the cost of one ton of liquid iron produced (Fick, et al., 2014).
- The lower ash yield of the biomass compared to Industrial coke improves the productivity of the blast furnace. This benefit was not taken into account in the economic evaluation.
- Assume no increase in productivity with the use of biomass.

In order to calculate the extra cost associated with the production of one ton of liquid iron, by substituting coke with biomass, the following equation proposed by Fick *et al.* (2014), was used.

$$Cost = SR \times CI \times \left(\frac{P_{biomass}}{RR} - P_{Fuel} - P_{CO2} \times EF_{Fuel} \right) \tag{22}$$

Where SR represents the substitution ratio, CI is the coal/coke input and RR is the replacement ratio of biomass. $P_{biomass}$ shows the price of the pre-treated biomass delivered with P_{Fuel} the estimated price of coke and P_{CO2} the carbon tax or cost of CO_2. EF_{Fuel} is the CO_2 emission coefficient for coke (Fick, et al., 2014). From the assumptions, a 20% substitution ratio for the blast furnace was used (Fick, et al., 2014). To account for the most extreme scenario possible, the price of coke was chosen as the highest in the given range, thus 8861.8 R/t. The CO_2 emission coefficient was chosen as 3.16 CO_2/t and the coke/coal input as 0.47 t coke/coal t (Fick, et al., 2014). Each replacement ratio has its own unique carbon tax, to take into account that biomass will release less CO_2 and thus less carbon tax is applicable. Table 4-11shows the extra cost of three different replacement ratios when using Equation (22) to calculate the cost of one ton of liquid iron.

Table 4-11: Extra cost associated when using different replacement ratios to produce one ton of liquid iron.

Replacement ratio	Cost of CO_2 R/t	Cost (R/t)
100 %	120	120
50 %	100	729.90
30 %	68	1801.20
10 %	48	7115.90

In order to calculate the cost associated with using coke and no biomass, a replacement ratio of 100% is used, this entails that only carbon tax will increase the cost. This results in an extra cost of R120/t of iron ore produced. A replacement ratio of 50% resulted in an additional cost of R729.90/t liquid iron produced. A 30% replacement ratio means that an additional R1801.20/t is needed to produce one ton of liquid iron ore and with a replacement ratio of 10%, an additional cost of R7115.90/t is needed for the production of one ton of liquid iron. All of the above extra costs are added to the price of coke in order to calculate a total cost for using biomass as a substitute. Table 4-12 shows the total cost associated with the production of one ton of liquid iron when using three replacement ratios for biomass.

Table 4-12: Total cost associated with producing one ton of liquid iron when using different replacement ratios.

Replacement Ratio	Total Cost R/t	Percentage change
100 %	8981.80	-
50 %	9591.70	6.80 %
30 %	10663.00	18.70 %
10 %	15977.74	77.90 %

A cost of 8981.80 R/t is considered as the base cost when no Industrial coke is replaced in the blast furnace. When 50% of the coke is replaced with biomass the cost per ton increased by 6.8%. When 70% of the coke is replaced with biomass the cost per ton increased by 18.7%, and when 90% of the coke is substituted with biomass the cost increased by 77.9%. The most economical option would be to only substitute 50% of the coke with biomass. Replacing 70% of the coke with biomass is the second most economical option. Increasing the biomass beyond this point will exponentially increase the cost per ton and thus will not be feasible. It might be advantageous to substitute only 20-30 % of the coke with biomass. The aforementioned may result in a lower cost per ton with a decrease in the plants carbon footprint. This is in accordance with what Fick *et al.* (2014) reported, where it was found that injected torrefied biomass through the tuyers resulted in a cheaper cost per ton. In order to identify which replacement ratio will result in a break-even point, a sensitivity analysis was conducted and resulted in a replacement ratio of 92.3% (Fick, et al., 2014). Meaning that using 7.7% biomass and 92.3% coke will result in breaking even. When using a replacement ratio of 88.2% coke the plant will start to show a profit (Fick, et al., 2014). The break-even ratio and profit ratio were determined using Microsoft Excel.

4.13 Summary

Table 4-13 shows a comparison between the chemical properties of metallurgical coke used in the industry and the coke substitute produced in this study.

Table 4-13: Comparing the chemical properties of metallurgical coke with that of the produced coke substitute.

Properties	Coke	Thermally treated wet oxidized biomass (coke substitute)
Ash yield (wt.%)	8-12	4.3
Moisture (wt.%)	1-6	0.7
Volatile matter (wt.%)	<1	2.6
Sulphur (wt.%)	0.5-0.9	0.1
CRI (x10^{-4} min^{-1})	20-30	132.4
CSR (%)	>60	97.3

Table 4-13 concludes that the produced coke substitute, having an ash yield of 4.3 wt.%, is within the range of that of coke. The aforementioned statement ensures a higher productivity in the blast furnace, as stated by literature (Díaz-Faes, et al., 2007). A moisture content of 0.7 wt. %, a bit lower than expected, will not have a negative influence on the coke properties. The volatile matter is not within in the range of that of coke, thus can be improved upon in future studies by increasing the thermal treatment temperature to a 1300 °C. The sulphur content is within the required range at 0.1 wt. %. The CRI of the produced substitute is significantly higher at 132.4 x 10^4 min^{-1}. This in accordance with literature where it is stated that biomass has a high reactivity due to the high BET surface area. The CSR value is within the required range of coke.

When looking at the economic analysis, the most economical option to use, will be to replace 50 % of the coke with biomass. The sensitivity analysis reported that when replacing 7.7 % of the coke with biomass the plant will reach a break-even point.

5. Conclusion and Recommendations

5.1 Introduction

In this chapter, the conclusion is based on the results obtained together with recommendations for future studies.

5.2 Conclusion

Based on the FSI results, the -75 µm particle size fraction showed a crucible swelling number (CSN) closest to that of metallurgical coke and was deemed the optimal particle size to be used for this study. The raw biomass showed an increase in its carbon content from 47 % to 56 % as a result of the pre-treatment method (torrefaction). The wet oxidized biomass yielded a decrease in its carbon content when compared to that of the torrefied biomass which can be ascribed to a decrease in the volatile matter of the sample and the incremental increase in oxygen is due to mild oxidation. All the thermally treated biomass samples showed sulphur contents in the desired range of less than 0.5 wt. %. All the biomass samples showed an ash yield below the desired range of 8-12 %, which is advantageous as less energy will be needed to melt the ash which will result in an increase in the productivity of the blast furnace. Theoretically, when replacing coke with the biomass as a reductant, the productivity of the blast furnace will increase by 2 to 3 %, when the ash yield is decrease by 1 wt. %. The thermally treated wet oxidized biomass showed the lowest moisture content (0.7 wt. %), which falls within the desired range of 4 wt. %. The volatile matter content of the raw biomass was very high (84.9 wt. %), but after the pre-treatment methods and the thermal treatment the volatile matter content was lowered to 4.3 wt. %, which falls outside of the desired range (<1 wt. %). This may be due to the lower temperature (900 °C) at which the biomass was thermally treated when compared to industrial coke, treated at 1300 °C. The thermally treated wet oxidized biomass had the highest CV value of 32.4 MJ/kg which falls within the desired range. The compressive strength of the biomass decreased as it was thermally treated from 40.2 MPa to 3.1 MPa. This may be due to the fact that no binder was used to bind the -75 µm particles or no equilent fusion compared to coking coal.

The maximum mass loss during CO_2 gasification (CRI) of the wet oxidation treated samples was observed to be lower when compared to the torrefied and the raw biomass samples, which are a result of reactions between mineral matter and the hydrogen peroxide, due to the wet oxidation method degrading the biomass. The remaining mass percentage of the raw biomass was found to be 14.5%, while the torrefied biomass and wet oxidation treated samples were observed to be 27.5% and 32.0%, respectively. After torrefaction, the biomass showed a decrease of 46% for cellulose while the hemicellulose was completely depleted, which indicates that the torrefaction process was successful, resulting in a significant increase in the energy density of the sample. These are in agreement with the CV values of the thermally treated wet oxidized samples, showing the highest CV value of 32.4 MJ/kg.

The surface area of the biomass samples was significantly higher than that of coke with the thermally treated wet oxidized biomass having a total surface area of 327.1 m^2/g compared with 8.8 m^2/g for industrial coke. This is evident when observing the CRI values of coke compared to biomass, as the biomass showed significantly higher reactivity towards CO_2 than for the coke at 132.4 x 10^4 min^{-1} and 21.2 x 10^4 min^{-1}, respectively. This is due to the larger surface area of biomass, which allows for easier reaction with CO_2. The coke has a low surface area resulting in less CO_2 reacting, and thus giving a lower reactivity. The reactivity is also influenced by the pore volume of the sample and thus the biomass, having a larger pore volume, displayed a higher reactivity. The CRI values of the biomass were not in the acceptable range of 20-30%, but the values reported are in accordance with values reported in literature. Degradation of coke can be prevented by using a coke with a higher reactivity culminating in the gasification reactions to be limited to the surface layer of the coke structure and thus leaving the stability of the coke intact.

The CSR of the coke lumps are in the acceptable range of above 60 %, whilst all the biomass samples reported values significantly higher than the prescribed 60 %. The low CSR value for the coke pellets may be due to the -75 µm particles being pelletized without the use of any binder.

The cost evaluation showed that when using 90 % biomass and 10 % coke there will be a 77.9 % increase in the production cost of one ton liquid iron. When substituting more than 50 % of the coke with biomass, the cost of production increased exponentially. The most economical option will be to substitute 50 % of the coke with biomass. A sensitivity analysis showed that when using 7.7 % of biomass and 88.2 % coke, a breakeven point is reached. Considering the use of biomass by means of PCI injection may be the most advantageous and economical due to lower cost of pre-treatment and less biomass needed, thus increasing the savings from using less coke whilst decreasing the greenhouse gas emissions.

5.3 Recommendations

To improve or better this investigation in the future, it is recommended that the pelletization step be improved by adding a binder in order to increase the compressive strength of the coke and biomass pellets. In order to improve the accuracy of the thermal treatment process, the set temperature may be increased to 1300 °C from 900 °C. This will mimic a coking oven better than the temperature of 900 °C used in this study. In order to understand the biomass behaviour during wet oxidation better, a Gieseler fluidity analysis and dilatometry can be added to the characterisation techniques used.

In order to determine the most effective wet oxidation conditions, the temperature and treatment time of the wet oxidation process can be varied.

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7. Appendix A

In Appendix A, figures of the washing process will be shown. This is to help the reader understand what equipment was used and to help the process to be replicated. Figure A 1 shows the drums that were used to wash all of the soft wood chips sample in order to prepare them for torrefaction.

Figure A 1: Drums used to wash the soft wood chips.

Figure A 2 shows how the water was added to the drums in order to wash all of the soft wood chips sample. The drums were filled three quarters of the way with water whereafter the wood chips was added for washing.

Figure A 2: Shows the water that was added to the drums in order to wash the soft wood chips.

Figure A 3 shows the wood chips after it was added to the water in the drum. The wood chips were left for a residence time of an hour before it was removed. Whilst it was left there, the wood chips were stirred every 10 minutes with a shovel.

Figure A 3: Soft wood chips being added to the water in the drums.

Figure A 4 shows the water after the wood chips were removed from it; it can be observed when comparing Figure A3 to Figure A 2 how much dirt was removed from the wood chips. After this step the wood chips were left to dry for a period of 72 hours before torrefaction.

Figure A 4: The water after the wood chips were removed.

Figure A 5 shows the wood chips being left to dry for a period of 72 hours whereafter, the sample was packed into sealed bags and prepared for the torrefaction process.

Figure A 5: Drying of wood chips.

The next few Figures will show the torrefaction set up used at Thermo Power Furnaces SA. Figure A 6 shows the torrefaction set up used. The rotary kiln can be seen in the middle of the Figure. On the left side is where the sample was fed to the set up and the tube in the middle is where the torrefaction takes place.

Figure A 6: Torrefaction set up used at Thermo Power Furnaces SA.

Figure A 7 shows the outlet of the torrefaction process. Rotary kiln can be seen in the middle of the figure. The box located on the ground is the catching box for the torrefied biomass. The torrefied biomass was removed from this box and then sealed in bags for the wet oxidation process. The CO_2 cylinder can be seen to the left of the catching box as well as the thermocouple used on top of the catching box.

Figure A 7: The outlet of the torrefaction set up together with the gas cylinder used.

Figure A 8 shows the feeding area which was used to feed the wood chips to the torrefaction process.

Figure A 8: The feed area to the torrefaction process.

Figure A 9 shows the biomass after torrefaction.

Figure A 9: The torrefied biomass.

8. Appendix B

This appendix section will show the FSI results and the biomass after pelletization. Figure B 1 shows the biomass in the crucible after the FSI test was done on the sample. The biomass was subjected to an FSI test in order to determine the CSN.

Figure B 1: The biomass in the crucible after the FSI test was conducted.

Figure B 2 shows a representation of the CSN number of the -1000 µm +500 µm (+500 µm), -500 µm +250 µm (+250 µm), -250 µm +150 µm (+150 µm) and the -150 µm +75 µm (+75 µm).

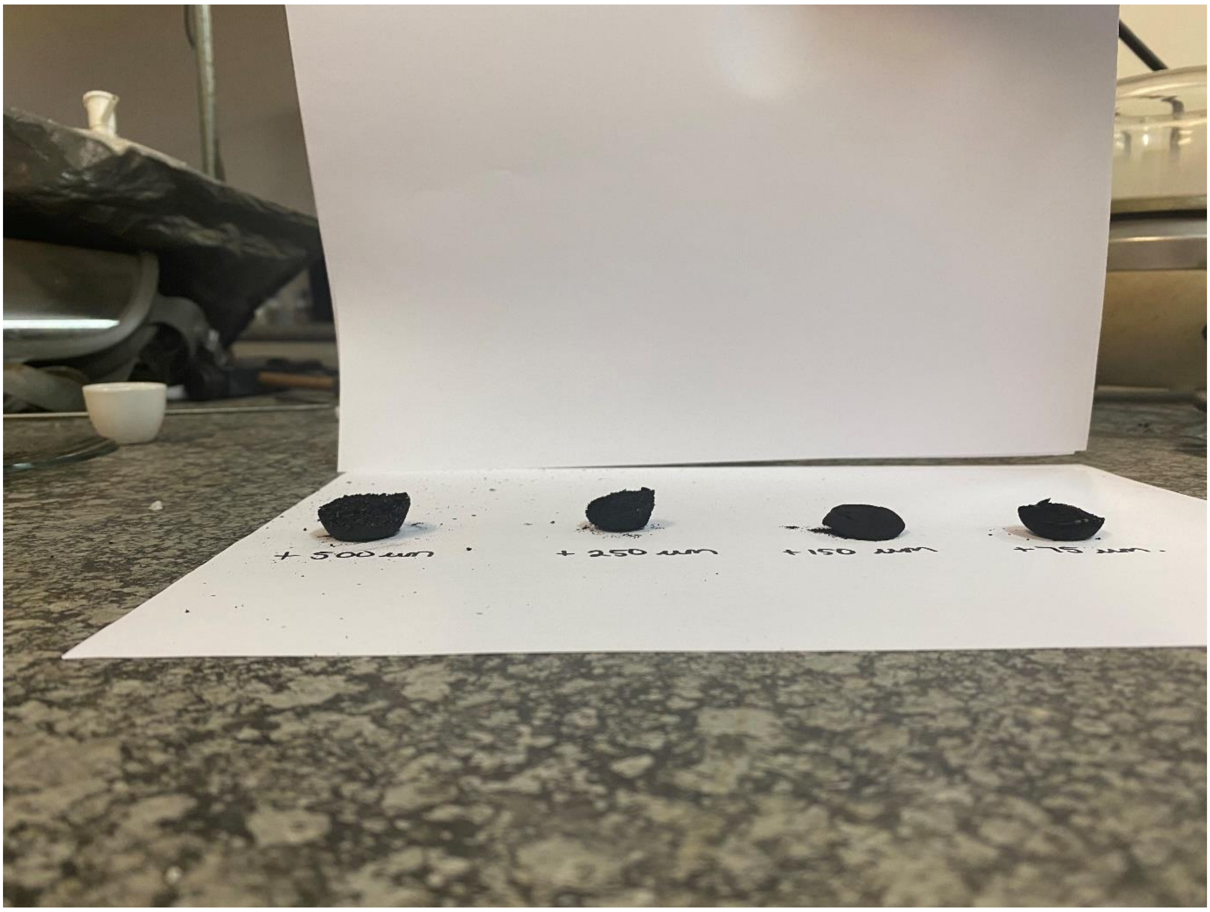


Figure B 2: Representation of the CSN number of different particle sizes.

Figure B 3 shows a representation of the CSN number for the -75 µm wet oxidized biomass.

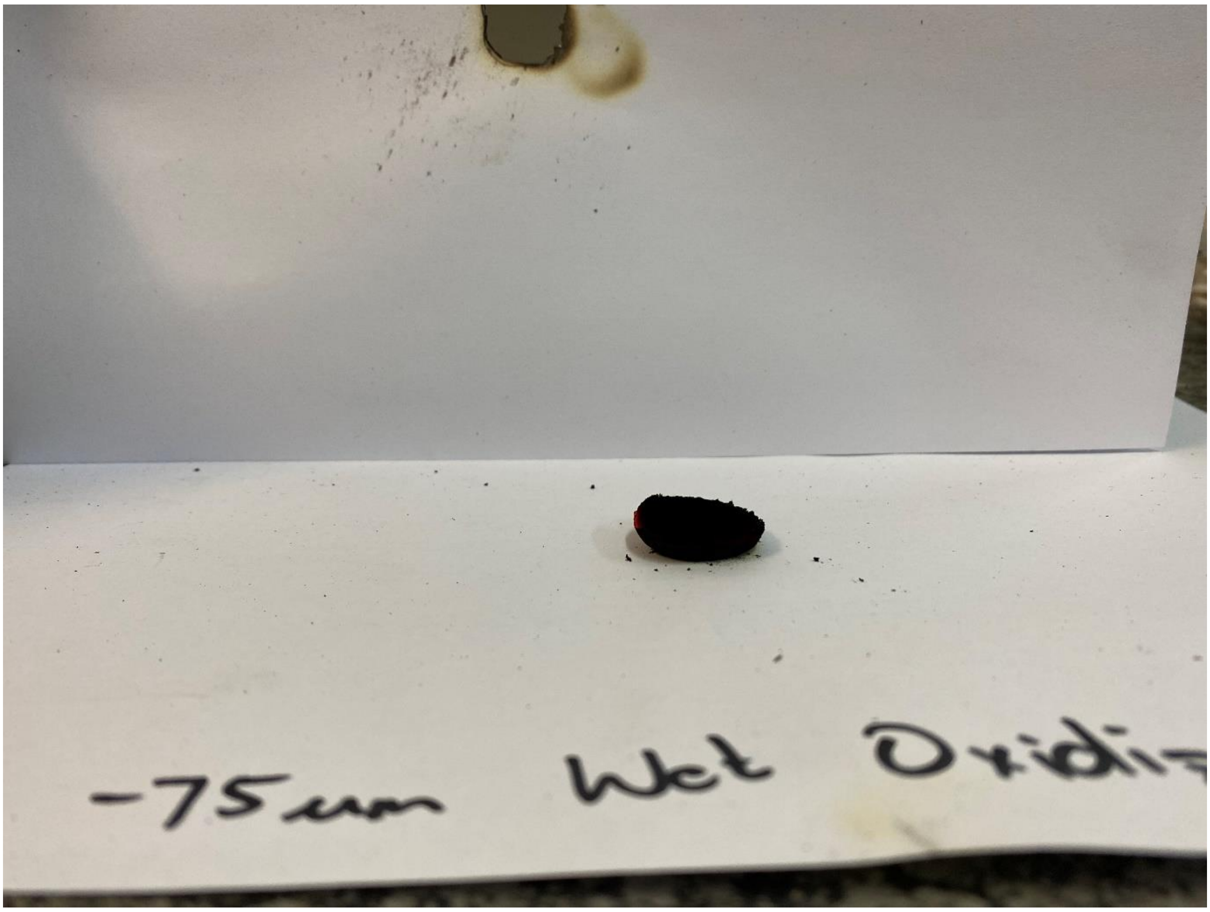
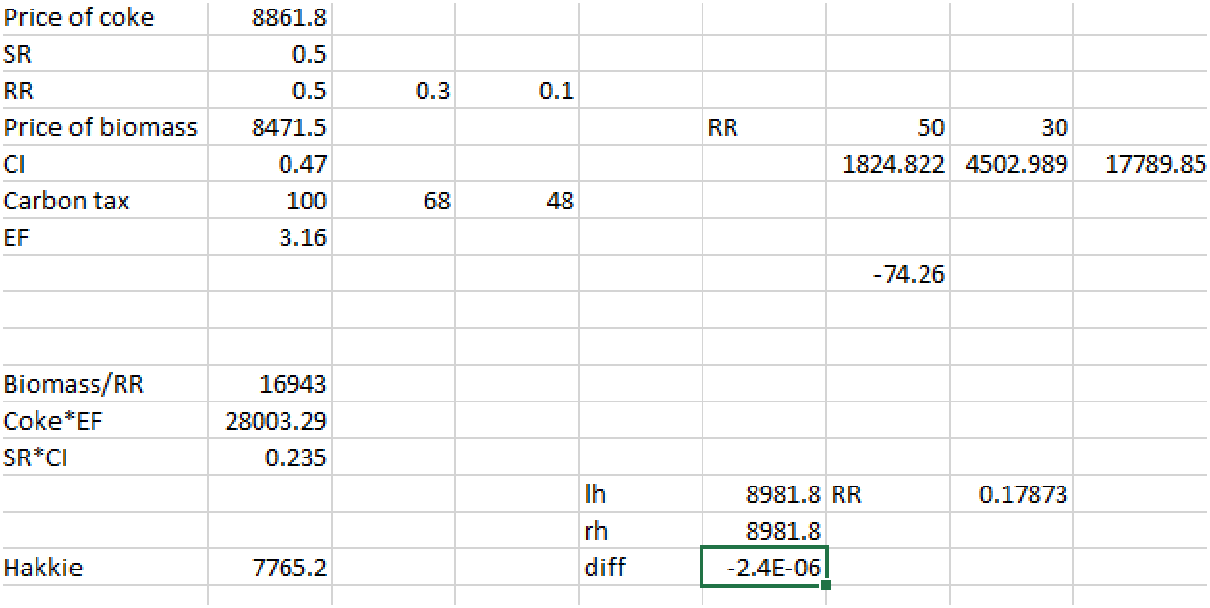


Figure B 3: CSN number of the -75-micron wet oxidized biomass.

9. Appendix C

Appendix C, shows the sensitivity analysis results. In order to complete the sensitivity analysis Microsoft Excel was used. The goal seek function was used in order to calculate a replacement ratio which will result in a break-even point. It was also used to find a point where the plant will start to show a profit. Figure C 1 shows the sensitivity analysis for the break-even point (RR=0.17).



Price of coke	8861.8							
SR	0.5							
RR	0.5	0.3	0.1					
Price of biomass	8471.5				RR	50	30	
CI	0.47					1824.822	4502.989	17789.85
Carbon tax	100	68	48					
EF	3.16							
						-74.26		
Biomass/RR	16943							
Coke*EF	28003.29							
SR*CI	0.235							
				lh	8981.8	RR	0.17873	
				rh	8981.8			
Hakkie	7765.2			diff	-2.4E-06			

Figure C 1: Sensitivity analysis for the break-even point.