



Development of a green reductant for high-temperature smelting

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Declaration of authorship

I, Keagan Velde, hereby declare that the report entitled “Development of a green reductant for high-temperature smelting”, submitted in the pursuit of a Master’s degree in Chemical Engineering, is my own work. All other contributors have been indicated clearly and literature has been referenced as necessary. This work has not been previously submitted in pursuit of a degree at any other tertiary institution.

Signed at Potchefstroom on the 27th day of November.



KM Velde

Acknowledgements

I would first like to acknowledge our Heavenly Father, with whom I am privileged to have become closer to through the course of 2024. Everything we do, we do to His glory, and I am truly blessed to have been afforded this opportunity to further my studies, and myself therefrom.

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1 Corinthians 10:31

So whether you eat or drink or whatever you do, do it all for the glory of God.

Abstract

Coal is a significant energy source worldwide, supplying 25% of global energy needs. In the smelting industry, coal is used as a reductant, typically in the form of anthracite or coke produced from bituminous coal. Coal releases CO₂ when burned and emits high levels of methane during mining. Despite coal being an exceptional energy source, the growing concern over global warming necessitates the exploration of greener alternatives to fossil fuels.

The study initially commenced with three biomass samples: pine sawdust, maize stover, and sugarcane bagasse. In addition to determining the most suitable biomass type for the development of a green reductant for high-temperature smelting, the biomass charring temperature was simultaneously investigated. Maize stover and sugarcane bagasse were subsequently excluded from the study due to the high ash content and low compressive strength of the pellets produced. Pine sawdust was selected for pyrolysis at 850 °C due to the high compressive strength and fixed carbon content of the resulting material. Following this initial pre-screening step, briquettes were produced using polyvinyl alcohol (PVA) and molasses (MOL) as binders, with 5%, 10%, and 15% addition.

The briquettes were cured in a temperature-controlled room for 0, 1, 3, 5, 7, and 10 days before undergoing compressive strength, drop shatter, and water resistance tests, which demonstrated improved quality due to curing. Additional tests such as abrasion resistance, proximate analysis, ultimate analysis, calorific value, X-ray fluorescence, and measurements of bulk, particle, and true density were performed on the cured briquettes and two imported anthracite materials (high volatile (HA) and low volatile (LA)) sourced from an industrial smelting company. The briquettes displayed similar chemical properties to HA and LA, with approximately 85% fixed carbon and 5% ash content, differing mainly in mineral composition. Mechanically, the briquettes outperformed HA and LA, with a compressive strength of 19 MPa for the 15% MOL addition, though performing poorly in water. The briquettes' bulk density was half that of HA and LA, potentially causing logistical issues. MOL briquettes were chosen for thermal tests due to their superior performance compared to PVA-bound briquettes.

During thermal shock tests, MOL briquettes performed exceedingly well, outperforming both HA and LA. However, the CO₂ reactivity of MOL was 100 times greater than HA and LA, potentially problematic for use in a smelter, as it would possibly react before entering the slag bath. Nonetheless, MOL displayed reducing capabilities comparable to anthracites HA and LA. Taken together, these findings suggest that MOL outperforms HA and LA in many areas but is hindered by low bulk density, extremely poor water resistance, and high CO₂ reactivity. Further

testing is required to understand the impact of reactivity, but MOL may still be suitable if stored correctly.

Keywords: biochar, anthracite, reductant, characterisation, smelting

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List of Abbreviations

A	Ash content
a.d.	Air-dried basis
AI	Alkali index
AR	Abrasion resistance
BF-BOF	Blast furnace-basic oxygen furnace
CapEx	Capital expenditures
CV	Calorific value
d.a.f.	Dry-ash-free basis
DC	Direct-current
EAF	Electric arc furnace
FC	Fixed carbon content
GHG	Greenhouse gas
HePyc	Micromeritics AccuPyc II 1340 Gas Pycnometer
HHV	Higher heating value
IEA	International Energy Agency
IRI	Impact resistance index
LHV	Lower heating value
LRX	LRXPlus instrument from Lloyd Instruments
M	Moisture content
N/D	No data
OpEx	Operating expenses
PSD	Particle size distribution
TGA	TA Instruments SDT-Q600 thermogravimetric analyser
VM	Volatile matter content
wt%	Weight fraction
XRD	X-ray diffraction
XRF	X-ray fluorescence

Nomenclature

Symbol	Unit	Description
h	cm	Height
m	g	Mass of a substance
M	g	Mass of the sample at time t
t	min	Time
r	cm	Radius
R	min^{-1}	Reactivity
V	cm^3	Volume

CHAPTER 1

INTRODUCTION

1.1. Overview

Chapter 1 provides a basic introduction to the topic. Section 1.2 offers a concise background on coal, smelting, and biomass-based pellet production, as well as the motivation for the study. The problem statement is presented in Section 1.3. Section 1.4 delineates the aim of the study and the specific objectives required to achieve this aim. Lastly, Section 1.5 outlines the study's scope, and Section 1.6 provides an overview of the dissertation structure.

1.2. Background and motivation

Coal is a significant energy source and one of the most widely used worldwide. This is illustrated in Figure 1, which shows the primary energy sources used globally, with coal supplying 25% of global energy needs.

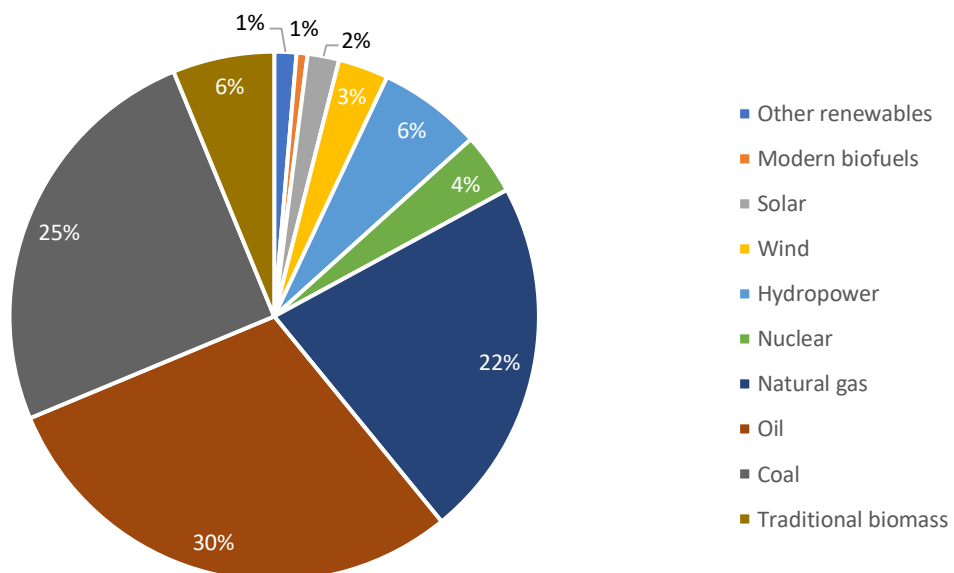


Figure 1: Primary sources of energy used worldwide (Energy Institute - Statistical Review of World Energy (2023); Smil (2017) – with major processing by Our World in Data, 2024)

Energy is a vital commodity for any emerging country and the backbone of developed countries (Srabani *et al.*, 2021). The largest consumers of coal as an energy source include China, India, the United States, Germany, Brazil, and South Africa (Yildizhan, 2017). These countries utilise coal in many sectors. Figure 2 illustrates the primary sectors in which coal is used globally, with its main applications being electricity generation and heat production, followed by its use in the iron and steelmaking industry. South Africa's dependence on coal significantly exceeds global averages, with coal supplying 72% of the country's energy needs and 92% of its electricity generation (Eskom, 2021; Strambo *et al.*, 2019). Coal is often discussed in the context of global warming due to its substantial carbon footprint.

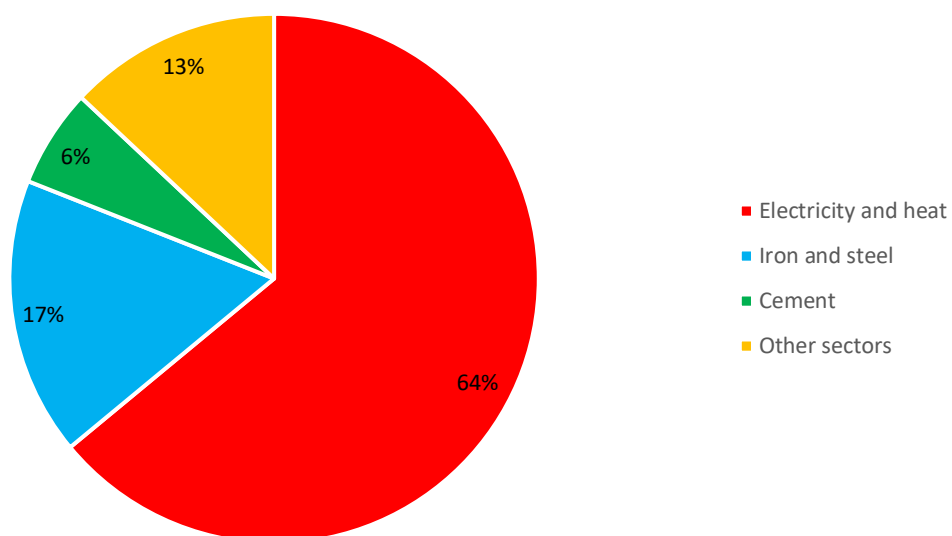


Figure 2: The global coal demand in 2020 separated by main sectors (Government of Canada, 2023)

Given its heavy reliance on coal for energy, it is unsurprising that South Africa is not only the largest CO₂ emitter in Africa but also the 15th largest CO₂ emitter worldwide (Global Carbon Budget (2023) – with major processing by Our World in Data, 2023). There has been global pressure for South Africa to adopt greener technologies. However, coal use is expected to continue for many years, as the country plans to extend decarbonisation targets (Sguazzin, 2023). A more feasible short-term goal (approximately 50 years) is to improve the methods and materials used in current processes to reduce carbon emissions.

Focusing on the metallurgy industry, it is well known that steel and ironmaking industries require coke for energy and as a reductant. Coke, a high-carbon content material, is primarily produced for the iron and steelmaking industries. In ilmenite smelting, anthracite is used as a

reductant (Pisilä *et al.*, 2015). Anthracite, like coke, is a high carbon content material (Li, Cao, *et al.*, 2012), while ilmenite is an ore with the composition FeTiO_3 , or more simply, $\text{FeO} \cdot \text{TiO}_2$ (Pistorius, 2008). Gous (2006) noted that 3 tons of CO_2 are generated per ton of ilmenite produced at a South African smelting plant. This is comparable to the 1.4 tons of CO_2 emitted per ton of crude steel produced via the blast furnace-basic oxygen furnace (BF-BOF) method, with an additional 0.8 tons of CO_2 indirectly produced per ton of steel (IEA, 2020). The International Energy Agency (IEA) states that direct CO_2 emissions need to decrease to 0.4 tons of CO_2 per ton of steel produced, representing a 60% reduction in CO_2 emissions. Therefore, a greener reductant needs to be utilised, particularly one with a fixed carbon content similar to that of anthracite and coke, which are currently used in high-temperature smelting environments.

Bertling (1999) reports that coke used in blast furnaces for steelmaking requires low ash content, low moisture content, and low chlorine content. Anthracite can have fixed carbon contents as high as 94% (Kaliakparov *et al.*, 2018). Therefore, a green reductant must have a high carbon content to effectively reduce the ores entering the smelter while introducing minimal impurities into the slag and metal phases. The release of greenhouse gases – CO and CO_2 – results from the reduction of ores in the smelter (Pistorius, 2008). Consequently, the CO and CO_2 emissions from the smelters will be the same regardless of whether anthracite, coke, or green reductant is used. The defining characteristic of a green reductant is its carbon neutrality.

Carbon neutrality means that the CO_2 emitted by a source is equal to the amount of CO_2 removed from the atmosphere (APTIV, 2021). To achieve net-zero CO_2 emissions, methods must be implemented to remove CO_2 from the atmosphere either before or after the emission process, directly or indirectly. A green reductant would indirectly remove CO_2 from the atmosphere as it is typically made from biomass materials. Plants absorb CO_2 through openings on the surface of leaves and produce glucose and oxygen by the process of photosynthesis (Taiz *et al.*, 2018). Consequently, a green reductant would absorb CO_2 from the atmosphere during its photosynthetic life cycle and subsequently emit an equivalent amount of CO_2 when used as a reductant – thus achieving net-zero CO_2 emissions. In contrast, coal releases CO_2 when used as a reductant and emits significant amounts of methane during mining (Tate, 2022).

A biochar substitute for anthracite will have a similar fixed carbon content resulting in comparable CO_2 and CO emissions. What makes biochar a green reductant is its lifecycle. Biochar starts as biomass, which absorbs CO_2 from the atmosphere. Therefore, biochar can

be considered CO₂ neutral, as it absorbs a similar amount of CO₂ during its growth as it releases when burned. In contrast, the lifecycle of coal is highly polluting. To effectively use biochar in the smelting industry, it must be densified into pellets or briquettes.

There are many methods of producing pellets from biochar. These include pelletisation, briquetting, and extrusion. These methods are used to replicate the mechanical attributes of coal. The characteristics of interest in this study include:

- Chemical
 - Proximate analysis (Fixed carbon content, volatile matter content, ash content, and moisture content)
 - Ultimate analysis (Carbon content, Nitrogen content, Oxygen content, Hydrogen content, Sulphur content)
 - Calorific value
 - X-ray fluorescence (Ash composition)
- Structural
 - Density (Particle, skeletal, and bulk)
- Mechanical
 - Compressive strength
 - Abrasion resistance
 - Drop shatter
 - Water resistance
- Thermal
 - Thermal shock
 - Thermogravimetric analysis
 - Sessile drop test

Pine sawdust was the primary biomass used in this study. Sawdust production in South Africa was 1 million tons in 2017, with sawdust comprising approximately 5% of all organic waste produced in the country (Department of Environmental Affairs, 2018). Pine trees make up 49% of land used for timber plantations in South Africa (Forestry South Africa, 2019) and sawdust is generally considered an unused wood portion (Udokpoh & Nnaji, 2023). In addition to the preliminary biomass pre-screening, this further substantiates the selection of pine sawdust.

Despite coal being an efficient source of energy, its detrimental environmental impact has driven research into cleaner energy alternatives. There is a multitude of studies where researchers have attempted to produce a biomass-based alternative to coal as a reductant

(Demus *et al.*, 2016; Fan *et al.*, 2015; Makgobelele *et al.*, 2021; Suman *et al.*, 2022; Xie *et al.*, 2024; Xu *et al.*, 2024; Ye *et al.*, 2019). This research seeks to advance the understanding of producing effective biomass-based replacements for carbon-rich materials used in high-temperature smelting processes.

1.3. Problem statement

Coal has proven effective as a reductant in high-temperature smelting. However, the global drive to mitigate greenhouse gas emissions necessitates the development of more environmentally friendly alternatives. This need arises from the substantial emissions generated during coal mining and smelting processes.

1.4. Aim and objectives

1.4.1. Aim

This study aims to develop an organic reductant to substitute conventional anthracite and coke materials currently utilised in high-temperature smelting applications, with a particular focus on ilmenite smelting.

1.4.2. Objectives

The objectives for this study are as follows:

1. Determine the primary biomass and charring temperature through a series of pre-screening tests.
2. Produce a large variety of biochar briquettes and assess the impact of curing time on the mechanical properties.
3. Determine a single binder based on chemical, structural, and mechanical tests conducted on anthracite and biochar briquettes.
4. Conduct thermal tests on anthracite and biochar briquettes produced using the chosen binder.
5. Compare the quality of biochar briquettes to anthracite and evaluate the potential as a replacement fuel.

1.5. Scope

This study investigates three distinct biomass sources, i.e. wastes from the agricultural and forestry industries. Table 1 presents the biomass, biochar, anthracite, and binders used. Additionally, their sample codes, what type of sample they are, and where they were sourced from are included in the table.

Table 1: The materials used in this study with material codes, type of material, and source.

Material code	Material	Type	Source
PS	Pine sawdust	Biomass	Local sawmill
SS	Sugarcane bagasse	Biomass	Local sugar refinery
MS	Maize stover	Biomass	Local maize farm
PC	Pine sawdust char	Biochar	Produced from PS
SC	Sugarcane bagasse char	Biochar	Produced from SS
MC	Maize stover char	Biochar	Produced from MS
LA	Anthracite (Low volatile)	Coal	Local smelting operation
HA	Anthracite (High volatile)	Coal	Local smelting operation
MOL	Molasses	Binder	Local sugar refinery
PVA	Polyvinyl alcohol	Binder	Sourced online
LIG	Lignin	Binder	Local papermaking factory

This study is split into 4 major steps. These steps help to achieve the objectives set out in Section 1.4.2. The steps include:

1. Literature study: A comprehensive literature review is undertaken to address several key aspects. This includes identifying suitable types of biomasses relevant to the South African market, exploring various methods of biochar production and summarising previous research findings, analysing the properties of current reductants and their

environmental impacts, and examining carbon neutrality to understand why biomass-based reductants are a viable alternative.

2. Lab-scale experimental work: The study begins with a broad scope, which is systematically narrowed by reducing the sample size. This step focuses the research on the selection of a single biomass type and the determination of a pyrolysis temperature.
3. With the study now more focused, experiments can be conducted on a larger scale. In this phase, a briquetting apparatus that allows for continuous operation is utilised.
4. Comparative tests: The anthracites and chosen biochar pellets will undergo numerous tests and then be compared with one another. These tests include:
 - a. Chemical: Proximate analysis; Ultimate analysis; Calorific value; XRF
 - b. Structural: BET analysis; Density (Bulk, particle, skeletal).
 - c. Mechanical: Compressive strength; Abrasion resistance; Drop shatter; Water immersion.
 - d. Thermal: Reactivity (Performed in TGA); Thermal shock; and sessile drop test.

1.6. Structure of the dissertation

Figure 3 shows the structure of the dissertation.

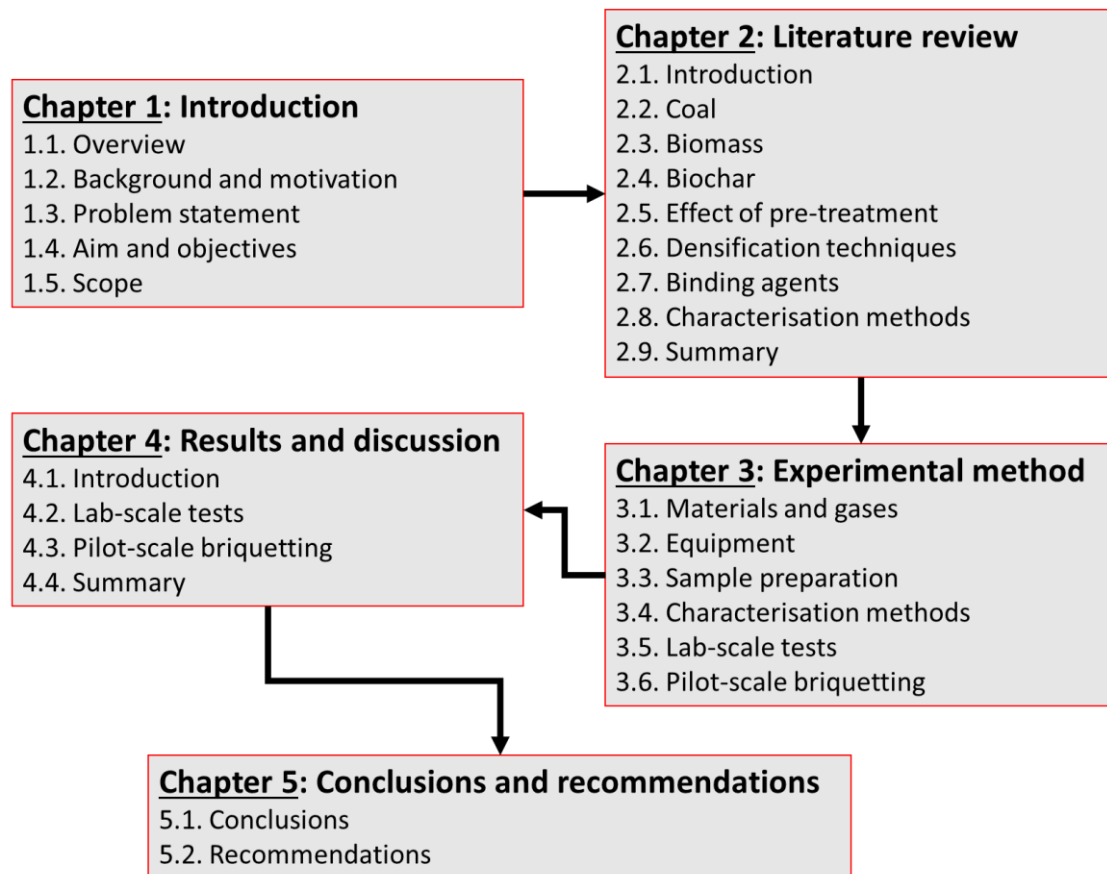


Figure 3: Structure of dissertation

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

The literature review explores the origin of coal and its various types. This leads to an examination of mining emissions from coal mines. These emissions are often overlooked when considering the greenhouse gas (GHG) emissions from fossil fuels. To mitigate these emissions, the potential of biomass-based alternatives is examined.

In the context of South Africa, biomass waste sources are identified, and their potential applications are assessed. The current use of biochar in the smelting industry, with a focus on steel, iron, and ilmenite smelting, is reviewed. The preparation of biochar involves pre-treatment of biomass followed by densification into solid biochar briquettes, and the factors influencing these processes are analysed.

The suitability of biomass-based briquettes for smelting operations presents several challenges. This review investigates various methods for testing briquettes to determine their appropriateness for smelting applications. The significance of mechanical, structural, chemical, and thermal tests in evaluating the performance of these materials is discussed in detail.

2.2. Coal

2.2.1. Origin, grade, rank, and type

Coal is a heterogeneous material comprised of macerals and minerals (O'Keefe *et al.*, 2013). The variation of these macerals and minerals among different types of coal is a result of differences during coal formation. Coal formation involves the metamorphism of organic matter. Coal begins as buried woody material which, under heat and pressure, transforms into peat through the process of peatification (Sekhohola *et al.*, 2013). An increase in the temperature and pressure results in coalification (Delrio *et al.*, 1994). During coalification, the peat transforms into coal. The mined coal therefore varies according to factors such as parent material, duration of formation, and the temperature and pressure of formation (Sekhohola *et*

al., 2013). These variations can be classified into 3 main categories: coal grade, coal type, and coal rank.

The coal grade is determined by the mineral matter present in the coal (O'Keefe *et al.*, 2013). The greater the mineral matter present in coal, the lower the grade, and vice versa. Major species that make up the mineral matter include aluminosilicates, carbonates, sulphides, and silicates, with iron, silica, and alumina compounds constituting the largest portion of mineral matter (Viswanathan, 2017). For smelting, mineral matter in reductants is undesirable. Additionally, mineral matter can be abrasive while potentially reducing binding capabilities and therefore a low-grade coal is generally undesired (Couch, 2002).

Coal rank signifies the degree of coalification of coal, ranging from low-rank peat to high-rank meta-anthracite (Mastalerz *et al.*, 2011). From lowest to highest rank, the four primary ranks of coal include:

- Lignite: Lowest fixed carbon content; Lowest heating value.
- Sub-bituminous: Steam coal with carbon content higher than lignite, but lower than bituminous coal.
- Bituminous: Steam coal with carbon content higher than sub-bituminous coal, but lower than anthracite.
- Anthracite: Highest fixed carbon content; Highest heating value.

Anthracite makes up 15% of all coal mined (IEA, 2023), while sub-bituminous and bituminous coals make up around 80% of all coal mined. They are called steam coals due to their primary use being for steam production in heat and electricity generation (IEA, 2023). The remaining 5% of all coal mined is lignite.

Coal type refers to the maceral composition of the coal i.e., how much vitrinite, inertinite, and liptinite the coal contains (Tiwary *et al.*, 2020). Vitrinite is a common indicator of high-ranking coals, with reflectance in between that of liptinite and inertinite (Ward, 1984). Inertinite is characterised by its high reflectance, high carbon content, and how it remains inert during carbonisation (Gupta *et al.*, 2012). Liptinite has the lowest reflectance and is often found in low-ranking coals (Tiwary *et al.*, 2020). From these factors mentioned that are used to identify and categorise coal, anthracite is a high-grade, high-rank, high- vitrinite and inertinite content coal. With all the variations that can be found in coal, it is no surprise that coal has found numerous applications in the industrial sector.

Section 1.2 provided insight into the uses of coal globally. The use of coal in industry has infamously high GHG emissions. A frequently overlooked factor, however, in coal use is the GHG emissions from coal mining operations.

2.2.2. Coal mining emissions

Coal is constantly under scrutiny for its CO₂ emissions (Cassidy, 2024; Li *et al.*, 2016; Petroni, 2024; Ray, 2024). Coal mining emits methane equivalent to CO₂ emissions from all the coal-powered electricity generation stations in China (Tate, 2022). That is to say, the 52 million tonnes of methane per year emitted from coal mining (Tate, 2022) is equivalent to CO₂ emissions from over 1100 coal-fired power plants (McKenna, 2022). The primary factors affecting the methane emissions are the type of mine as well as the type of coal.

Deeper coal seams tend to contain more methane than shallow coal seams, therefore, the methane emissions from underground mining are typically significantly higher than the methane emissions from surface mining (IEA, 2023). Moreover, higher-ranking coals emit more methane from mines (IEA, 2023). Tate (2022) backs up these claims with an investigation both into the coal type and the depth at which the coal is found. At a depth of 100 m the methane content in an anthracite seam is 11.4 m³/tonne of anthracite mined, with bituminous and sub-bituminous coals having a methane content of 5.3 m³ and 1.4 m³ per tonne of coal mined respectively. By comparison, at a depth of 500 m, the methane content per tonne of anthracite mined is 24.2 m³/tonne with bituminous and sub-bituminous coals showing methane contents of 13.8 m³ and 4.5 m³/tonne respectively. The methane present in coal seams was formed when the coal was formed through the coalification of plant material. What makes methane so harmful is that it has up to 36 times more of an environmental impact than CO₂, on a mass basis, over 100 years (EPA, 2023).

Tate (2022) exclaims that methane from coal mining needs to be reduced by 11% per year until 2030 to reach the 2030 goal of net-zero emissions as set out by the IEA. However, there are more coal mine projects underway that will emit an additional 11 million tonnes of methane per year; and the cancellation of these projects may be the only way to adhere to the net-zero emissions goals from the IEA. Biomass may help lower GHG emissions while acting as an interim alternative to coal as technology develops away from the use of fossil fuels.

2.3. Biomass

2.3.1. General characteristics

Biomass is an organic material derived from plants and animals (EIA, 2023). It may be used as a fuel in several processes, making it a renewable source of energy. Higher quality fuels can be created through pyrolysis or charring of the biomass. This is due to the high volatile matter content often present in biomass materials (García-Pérez *et al.*, 2002; Reed & Gaur, 1994; Wang, Zhao, *et al.*, 2023; Zhang *et al.*, 2021; Zhou *et al.*, 2022). Different processes may require different amounts of volatile matter content. With each source of biomass, there comes a change in composition. Resultantly, GHG emissions differ depending on the biomass source used as well as the conditions under which the biomass has been prepared.

Borowski and Hycnar (2013) examined the effect that woody biomass had on the following gas emissions in a coal and biomass blend. The authors reported that varying the biomass addition to the coal/biomass blends had the following effects on greenhouse gas emissions when burning the blends:

- NO_x – Shows a decrease with an increase in biomass addition.
- SO₂ – Shows a decrease with an increase in biomass addition.
- CO – Shows an increase with an increase in biomass addition.
- CO₂ – Shows a decrease with an increase in biomass addition.
- H₂S – Shows an increase with an increase in biomass addition.

Therefore, biomass addition may be beneficial in certain processes; and it is important to study the biomass in depth beforehand. To effectively introduce biomass into industrial applications there should be a sufficient supply of biomass. There are a great number of different sources of biomass.

2.3.2. Sources

Some of the more well-known biomass sources are listed below (EIA, 2023):

- Wood and wood processing waste: This includes all wood waste produced from producing firewood, lumber and furniture, as well as black liquor produced from the papermaking industry.

- Crops and waste materials: Crops such as corn, sugarcane, soybeans, and wood plants leave large amounts of organic matter after harvesting. Some other waste includes used vegetable oils.
- Biogenic materials in municipal solid waste: This is waste the government is responsible for, and it includes paper products, cotton and wool, and food waste.
- Animal manure and human sewage: These can be used for producing biogas.

There needs to be sufficient amounts of these wastes to be useful in producing fuels. Nyika *et al.* (2019) describe different types of general waste present in South Africa such as Municipal; Commercial and industrial; Organic; Construction and demolition; Paper; Plastic; Glass; Metals; Tyres; and all other wastes. Organic waste makes up 34.6% of the general waste generated in South Africa, with approximately 19 million tons produced in 2017 (Department of Environmental Affairs, 2018). The organic waste stream primarily consists of biomass from the sugar, timber, and paper industries. Regrettably, half of the organic waste generated ends up in landfills (Department of Environmental Affairs, 2018). Table 2 presents the types of organic waste which make up the organic waste stream generated in South Africa in 2017.

Table 2: The amounts of different types of organic wastes generated in South Africa in 2017 (Department of Environmental Affairs, 2018).

Type of organic waste	Amount (million tons)
Garden waste	4.2
Food waste	2.5
Wood waste	2.4
Sugar bagasse	4.5
Black liquor from paper industry	4.9
Bark from paper industry	0.2
Sludge from paper industry	0.3
Total	19.0

Garden waste that is sent to the landfill is often diverted to composting facilities (Department of Environmental Affairs, 2018). Thus, reducing the strain on landfill capacity as well as producing a marketable product. The food waste comprises household kitchen and restaurant

waste. Much of this waste stream still requires methods of recycling. The wood waste stream can be further divided into wood chips (1.0 million tons), bark (0.4 million tons), and sawdust (1.0 million tons) (Department of Environmental Affairs, 2018). The majority of wood chips generated are recycled, however, the bark and sawdust are potential biomass waste streams which have yet to be properly utilised.

Black liquor, sludge, and bark are produced from the papermaking industry. Black liquor is often used to generate energy for the paper and pulp mills (PAMSA, 2021) and the bark is sold as is for mulch or compost (Department of Environmental Affairs, 2018). The sludge is produced from paper and pulp mills and is often disposed of through incineration or landfill (Haile *et al.*, 2021). Haile *et al.* (2021) mention the main route for recycling sludge, namely, as an energy source in construction and energy generation.

Sugarcane bagasse is a by-product of the sugar industry. Significant amounts of sugarcane bagasse are produced with as much as 280 kg of bagasse produced per ton of sugarcane processed (Melati *et al.*, 2017). In South Africa, large and medium-sized mills utilise the bagasse by-product as an energy source, generating heat and electricity (Mkhwanazi *et al.*, 2023). This process minimises waste with up to 75% of the bagasse used in energy production.

There is a multitude of ways of recycling the wastes described in Table 2, however, for application in a smelting environment a high carbon content is required and thus biochar would need to be produced from these biomass sources.

2.4. Biochar

Biochar is the solid product resulting from the thermal treatment of biomass. During this carbonisation process, volatile matter and moisture are removed, leaving behind a carbon-rich material. Biochar has demonstrated significant effectiveness, particularly when compared to traditional biomass energy sources (Wild & Calderón, 2021). However, its adoption in industrial applications has only recently begun to gain momentum (Wild & Calderón, 2021).

2.4.1. Use of biochar in high-temperature smelting

In the smelting industry, a reductant is required to extract the desired products from various ores. To ensure reduction results in high-purity products, carbon-rich materials are used such as coke, coal, oil, and gas (Suopajarvi *et al.*, 2013). Biomass is unsuitable as a reducing agent as it contains high moisture and volatile matter content, as well as a low carbon content. High

volatile matter content culminates in a reductant that reacts more readily with a lower ignition temperature (Miller, 2013). Consequentially, biomass may burn too quickly producing gases and decreasing reducing ability. Biomass that has undergone pre-treatment – such as pyrolysis – will form a more suitable coke replacement if prepared at a high temperature. When compared to coal, biochar may have more favourable characteristics including a higher fixed carbon content as well as lower impurities, such as sulphur (Ren *et al.*, 2007). However, when compared with coke, the biochar may have lower fixed carbon content and calorific value (Ye *et al.*, 2019). Depending on the base biomass, biochar could still prove to be an effective substitute for fossil fuels as it may have decidedly lower ash content.

a) Ironmaking and steelmaking

Ironmaking is a process whereby iron is extracted from its natural ore by reducing iron oxides to produce molten iron, commonly known as pig iron – which can then be further smelted, through steelmaking, to produce steel (Ghosh & Chatterjee, 2008). The most common method of steelmaking is the blast furnace-basic oxygen furnace (BF-BOF) process, which makes up approximately 70% of all steel production (worldsteel, 2023b). This process involves producing pig iron in a blast furnace (BF), before undergoing further processing in a basic oxygen furnace (BOF). During ironmaking, layers of iron ore, coke, and fluxes (materials used to rid the iron of impurities) are fed into the top of the furnace (Tupkary & Tupkary, 2017). Hot air is blasted through openings at the bottom of the furnace igniting the coke to generate high temperatures and produce carbon monoxide, which in turn reduces the iron ore to metallic iron (Ishii, 2000). BOF follows on from BF operation to produce steel. BOF primarily relies on the oxidation of elements in the pig iron for energy, however, pulverised coke may be injected into the furnace to adjust carbon content or temperature (Fruehan & Foundation, 1998). Electric arc furnaces (EAF) utilise anthracite coal, or coke breeze, for several reasons, including, the formation of CO gas (Matsuura & Fruehan, 2009), which helps to foam the slag, thereby protecting the furnace lining; and adjusting the carbon content of the steel (Shiqi *et al.*, 2022)

A reported average of 2.33 tonnes of CO₂ is produced per tonne of crude steel cast (worldsteel, 2023a). Tian *et al.* (2013) confirm this by finding the average emissions for steelmaking to be 2.27 tonnes of CO₂ per tonne of steel produced. The average across all production methods is 1.91 tonnes of CO₂ per tonne of crude steel cast. The coke materials utilised in these processes are produced through a high-temperature carbonisation process, exceeding 1100 °C, which employs coking coal as the primary feedstock (Kamyab *et al.*, 2017). Hence, a material with extremely high carbon content is required. Biochar shows potential with its characteristically good combustibility and reducing ability (Ye *et al.*, 2019).

However, biochar exhibits significant limitations that currently prevent it from substituting coke, including low density, inadequate mechanical strength, and high particle reactivity (Riva *et al.*, 2019).

Despite its limitations, biochar has been used in ironmaking for some time. It is directly added to blast furnaces as a substitute for coke and coal reductants (Mathieson *et al.*, 2012). Biochar performs effectively in this application, and without any changes to the current technology, the furnaces can handle 200 kg per ton of hot metallic iron produced (Hooey *et al.*, 2010). The use of tuyere injection further enhances the versatility of biochar types that can be employed. Suopajarvi *et al.* (2018) demonstrated that powdered biomass could be used in BF-BOF processes. Mechanical strength is not a concern with this method, as pellets are unnecessary; the primary requirement is producing biochar with a similar carbon content comparable to that of coke and coal reductants currently in use.

Seo *et al.* (2020) investigated the production of biochar-coke from yellow poplar wood by blending it with coking coal in ratios of 0, 10, 15, 20, and 30% and subjecting the mixtures to charring at temperatures ranging from 500 to 800 °C. The resulting biochar-coke blends exhibited calorific values of 7200 to 7560 kcal/kg, which are higher than the 7000 kcal/kg reported for conventional coke. The researchers suggest that biochar could be a viable replacement for coke in smelting applications. The size fractions of the charcoal used can significantly impact the quality of coke produced (MacPhee *et al.*, 2009). When 10% of charcoal with a particle size below 250 µm was blended with coking coal, the resulting coke blend was of lower quality compared to the base coals. Conversely, charcoal with a particle size fraction of -9.5 + 6.4 mm produced higher-quality coke blends than the base coals (MacPhee *et al.*, 2009). This phenomenon is attributed to the ash content, with higher calcium content and other minerals being more prevalent at smaller particle sizes, thereby enhancing CO₂ reactivity.

With a focus on the steel industry Wang, Wang, *et al.* (2018) investigated the co-combustion of anthracite and biochar produced from palm kernel shells. The biochar was prepared by pyrolyzing a sample of palm kernel shells at 600 °C for 60 min under a continuous stream of nitrogen. The biochar sample was then crushed and sieved to -74 µm. The anthracite studied in this article had a fixed carbon content of 79.6% and an ash content of 12.4%. Comparatively, the palm kernel char had a fixed carbon content of 81.3% and an ash content of 11.0%, a slight improvement on the anthracite. The ash composition between the biochar and anthracite coal varied significantly. The coal ash predominantly consisted of SiO₂ and Al₂O₃, 49.6% and 37.3% respectively. By comparison, the main components in the ash of the biochar were 25.9% CaO, 38.4% MgO, and 22.2% K₂O (Wang, Wang, *et al.*, 2018). The reactivity of the

biochar and coal was studied, and the biochar exhibited higher reactivity with a significantly lower ignition temperature. The higher reactivity is likely due to the high alkali and alkaline earth metal content in the ash, which act as catalysts for reactions with carbonaceous materials (Du *et al.*, 2014).

b) Iron ore sintering

Iron ore sintering is the process of creating sinter which is more suitable for the BF-BOF process versus lump iron ore (Zandi *et al.*, 2010). This process utilises coke breeze – fine (<5 mm) coke particles – as an energy source. Partial replacement of some of the coke breeze with biochar yields an increase in CO₂ but a lower concentration in SO_x and NO_x in the off-gas (Gan *et al.*, 2012).

c) Ilmenite smelting

An ilmenite smelter was found to produce approximately 3 tons of CO₂ per ton of ilmenite smelted (Gous, 2006). There are many methods for producing TiO₂ from ilmenite ore, including the Becher process; Murso process; Laporte process; Benelite process; Auspact process; Dunn process; Kataoka process; Altair process; and the BHP Billiton process (Nguyen & Lee, 2019). EAF smelting of ilmenite is common worldwide (Jones *et al.*, 2011; Nguyen & Lee, 2019; Pistorius, 2008), with DC arc furnaces being the superior technology (Jones, 2016). The reducing agent customarily used in ilmenite smelting is anthracite (Spencer *et al.*, 2022; Zietsman & Pistorius, 2006). The TiO₂ ore produced from the smelter undergoes one of two further processes: sulphate process; or chloride process (Gázquez *et al.*, 2014). These two processes make up 40% and 60%, respectively, of the total TiO₂ production (Gázquez *et al.*, 2014). Which process is used is dependent on the quality of the TiO₂ product produced from the smelting process, with the sulphate process handling lower quality (72% - 85% TiO₂) ore and the chloride process handling higher quality (>85% TiO₂) ore (Gázquez *et al.*, 2014; Guo *et al.*, 2014). There are fewer articles published on the use of biochar in ilmenite smelting.

Lamandasa *et al.* (2021) used palm kernel shells to reduce ilmenite at high temperatures in a tube furnace with a constant flow of Argon gas (0.6 L/min). The palm kernel shells were initially dried at 100 °C before undergoing torrefaction at 300 °C for 1 h and subsequently charred at 750 °C for 3 h. The charred biomass was crushed and combined with carboxymethyl cellulose – to act as binder – and ilmenite with ratios of 6 - 10% biomass addition. The reduction reactions occurred at 1000 °C, 1100 °C, and 1200 °C for 0.5, 1, 2, and 3 h. A temperature of 1200 °C and reaction time of 1 – 2 h was best for the creation of rutile (TiO₂) and metallic iron.

Using a temperature of 1200 °C and a reaction time of 2 h the effect of the biomass addition was determined (Lamandasa *et al.*, 2021):

- With 6% biomass addition, ilmenite (FeTiO_3), pseudobrookite (FeTi_2O_5), metallic iron, rutile (TiO_2), and spinel (MgAl_2O_4) formed.
- At 8 – 9% biomass addition more metallic iron and rutile (TiO_2) were formed along with a decrease in pseudobrookite (FeTi_2O_5) and almost no ilmenite (FeTiO_3) and spinel (MgAl_2O_4) present.
- With 10% biomass addition, there was a decrease in rutile formed as the additional carbon allowed for increased reduction reactions, resulting in the formation of anosovite (Ti_3O_5) according to the reducing chain:
 - Ilmenite (TiFeO_3) $\rightarrow$ pseudobrookite (FeTi_2O_5) $\rightarrow$ metallic iron and rutile (TiO_2) $\rightarrow$ rutile reduced to anosovite (Ti_3O_5)

Setiawan *et al.* (2021) confirm this with a similar report conducted on ilmenite reduction with palm kernel shells. Spencer *et al.* (2022) investigated the efficacy of biomass as a reductant for ilmenite smelting. They evaluated the reducing performance of charcoal, wood kindling, and gum tree sticks. The fixed carbon content of these three materials was 64%, 57%, and 16% respectively. The ilmenite sample was combined with the biomass in a 1:1.5 ratio and placed into a rotating tube furnace where it was heated to 1100 °C and was kept isothermal for 3 h. Once completed and the furnace had cooled, the sample was taken out and separated to produce a reduced ilmenite which undergoes acid leaching utilising a hydrochloric acid solution. The reduction results obtained to produce synthetic rutile (TiO_2) using various carbon sources in this study are summarised below (Spencer *et al.*, 2022):

- | | |
|----------------------------|------------------------------|
| • 93.8% with coal | • 95.4% with charcoal |
| • 94.9% with wood kindling | • 93.4% with gum tree sticks |

It is noted that the charcoal has a higher carbon content than that of the wood kindling and gum tree sticks, which affects the quality of the resultant product.

2.4.2. Carbon neutrality of biochar

The emissions from the use of fossil fuels as a reducing agent have been mentioned and the emissions from mining these materials have also been discussed. As a reducing agent, biochar will have similar carbon emissions to that of fossil fuels. The biochar should have similar quantities of carbon as traditional fossil fuels, leading to similar carbon emissions from

high-temperature smelting operations. Therefore, to lower carbon emissions, the idea behind carbon neutrality is that the life cycle of the biochar – from plant to use as a reductant – absorbs adequate amounts of CO₂ to sufficiently counteract the CO₂ it releases during combustion (APTIV, 2021).

Wang, Chai, *et al.* (2023) note that there is research that shows potential CO₂ emission reduction in coal injection smelting processes (such as blast furnace operation), namely, the injection of charcoal and sawdust, which respectively give annual CO₂ savings of 1140 kton and 260 kton. As noted by Pan and Sun (2023) the biggest savings come from the fact that the plant material absorbs CO₂ before becoming waste and is used as a source material for biochar or industrial processes. They note that the CO₂ absorbed through photosynthesis forms a balance with the CO₂ released once the material has died or burned. While mining the ores used in high-temperature smelting operations greenhouse gases are released; using biomass-based reductants will significantly decrease the overall impact. Producing biochar reductants requires processing of the biomass. Thermal treatment will allow the biomass to reach a high carbon content similar to that of the fossil fuels in use.

2.5. Effect of pre-treatment

Several methods for producing biochar are described in literature, varying in terms of temperature, pressure, equipment, residence time, and sample material and size. Despite these differences, the core principle remains the same: the material must be heated to remove moisture and volatile matter content.

2.5.1. Torrefaction and pyrolysis

Torrefaction and pyrolysis are similar processes, both involving the heating of a sample in an inert atmosphere. Torrefaction typically occurs around 280 °C, while pyrolysis refers to heating at temperatures above 300 °C. Ghiasi *et al.* (2014) investigated the effects of pelletising wood chips before versus after torrefaction. Torrefaction was conducted at 260 °C using a large thermogravimetric analyser, with an isothermal residence time of 15 minutes, followed by pellet production. The torrefied material exhibited poor binding characteristics, necessitating the addition of a binder (7% wheat flour) when producing pellets after torrefaction. Testing the effect of pelletising before torrefaction, it was found that no binder was required as the raw wood chips were able to bind effectively. This route produced pellets with a lower density and durability, but they had greater hydrophobic properties.

Siyal *et al.* (2021) produced biomass pellets from wood sawdust. Initially, the wood sawdust was torrefied at temperatures of 200 °C and 300 °C. Thereafter, pellets were produced using a moisture addition of 5.5%, and under a constant heat of 130 °C, and a compaction pressure of 130 MPa. The heat during compaction of pellets cures the material, and with the addition of high compaction pressure, a mechanically strong pellet is produced. The residence time was shown to have an insignificant effect on the torrefaction process; however, the torrefaction temperature had a notable impact: at 300 °C, the pellets exhibited notably lower density, strength, and durability compared to those torrefied at 200 °C. Li, Liu, *et al.* (2012) demonstrated similar results when preparing biochar from wood sawdust in a bubbling fluidised bed reactor, observing a decrease in pellet hardness with increasing biochar production temperatures. Hu *et al.* (2016) also noted a decrease in the compressive strength of pellets produced from charred biomass. However, the compressive strength began to improve at 450 °C reaching a maximum at the study's maximum temperature of 650 °C. The durability of biomass pellets also deteriorates with higher torrefaction temperatures (Larsson *et al.*, 2013; Siyal *et al.*, 2021). Additionally, Basu *et al.* (2013) reported a decrease in the apparent density of poplar wood biomass from 500 kg/m³ to 297 kg/m³ at a torrefaction temperature of 300 °C with a residence time of 180 min.

2.5.2. Hydrothermal pre-treatment

Wu *et al.* (2018) subjected corn stalk and pine wood sawdust to hydrothermal pre-treatment. To ensure an inert atmosphere, an autoclave was flooded with nitrogen. Then, 20 g of biomass was mixed with 100 mL of deionised water, placed in the autoclave, and heated to 200, 230, and 260 °C with a holding time of 20 min at each temperature. After cooling to room temperature, the samples were removed from the autoclave and washed with deionised water. Raw biomass was also torrefied at the same temperatures. Hydrothermal pre-treatment resulted in greater mass loss of the biomass, indicating that more components were released into the gaseous and liquid phases during the process (Wu *et al.*, 2018). Additionally, it was found that the compressive strength of briquettes produced from the hydrothermally pre-treated biomass far exceeded that of the torrefied materials and raw biomass.

2.6. Densification techniques

The biochar must be pelletised due to the low bulk density. Densification techniques provide many benefits, such as (Mohammadi, 2021):

- Increases the density, thereby lowering the volume, allowing for improved logistics of the material.

- Can lower dust creation.
- Allows for variable sizing of the material for specific industrial purposes.

Two common methods for material densification are pelletisation and briquetting. However, these terms are used interchangeably for similar methods of production in literature. Both briquettes and pellets can be produced in various sizes and under different conditions using a die.

Siyal *et al.* (2021) pelletised raw sawdust at varying pressures, temperatures and moisture contents. Four pressures were tested, namely: 70, 100, 130, and 160 MPa. The higher pressures produced mechanically superior pellets at lower production temperatures; however, once reaching production temperatures of 200 °C the lower pressures (70 and 100 MPa) were better. When varying the moisture content Siyal *et al.* (2021) found 18% water to be optimal with a test range from 5.5% to 28%.

Water addition significantly affects pelletising. Hu *et al.* (2016) investigated the impact of varying water content on pelletising wood chips charred at 450 °C. They found that adding water up to 35 % of the total weight significantly increased the compressive strength of the pellets. However, adding more than 35% water resulted in a decrease in compressive strength. Additionally, they observed that higher water content reduced the energy required for pellet production.

It is logical to expect that higher pelletising pressure would enhance the mechanical properties of produced pellets, as greater pressure reduces gaps and voids between material particles (Hu *et al.*, 2016). Hu *et al.* (2016) observed that volume density increased with pressure, leading to fewer voids and improved particle binding. However, there was a threshold beyond which further increases in pressure led to a decrease in pellet compressive strength. Siyal *et al.* (2021) reported a similar increase in compressive strength with rising production pressure but noted a decrease in compressive strength beyond a certain point, which was attributed to production at elevated temperatures of 160 – 200 °C. Both studies focused on wood shavings or sawdust; Siyal *et al.* (2021) produced biomass pellets before exerting them to temperatures up to a maximum of 300 °C, while Hu *et al.* (2016) investigated pellets from biomass produced up to 650 °C.

The conditions of pelletising equipment can significantly impact the compressive strength of pellets produced. Li and Liu (2000) investigated how compaction pressure, compaction speed, and pressure holding time affect the properties of pellets produced from various woody biomass wastes. It was found that increasing compaction pressure resulted in higher pellet

density. In contrast, higher compaction speeds decreased pellet density; a speed of 0.24 MPa/s yielded greater density than a speed of 5 MPa/s, although the difference was marginal. The pressure holding time had a more pronounced effect on density, with improvements becoming insignificant beyond 20 – 30 s. Increasing density, in turn, enhances pellet compressive strength (Bajo & Acda, 2017). Therefore, using a holding time of 30 seconds, with high pressure and slow compaction speed, optimises the mechanical properties of pellets.

Wu *et al.* (2018) produced briquettes from torrefied, raw, and hydrothermally pre-treated biomass by keeping the samples at 75 °C for 3 minutes. Briquettes were produced using a 16 mm die with a pressure of 80 MPa and a holding time of 30 s. The raw briquettes exhibited better mechanical properties compared to the torrefied material, but the hydrothermally pre-treated briquettes demonstrated the highest compressive strength. This trend persisted even after all briquettes underwent carbonisation at 400 °C. None of the samples required a binder with this briquetting method, and the resulting biochar briquettes were stronger than commercially available briquettes.

Borowski *et al.* (2017) used a roller press unit to produce briquettes from charcoal, incorporating 8% wheat starch as a binder. The initial moisture content of the material was 28 – 32%, which was reduced to 6% after briquetting. This process resulted in briquettes with a compressive strength of 24.5 MPa and a density of 700 kg/m³.

In a further study, water hyacinth was carbonised at an average temperature of 425 °C before being briquetted using molasses at a 30:70 mass ratio (Carnaje *et al.*, 2018). This ratio yielded briquettes with the highest calorific value and compressive strength, measuring 16.6 MJ/kg and 1.87 MPa, respectively. The briquettes were pillow-shaped with dimensions of 50 × 60 × 25 cm for these analyses.

2.7. Binding agents

Products formed through binderless densification techniques tend to exhibit low mechanical strength, making storage and transport of these products challenging (Siyal *et al.*, 2021). To improve the mechanical properties of pellets, binding agents are often used. Obi *et al.* (2022) explain that there are 3 main categories of binders: organic, inorganic, and compound (organic and inorganic) binders. Organic and inorganic categories of binders are tabulated below in Table 3 along with examples, advantages, and disadvantages for each:

Table 3: Organic and inorganic binders along with advantages and disadvantages for each.

Binder classification	Examples	Advantages	Disadvantages	Source
Organic	Molasses, PVA, starch, lignin	High impact and abrasion strength, high water resistance ¹ , good availability, low price, high heating value, low ignition temperature ²	Poor thermal stability, low mechanical strength ³	¹ (Zhang <i>et al.</i> , 2018), ² (Obi <i>et al.</i> , 2022), ³ (Han <i>et al.</i> , 2014)
Inorganic	Clay, bentonite, limestone, cement	Strong adhesion, good hydrophilicity	High ash content, low combustion efficiency	(Shu <i>et al.</i> , 2012)

Both organic and inorganic binders have been extensively studied in literature. Hu *et al.* (2015) evaluated four different binders: two organic and two inorganic. The inorganic binders displayed superior binding properties compared to the organic binders. Inorganic binders are less suitable for smelting applications as they introduce additional unwanted minerals and increase the ash content of the reductant (Hu *et al.*, 2015). The two organic binders used in the study were lignin and starch, combined with a biochar prepared from rice husks. Although the specific biochar preparation conditions were not provided, the lignin-based pellets exhibited better compressive strength compared to those made with starch. Both types of pellets showed similar characteristics in terms of moisture resistance.

One of the most well-known commercial applications of biochar is in charcoal production, where binders are required. Common binders include molasses, starch, and tar (Zakari *et al.*, 2013). Borowski *et al.* (2017) investigated the effects of varying a single binder, focusing on starch, both modified and native. Native wheat starch is obtained directly from the wheat plant, whereas modified wheat starch is derived from native starch through physical, enzymatic and chemical transformations (Borowski *et al.*, 2017). Both binders produced sufficiently strong briquettes, but there were differences in burning properties. Briquettes made with native starch reached higher temperatures and burned for a shorter duration compared to those made with modified starch. Ghiasi *et al.* (2014) found that wheat starch reduced the CV and fixed carbon yield of products formed through densification techniques when compared with lignin. Similarly, Wirabuana and Alwi (2021) observed that using starch in the production of durian fruit peel charcoal briquettes resulted in lower CV and fixed carbon content, while ash and volatile matter content increased. Starch is among the most common organic binders, alongside molasses, glycerol, lignin, and algae (Obi *et al.*, 2022).

Molasses is produced at a rate of 4 tons per 100 tons of wet sugarcane (Rein & Attard, 2007). Given the large annual production of sugarcane, this could amount to approximately 70 million tons of molasses each year (Dirbeba *et al.*, 2021). While molasses is traditionally used in ethanol production, its use in this context has proven inefficient, leading to investigations into alternative applications (Dirbeba *et al.*, 2021). Several studies have explored the use of molasses as a binder for coal briquette production (Benk & Coban, 2011; Blesa *et al.*, 2003; Das *et al.*, 2015; Kambo & Dutta, 2014). Carnaje *et al.* (2018) found that combining molasses with carbonised water hyacinth in a 30:70 biomass-to-molasses ratio produced the most robust briquettes. Additionally, Jittabut (2015) reported that a 100:50 biomass-to-molasses ratio resulted in high structural and mechanical properties for briquettes made from straw and sugarcane leaves.

Glycerol is a by-product of biodiesel production and can be purified for use in the cosmetic, food, and pharmaceutical industries (de Almeida Moreira *et al.*, 2020). It is a vital chemical in these industries, despite how expensive and inefficient it is to purify due to the wide variety of impurities it contains. The selling price of glycerol continues to decline (Bala-Litwiniak & Radomiak, 2019) with the market being saturated and the disposal of glycerol environmentally unsustainable (Ayoub & Abdullah, 2012). This makes glycerol an economically attractive binder. de Almeida Moreira *et al.* (2020) mixed sugarcane and sorghum residues to produce briquettes. It was found that glycerol addition resulted in briquettes with greater hygroscopic properties whilst being less energetic and mechanically unstable.

Lignin has been shown to have widespread application as a binder (Mili *et al.*, 2022; Tawaf Ali *et al.*, 2022). Manouchehrinejad *et al.* (2018) explored the use of lignin extracted from energy cane and napier grass to produce torrefied briquettes. It was found that adding 10% lignin increased the bulk density of the torrefied briquettes by 11% for energy cane (a specially bred type of sugarcane) and 38% for napier grass. Additionally, the compressive strength of the briquettes was tripled, with a slight increase in durability. However, lignin used in densification processes is often sourced from the papermaking industry, resulting in impure lignin, or sodium lignosulphonate – a compound with high sulphur content.

Algae, widely distributed and easily cultivated, grow 50 times faster than most terrestrial plants (Haykiri-Acma *et al.*, 2013). Beyond its binding properties, algae is an attractive binder due to its availability, ease of production, and environmental benefits (Costa *et al.*, 2017; Savage & Hestekin, 2013). Muazu and Stegemann (2017) found that using 6% algae as a binder in briquettes made from a blend of rice husk, corncob, and bagasse improved density and compressive strength compared to starch and biosolids binders. Costa *et al.* (2017) utilised seaweed (macroalgae) as the biomass carbonising it at 900 °C and before cooling. The

seaweed biochar was combined with various binders, including molasses, sulphide liquor, and Linobind. A blend of 95% seaweed biochar and 5% molasses yielded the most promising results, showing high mechanical stability. However, it was noted that the use of algae significantly increases the ash content, with seaweed biomass having an ash content of 22.5%.

PVA is a synthetic organic polymer which has found success in various applications, including the textile industry (Dong *et al.*, 2020; Wu *et al.*, 2015), composite synthesis (Xianhua *et al.*, 2019; Zhang *et al.*, 2023), and in the preparation of hydrogels (Kumar & Han, 2017; Macias *et al.*, 2013). It has also been used as a binder in pellet preparation of coals and biomass. Rajput and Thorat (2019) utilised PVA to produce coke breeze briquettes. Pregelatinized starch is commonly used as a binder for coke breeze briquettes, but it can have a high cost and low availability due to its popularity in the food industry. Testing both binders, Rajput and Thorat (2019) found that PVA formed a briquette equally as strong as briquettes formed with pregelatinized starch. Similarly, Lu *et al.* (2015) found that PVA addition could improve the strength and durability of coal briquettes. Working with biomass, Dai *et al.* (2019) and Makgobelele *et al.* (2021) produced strong pellets from wood-based char with PVA as a binder. When considering water resistance, Dai *et al.* (2019) and Makgobelele *et al.* (2021) both note the hydrophobic capabilities of pellets when using PVA as a binder. Wang, Yu, *et al.* (2018) reach a similar conclusion, noting an increase in strength and improved hydrophobicity with the addition of PVA addition to particleboards. A short list of binders not yet mentioned is shown in Table 4, compiled with aid from the table in Obi *et al.* (2022). It is worth noting that sawdust has been used as the substrate for binder addition and as the binder.

Table 4: Other binders used for biomass densification as well as their source and alternative uses.

Biomass	Binder	Binder source	Alternative uses	Source
Rice husk, corn cob, and bagasse blend	Biosolids	Nutrient-rich by-product of municipal wastewater treatment.	Valuable source of fertiliser in agriculture.	(Muazu & Stegemann, 2017)
Sawdust	Neem powder	Crushed leaves of the neem tree.	Herbal medication, and hygiene.	(Rajaseenivasan <i>et al.</i> , 2016)
Rice straw	Sawdust	By-product of timber industry.	Largely waste, with small use in construction and livestock farming.	(Rahaman & Salam, 2017)
Spent coffee ground	Guar gum	Powder from milling guar beans.	Used as a thickening agent in the food industry.	(Espuelas <i>et al.</i> , 2020)

2.8. Characterisation methods

This section evaluates the relevance of the characterisation tests and techniques selected for this study. The tests are categorised into four main groups: Chemical tests, Structural tests, Mechanical tests, and Thermal tests.

2.8.1. Chemical tests

a) Proximate analysis

The proximate analysis determines the amount of moisture content, volatile matter content, ash content, and fixed carbon content present in a sample. High moisture content in biomass materials can be problematic as it could lead to degradation of the material if stored incorrectly (Karunanithy *et al.*, 2013). It could also affect the conversion of biomass to biochar. As previously mentioned, high moisture content affects the structural integrity of briquettes or pellets produced. A low moisture content is therefore always desired.

Ash content is the solid residue remaining after a material has undergone complete combustion. Primary elements often found in the ash content of biomass include Si, Al, Fe, Ca, Mg, Ti, Na, and K (Vassilev *et al.*, 2013). Knowing the ash content helps to predict the tendency to form deposits and how the elements may contaminate products in industrial processes (Nunes *et al.*, 2016).

Volatile matter content is made up of all the condensable vapour and permanent gases expelled when a material is heated (Cai *et al.*, 2017). This excludes the moisture content that would have heated off at lower temperatures. A material with high volatile matter content will burn more readily, and quicker. Hence, biochar products with varying characteristics can be produced by a large assortment of biochar can be produced based on the requirements of an application by changing the volatile matter content. Altering the pyrolysis temperature, heating rate, and residence time in a furnace allows for control of the volatile matter content of a biomass material (Singh Chouhan & Sarma, 2013).

During pyrolysis of a sample, volatile matter content is expelled along with the moisture content. What remains is the fixed carbon content and ash content. As the main reducing agent in smelting, the biochar materials must have a high fixed carbon content.

b) Ultimate analysis

Elements that are in abundance in biomass, in decreasing order, include C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, and Ti with all elements after N reporting primarily to the ash content of the material (Vassilev *et al.*, 2010). The objective of an ultimate analysis is to determine the quantities of C, O, H, N, and S in a sample. This gives a relatively good idea of the composition of the sample. These are displayed nicely using a Van Krevelen diagram, which also helps to show the quality of a material (Cai *et al.*, 2017).

c) Calorific value (CV)

The calorific value measures the energy content of a material per unit mass. There are two common heating value types, higher heating value (HHV) and lower heating value (LHV) (Cai *et al.*, 2017). HHV is a measure of the total amount of heat available in a sample including the latent heat of vaporisation of water and the reaction products. LHV is a measure of the total heat available from the reaction products and excludes latent heat of vaporisation of water. Producing biochar creates a product with an improved energy density or greater calorific value.

d) X-ray fluorescence analysis

X-ray fluorescence (XRF) analysis is an elemental analysis of the ash content of a biomaterial. González *et al.* (2024) state that XRF is a non-destructive analytical method to detect elements with atomic numbers from 11 (Na) and beyond 92 (U). They also note the wide range of industries that XRF is applied to, namely, mineralogy, geology, the food industry, and the pharmaceutical industry. It is vital to understand the ash composition to prevent unwanted reaction mechanisms or deposits forming within equipment or processes, as previously stated (Nunes *et al.*, 2016)

2.8.2. Structural tests

a) Particle density

The particle density is the mass of the particle, as measured on a scale, divided by the envelope volume of that particle (Deng *et al.*, 2021). Calculating the particle density requires accurate measurement of the volume of the particle. Deng *et al.* (2021) list numerous ways of calculating particle density: (1) caking end-point measurements; (2) gas flow measurements; (3) minimum fluidisation velocity measurements; (4) comparative measurements; (5) mercury porosimeters; (6) powder displacement measurements; (7) and photographic measurements. If the particles being investigated are of a uniform shape, then a simple volume calculation may be used.

b) Skeletal density

Gilvari *et al.* (2019) note that the skeletal density is mostly measured with the use of a gas displacement pycnometer. It works by determining the pressure difference between a reference volume and a volume filled with a sample. Helium is typically used as the gas for the pycnometer. The skeletal density only indicates as to the porous nature of the material and may help to ascertain why a structure performs poorly in water submersion tests. A very porous structure will yield a skeletal density much higher than that of the particle density (Deng *et al.*, 2021).

c) Bulk density

A particle from a larger sample will have a different density than that of the bulk sample. Therefore, the bulk density determines the mass of the sample in relation to the bulk volume of the sample (Deng *et al.*, 2021). The handling of a material can be influenced considerably

by the bulk density of a material. Kalyankar *et al.* (2016) note that low bulk densities increase the packaging and shipping costs of items. Lam *et al.* (2008) confirm this by stating that logistic systems currently in use may not be capable of handling biomass with a low bulk density. Hence, feed systems designed for fossil fuels may not be sufficient if a low bulk-density alternative is to be used as a drop-in product. A bulk density similar to that of the carbonaceous reductants currently in use in high-temperature smelting is therefore desired. Improving the bulk density of a sample may simply require a change in the size or shape of the particles. Cannova *et al.* (2020) found that changing the sphericity and convexity of petroleum coke had a massive impact on the bulk density of the sample. The size may even have an impact on powdered materials. Particles with irregular shapes and pointed edges, which may result in looser packing, and particles which are so small that adhesive forces outweigh the force of gravity result in lower bulk-density powders (Elmsahli & Sinka, 2021).

2.8.3. Mechanical tests

a) Compressive strength

Compressive strength is used to simulate the maximum compressive force an object can experience before failure. This is especially useful when deciding how to store, handle, and transport products. Kambo and Dutta (2014) describe the compressive strength of biomass-based materials to be a measure of the internal bonding strength. The simplest and most commonly used method for determining the compressive strength of materials is to place the material between two parallel plates that compress until the mechanical failure of the sample occurs (Obi *et al.*, 2022). Something to keep in mind when testing the compressive strength is what axis is tested. Bazargan *et al.* (2014) note that the compressive strength of a vertical cylindrical material is often greater than the strength when placed on its side. Figure 4 shows the orientation when (a) pellets experience greater compressive strengths, and (b) when the compressive strength is lowered. Pillow-shaped briquettes are tested according to (b) Figure 4 due to the shape.

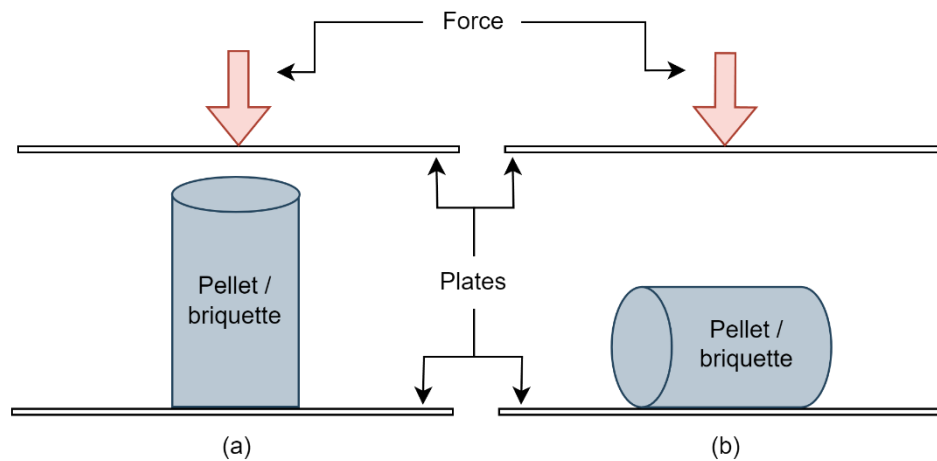


Figure 4: (a) Pellet placed vertically; (b) Pellet placed horizontally for compressive strength tests between two plates (Adapted from Bazargan *et al.* (2014)).

b) Drop shatter test

The drop shatter test measures the resistance of a material to shatter/break when dropped from a specified height onto a solid surface. Kambo and Dutta (2014) believed that the drop shatter test was a good indication of a material's likelihood of breakage when being offloaded from trucks or falling from chutes or conveyors. Richards (1990) introduced the impact resistance index, a value based on the number of times a particle can be dropped without breaking, and how many pieces it breaks into when it breaks. While this method has been commonly used, it varies in the number of drops, the surface the materials are dropped onto, and the height at which the drop occurs (Obi *et al.*, 2022). It is important to report the method well and ensure that the experiments are carried out accordingly.

c) Abrasion resistance

Abrasion resistance is directly related to the handling of materials. During transportation of materials, they are prone to wear from scraping against each other, container walls, and conveyor belts (Dohm *et al.*, 2012). Durability is important in understanding the dust generation of materials to prevent a possible dust explosion (Obi *et al.*, 2022). Two common pieces of equipment used in assessing abrasion resistance are the rotating drum and tumbler tests. The primary difference between these is that the rotating drum is a cylinder with baffles inside which rotates along its cylindrical axis (Gilvari *et al.*, 2019), while the tumbler test is a cylinder which rotates against its cylindrical axis (Ueki *et al.*, 2014). Richards (1990) notes that the shape of particles affects the abrasion resistance, observing that more rounded particles

have increased durability. Comparing durability can be difficult due to the lack of a conventional testing standard (Obi *et al.*, 2022).

d) Water resistance

Biomass-based materials tend to be hydrophilic. An increase in moisture content could degrade biomass materials (Kymäläinen *et al.*, 2014). This makes the water resistance of biomass materials an important factor in ensuring the structural integrity of samples in high-moisture areas. There are two main ways of testing the hydrophobicity of a sample; moisture absorption tests and water resistance tests (Gilvari *et al.*, 2019). Moisture absorption is used to test the readiness of a material to absorb water in a high-moisture atmosphere. Water resistance tests the materials' ability to resist absorption of water when fully submerged. Binder type and quantity have been shown to improve the hydrophobicity of biomass samples (Fadele *et al.*, 2021). Additionally, pore size affects water uptake, with larger pores resulting in poorer water resistance (Anggraeni *et al.*, 2021). Water resistance is a critical factor to ensure that samples remain intact under wet storage conditions.

2.8.4. Thermal tests

a) Thermal shock test

A thermal shock test is used to assess the breakability of a material that experiences sudden high temperatures (England, 2000). Nieto-Delgado *et al.* (2014) found that large lumps of anthracite disintegrate into smaller pieces when undergoing thermal shock. They did, however, find that proper binding of coal fines with lignin, collagen, and silicate, produced briquettes with a greater immunity to thermal shock. Baisanov *et al.* (2023) tested the thermal shock of coal briquettes produced using microsilica. They exposed the briquettes to a temperature of 900 °C for 1 h. Thereafter, they conducted an abrasion test to determine the thermal stability of the briquettes. A similar test, thermal fragmentation, utilised by Leokaoke *et al.* (2019), is conducted by placing a sample into a preheated oven at 100 °C. The temperature then rises at 5 °C/min until 700 °C is reached, where it remains isothermal for 60 min. The samples are then weighed to determine the thermal fragmentation. A combination of these methods is required in this study. When coal samples are used in the furnace they are exposed to sudden high temperatures and are then consumed. To ensure that the material makes it to the smelter's top liquid layer the materials must remain intact for a short period as they enter the furnace and experience sudden thermal stress.

b) Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a quantitative analytical method that allows the user to monitor a change in mass of a sample as it heats from ambient to 1600 °C under a constant or changing flow of gas (Saadatkhan *et al.*, 2020). TGA can be used to conduct many different tests. Garcia *et al.* (2013) used a TGA to conduct a proximate analysis on a biomass sample, and Carrier *et al.* (2011) developed a kinetic method to calculate the cellulose and hemicellulose content of a woody sample using TGA. Saadatkhan *et al.* (2020) state that researchers use TGA's to derive conversions, kinetics, and mechanisms for any process with a change in mass when thermally treated. When investigating biofuels, TGA is a simple, fast, and efficient way of determining the reaction kinetics and properties of the samples (Aniza *et al.*, 2024). The quality and quantity analyses of biofuel properties and reactivity can be investigated comprehensively using the thermogravimetric curves and data obtained from a TGA. It is important to understand the combustion performance of biofuels to suitably replace fossil fuels as a carbon-neutral alternative (Aniza *et al.*, 2024).

c) Sessile drop test

The sessile drop test involves placing a sample inside a furnace which can be operated at temperatures up to 2000 °C. Operational parameters which can be varied include the type of gas used, the rate of heating, and the holding time, in addition to the loaded sample. This test can be used to evaluate a multitude of material characteristics, including wetting, softening, melting, volume change, reduction, gas production, foaming, and kinetics of the materials. The method of conducting the sessile drop test is consistent throughout literature (Bao *et al.*, 2021; Lu *et al.*, 2017). A sample is placed into a chamber with heating coils. The chamber is connected to a vacuum pump. The vacuum pump ensures no air is present before an inert gas, either argon or nitrogen, is allowed to enter. A digital camera is used to capture images as the vessel heats up, and the sessile drop begins softening and melting. Typically, the wettability of materials is determined using this test, however, the softening, melting, and volume change may also be determined (Ringdalen *et al.*, 2019). Safarian *et al.* (2008) studied the reduction kinetics of MnO by carbonaceous materials in Ar and CO atmospheres. For this purpose, a sessile drop of high-carbon ferromanganese slag was placed on a carbon substrate – made of synthetic cokes, industrial cokes, or eucalyptus charcoal – and then placed into a sessile drop furnace. Using an electron probe microanalyzer (EPMA), the slag MnO composition was measured before and after the sessile drop test, revealing that the charcoal reduced the MnO to Mn just as effectively as the industrial cokes tested. Canaguier and Tangstad (2021) tested the carbothermic reduction of silicomanganese slags. Various

silicomanganese slags were produced and crushed before being placed onto a graphite substrate and then placed into a sessile drop furnace. Operating at a maximum of 1660 °C under a CO gas atmosphere and using wavelength-dispersive X-ray spectroscopy (WDS), it was found that an increase in temperature and holding time resulted in greater reduction of MnO to Mn across all the slags produced.

2.9. Summary

For smelting purposes, a high coal quality is required. This correlates to the use of anthracite or coke products as reductants in smelting operations. The use of fossil fuels has led to concerns over the greenhouse gas emissions from the smelting industry, with a particular focus on steel and iron production. The use of alternative carbon-neutral reductants will lower GHG emissions, but not directly through the smelting process. Instead, carbon-neutral reductants will help lessen the effect of mining coal resources, noting that coal mining has GHG emissions equivalent to that of all of China's 1100+ coal power plants (McKenna, 2022).

There are a wide variety of sources for biomass waste, including wood and wood processing waste, agricultural waste, biogenic materials in municipal solid waste, and animal manure and human sewage (EIA, 2023). Many of these waste streams have uses, but a substantial amount of waste still ends up in landfills. Hence, in addition to potentially lowering GHG emissions in the smelting industry, the use of biomass waste may free up land and utilise fewer resources. For the biomass to be used in a smelting environment, it needs to undergo thermal treatment.

Biochar can be produced through a variety of techniques such as torrefaction, pyrolysis, and hydrothermal pre-treatment. The temperature at which biochar is produced should be carefully considered for the operation in which it is required. The production temperature of biochar affects the chemical composition and mechanical properties of briquettes. Biochar requires densification for use in smelting operations.

Densification of biochar is vital for the operation of smelters. Firstly, it is used to improve the density of the biochar materials for easier transport and prevent the generation of fines. Fine particles are not feasible in certain smelters as the gas stream would transport any fine particles out of the smelter. There are numerous methods and variables used in the densification of biomass-based materials. An important factor is the addition of a binder. A binder helps improve the mechanical stability of a sample and may potentially improve hydrophobicity whilst improving the chemical composition depending on the operation and binder used.

To assess the suitability of biochar briquettes in smelting, mechanical, structural, chemical, and thermal tests are investigated. Many of the mechanical tests do not have a universal standard that researchers conform to, and it is, therefore, important to accurately and thoroughly state the methods used in conducting those tests. It is also important to produce a mechanically stable product to prevent the generation of fines. To have a similar composition as that of anthracite or coke, biochar requires a high fixed carbon content, with low volatile matter and ash content.

The methods in use are well adapted for using coal as the primary reductant. Hence, the substitution of coal with biochar requires the biochar to have as similar properties to the coal in use as possible. The properties of anthracite are displayed in Table 5. Many of the specifications set out in this table are desired characteristics of biochar pellets.

Table 5: Properties of anthracite as found in literature.

	Property	Specification	Source
<u>Mechanical</u>	Compressive strength	7 – 51 MPa	(Agioutantis <i>et al.</i> , 2023)
	Abrasion resistance	95%	(Richards, 1990)
	Drop shatter test	IRI > 50% FR > 80%	(Richards, 1990) (Kaliyan & Morey, 2009)
	Water resistance	95%	(Richards, 1990)
<u>Structural</u>	Bulk density	800 – 929 g/cm ³	(Speight, 2012)
	True density	1.6 g/cm ³	(Krzysińska <i>et al.</i> , 2005)
<u>Chemical</u>	Fixed carbon content	86%	(Grammelis <i>et al.</i> , 2016)
	Ash content	6%	(Bratek <i>et al.</i> , 2002)
	Ash composition	SiO ₂ ~ 63% Al ₂ O ₃ ~ 28%	(Strakhov <i>et al.</i> , 2022)
<u>Thermal</u>	Thermal shock	~ 80%	(Strakhov <i>et al.</i> , 2022)
	Sessile drop test	Reduction in FeO	-

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHOD

3.1. Materials and gases

3.1.1. Materials

The materials selected for this research were required to be organic due to the potential influence of inorganic compounds during the smelting process, which can lead to lower-quality products as a result of the introduction of significant quantities of inorganic substances. The materials have been described in Table 1 in the scope of the project, Section 1.5. A quick summary is provided in Table 6. The imported low and high-volatile matter content anthracites were retrieved from industry and are both used in high-temperature smelting applications.

Pine sawdust was selected due to the substantial quantity generated annually in South Africa, amounting to 1 million tons in 2017 (Department of Environmental Affairs, 2018). According to Udokpoh and Nnaji (2023), sawdust is an underutilised wood portion. Looking at Nigerian wood production, Udokpoh and Nnaji (2023) found that, despite various applications for sawdust, more than 1.5 million tons of sawdust are either burned or misused each year. This finding indicates significant wastage, given that Nigeria produces 1.8 million tons of sawdust annually. Pine was specifically chosen for this study as it constitutes 49% of all timber plantations in South Africa, with an extensive 584,000 hectares dedicated to pine plantations (Forestry South Africa, 2019). In practical scenarios, sawdust typically comprises a mixture of different tree species, as sawmills rarely process a single type of wood exclusively. However, for this study, the focus is solely on pine sawdust.

Sugarcane bagasse was also investigated due to its abundance. Sugarcane is among the most important crops globally, with the largest crop volume produced annually, representing 21.1% of global crop production (Figueroa-Rodríguez *et al.*, 2019). South Africa ranks among the top 15 sugar-producing countries worldwide (SASA, 2024). Approximately 280 kg of sugarcane bagasse is produced per ton of sugarcane processed (Melati *et al.*, 2017). While much of this bagasse undergoes combustion at sugarcane plants to generate electricity, mechanical properties warrant investigation for potential use as a hardwearing reductant.

Similar to sugarcane bagasse, maize is a highly prevalent crop in South Africa. Annually, approximately 10 – 12 million tons of maize are produced, making South Africa the largest maize producer on the African continent (Syngenta, 2024). Adeoye *et al.* (2011) determined the grain-to-waste ratio of maize to be 128:100, indicating that for every ton of maize produced, 780 kg of waste is generated. This waste, known as maize stover, includes stalks, cobs, husks, and leaves of the maize plant. Maize stover is typically used as livestock feed or left to decompose to enhance soil quality. However, there has been renewed interest in maize stover due to its potential for biofuel production (Casperson *et al.*, 2018). This material was readily available from a farmer who faced challenges in effectively disposing of the stover. Consequently, it represents an organic waste that warrants further investigation.

Table 6: A summary of the samples used in this study.

Samples			
Coal	Biomass	Biochar	Binder
LA – Anthracite (Low volatile)	PS – Pine sawdust	PC – Pine sawdust char	MOL – Molasses
HA – Anthracite (High volatile)	SS – Sugarcane bagasse	SC – Sugarcane bagasse char	PVA – Polyvinyl alcohol
	MS – Maize stover	MC – Maize stover char	LIG – Lignin

3.1.2. Gases

The gases utilised in completing this study include:

- Nitrogen: An inert gas used for TGA work and when producing biochar on lab-scale.
- CO₂: Reactive gas which is used for TGA gasification tests.
- Helium: An inert and light gas used in determining skeletal density.
- Argon: Inert gas used in sessile drop tests.

Summarised in Table 7 are the gases used along with their respective purities.

Table 7: Gases used and their purity.

Gas	N ₂	CO ₂	He	Ar
Purity (%)	99.999	99.9	99.999	99.9999

3.2. Equipment

Some of the more notable equipment used in this study is displayed in Table 8.

Table 8: Some important equipment used in this study.

Equipment	Application
Elite Thermal Systems Limited tube furnace (Model: TMH16/75/610 3x3216 + 3216i)	Prepare biochar and conduct thermal shock tests. Vertical tube furnace used for large particle TGA.
Micromeritics AccuPyc II 1340 Gas Pycnometer	Skeletal density of particles.
TA Instruments SDT-Q600 thermogravimetric analyser (TGA)	Used for the thermogravimetric analysis under CO ₂ and N ₂ .
Drum roller built at NWU Engineering	Used to determine abrasion resistance (tumbler test).
LRXPlus instrument from Lloyd Instruments	Produce pellets and compressive strength tests.
K.R. Komarek Inc. B050 roll press	Produce biochar briquettes.
Wetting furnace (NTNU)	Sessile drop tests.

Photos of all the equipment used are displayed in Table 22 in the Appendix.

3.3. Sample preparation

A photo of all the samples used in this study is available in Table 23, Appendix A.2. Sample preparation for each raw material is described below. Additionally, the particle size distribution (PSD) for each sample is given in Table 9 on an as-received basis.

3.3.1 Pine sawdust (PS)

Approximately 150 kg of pine sawdust was received from a local sawmill. The pine sawdust did not require any preparation before undergoing pyrolysis.

3.3.2 Sugarcane bagasse (SS)

A local sugar company was willing to provide approximately 100 kg of sugarcane bagasse which required washing due to the dirt, ~5 wt.%, present in the sample. The washing procedure is:

- A small sample of bagasse was placed into a bucket filled with water.
- The bagasse was then mixed every 20 min for a total washing time of 60 min.
- After 60 minutes, the bagasse was taken out of the water and allowed to air dry on a clean area of concrete floor. The drying time was dependent on the thickness of the sample bed. The bagasse was layered approximately 5 cm thick and required a week to air dry with thorough mixing once per day.

There was a weight loss of ~5 wt% after washing, which is due to the loss of dirt and small bits of plant material. As can be seen in the photograph of sugarcane bagasse in Table 23, it is a grass-like material. This made determining the particle size difficult, however, the sample was pulverised and sieved to a passing size of -500 µm before being subjected to pyrolysis.

3.3.3 Maize stover (MS)

Maize stover, approximately 110 kg, was retrieved from a local farm where the material had been baled from the fields. This material was large and required crushing before use. A hammer mill was utilised to reduce the particle size of the maize stover. The initial sample size contained pieces of corn stalk which were up to a metre in length. After milling, the sample was sieved to a passing size of -500 µm before being pyrolyzed.

3.3.4 Biochar

For lab-scale testing (Section 3.5), biochar was produced using an Elite Thermal Systems Limited tube furnace (Model: TMH16/75/610 3x3216 + 3216i) as described in Section 3.5.1. Producing sufficient quantities of biochar for pilot-scale briquetting (Section 3.6) required larger equipment. For this reason, pine sawdust biochar for pilot-scale testing was produced in a continuous biochar kiln. This is further discussed in Section 3.6.1.

3.3.5 Low and high volatile anthracites (LA and HA)

A local high-temperature smelting facility provided 200 kg each of LA and HA which are used in daily operation. The anthracite materials were used as received by finding similarly sized particles to the briquettes or pellets tested. However, the sessile drop test required thin disks. Cutting the anthracite into disks required an 11 mm Tork Craft diamond drill bit. Drilling anthracite samples with the diamond drill bit allowed for 8.5 mm anthracite disks to be created.

Table 9: PSD of biomass, PC, and anthracite samples.

Sample	Particles in each size range (%)							
	-212 μm	-500+212 μm	-1+0.5 mm	-2+1 mm	-5+2 mm	-10+5 mm	-20+10 mm	+20 mm
PS	0.5	1.9	1.6	12.3	83.5	0.1	0.3	0.0
SS	0.1	1.9	13.0	7.1	3.2	72.2	2.5	0.0
MS	0.1	0.1	0.6	2.8	4.5	2.4	3.0	86.5
PC	1.0	0.9	2.4	92.1	3.5	0.1	0.0	0.0
LA	0.0	0.0	0.0	0.0	0.0	1.5	64.7	33.7
HA	0.2	0.1	0.2	1.1	8.7	25.7	63.9	0.0

3.4. Characterisation methods

Numerous tests are conducted to characterise the biochar and anthracite materials. The broad categories of characterisation include mechanical, structural, chemical, and thermal tests. This chapter describes the methods used in conducting each test.

3.4.1 Chemical tests

a) Proximate, ultimate, CV, and XRF analyses

Proximate, ultimate, CV and XRF analyses were conducted at Bureau Veritas, a certified testing company. The standards used in performing these analyses are all displayed in Table 10. The fixed carbon content was determined by calculation. The calculation is shown in Equation E-1.

$$FC (\%) = \frac{m_o (g) - [M (g) + A (g) + VM (g)]}{m_o (g)} \times 100 \quad \text{E-1}$$

Where FC is the fixed carbon content, m_o is the original sample mass, M is the moisture content, A is the ash content, and VM is the volatile matter content. The oxygen content in the ultimate analysis is also calculated by difference. The calculation is shown in Equation E-2.

$$O (\%) = 100 - [N (\%) + H (\%) + C (\%) + S (\%)] \quad \text{E-2}$$

Where each letter is the corresponding element on the periodic table, namely, nitrogen (N), hydrogen (H), carbon (C), and sulphur (S).

Table 10: The analyses performed by Bureau Veritas and the standards used.

	Description	Standard
Proximate analysis	Sample preparation	BV-TPM-001 based on ISO 13909-4: 2001
	Moisture content (%)	BV-TPM-010 based on ISO 11722: 1999
	Ash content (%)	BV-TPM-011 based on ISO 1171: 2010
	Volatile matter content (%)	BV-TPM-012 based on ISO 562: 2010
	Fixed carbon content (%)	Determined by calculation.
	Ultimate analysis	Based on ISO 12902 – CHN Instrumental method
	Sulphur content (%)	BV-TPM-013 based on ISO 19579: 2006
	Gross CV (MJ.kg ⁻¹)	BV-TPM-014 based on ISO 1928: 2020
	XRF analysis	ASTM D4326 XRF

3.4.2 Structural tests

a) Particle density

Particle density is the mass of a particle divided by the envelope volume of the particle (Deng *et al.*, 2021). This can be calculated by weighing a single pellet and calculating the dimensions. While there are many methods for calculating the particle density, having a uniform shape allows for the calculation to be as simple as Equation E-3 shown below.

$$\text{Particle density (g/cm}^3\text{)} = \frac{\text{Mass of particle (g)}}{\text{Volume of particle (cm}^3\text{)}} \quad \text{E-3}$$

Where the volume of the particle is calculated by Equation E-4:

$$\text{Volume (cm}^3\text{)} = \pi \times r^2 \times h \quad \text{E-4}$$

With r being the radius of the cylindrical particle and h being the height. However, when the particle is not uniformly shaped, alternate methods are required to calculate the volume. A well-known method of calculating the volume of an object is the water displacement method.

Gupta *et al.* (2017) found the water displacement method to have an error of 1.74%. Proposing a sand displacement method, Gupta *et al.* (2017) found an error of 1.21% from the real volume. Due to the poor stability in water, a similar methodology was followed in this study; sand was initially sieved to collect a uniform sample between -500+212 μm . The sand was then placed into a container of known volume ($V_{s,\text{max}}$) and levelled. The container was tapped to settle the sand and then more sand was added; this procedure was repeated until repeated tapping yielded no movement. Once settled, the sand was weighed, and this was taken as the maximum weight of sand ($m_{s,\text{max}}$) that can be in the container. The density of the sand (ρ_s) could be calculated using Equation E-5.

$$\rho_s \text{ (g/cm}^3\text{)} = \frac{m_{s,\text{max}} \text{ (g)}}{V_{s,\text{max}} \text{ (cm}^3\text{)}} \quad \text{E-5}$$

The container was then emptied, and sand was poured till the container was filled halfway. A test sample was initially weighed (m_t) before being placed into the container and twisted to ensure no air gaps remained at the base of the sample. The container was then filled with sand and tapped and refilled until the sand was completely settled. Weighing this container (m_{s+t}) allowed for the calculation of the mass of the sand (m_s) as shown in Equation E-6.

$$m_s \text{ (g)} = m_{s+t} \text{ (g)} - m_t \text{ (g)} \quad \text{E-6}$$

The volume of the sand (V_s), and therefrom, the volume of the test sample (V_t) can be calculated as shown in Equations E-7 and E-8.

$$V_s \text{ (cm}^3\text{)} = \frac{m_s \text{ (g)}}{\rho_s \text{ (g/cm}^3\text{)}} \quad \text{E-7}$$

$$V_t \text{ (cm}^3\text{)} = V_{s,\text{max}} \text{ (cm}^3\text{)} - V_s \text{ (cm}^3\text{)} \quad \text{E-8}$$

The volume of the particle allowed for calculation of the density using Equation E-3.

b) Skeletal density

Skeletal density is an intrinsic property of a material and is calculated by dividing the mass of the sample by the volume of the sample, excluding the pore volume (Boateng, 2016). The skeletal density of the samples was determined using a Micromeritics AccuPyc II 1340 Gas Pycnometer (abbrev. HePyc) with Helium. A 10 cm^3 sample cup was tared and then weighed with a single pellet inside before being placed into the HePyc. Once sealed and the weight of the sample was input into the HePyc program panel, the test could begin. The equipment

follows the standard ISO 12154 for the determination of density by volumetric displacement – skeleton density by gas pycnometry (Micromeritics, 2024). The general calculation which describes skeletal density well is shown in Equation E-9.

$$\begin{aligned} \text{Skeletal density (g/cm}^3\text{)} \\ &= \frac{\text{Mass of particle (g)}}{\text{Volume of particle (cm}^3\text{)} - \text{Pore volume (cm}^3\text{)}} \end{aligned} \quad \text{E-9}$$

c) Bulk density

Bulk density accounts for voids between particles when multiple particles are packed together. The method followed is based on bulk density calculations by Lee *et al.* (2020) and Theerarattananon *et al.* (2011). A box with dimensions 100 × 100 × 100 mm was initially weighed. The pellets were then poured into the centre of the box and the excess was scraped off with a flat edge to ensure the sample was wholly contained in the box. The box, filled with pellets, was then weighed and the bulk density could be calculated according to Equation E-10.

$$\begin{aligned} \text{Bulk density (g/cm}^3\text{)} \\ &= \frac{\text{Mass of sample and box (g)} - \text{Mass of box (g)}}{\text{Volume of box (cm}^3\text{)}} \end{aligned} \quad \text{E-10}$$

3.4.3 Mechanical tests

a) Compressive strength

To determine compressive strength the LRX press was utilised. The LRX was configured for compressive strength testing before placing a particle on the machine. Firstly, a large plate was set to move down at 20 mm/min until it reached the particle. Thereafter, a force was applied until breakage of the particle. The force measured at the breaking point was used in calculating the compressive strength of the particle. If the particle is cylindrical, such as pellets, then the compressive strength (MPa) can be calculated from the force (kN) by knowing the diameter of the pellets, according to Equation E-11.

$$CS \text{ (MPa)} = \frac{\text{Force (kN)}}{\text{Top area of pellet (mm}^2\text{)}} \times 1000 \quad \text{E-11}$$

This method is useful for particles with a well-defined shape. For this reason, for particles with irregular shapes, such as the briquettes and anthracite particles used in this study, a different method was required. A 2×12 mm stainless steel rectangular head was placed onto the LRX press. A sample was then placed parallel to the length of the rectangular head. The same procedure as previously discussed was followed to determine the compressive strength. Figure 5 depicts the procedure described. This method attempts to mimic the forces a particle may experience during heap storage.

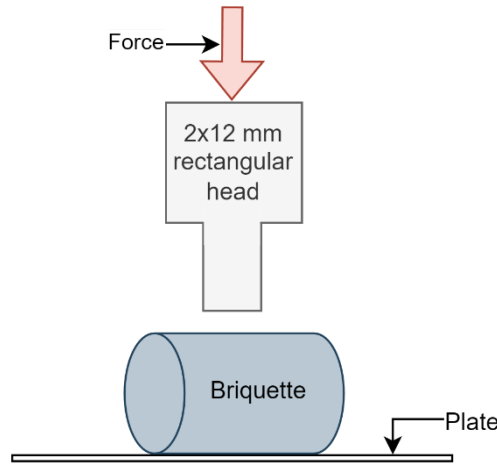


Figure 5: Depiction of compressive strength testing procedure for briquette and anthracite materials.

b) Drop shatter test

The drop shatter test utilised in this study is based on the work done by Richards (1990). A single particle was dropped onto a concrete floor from a height of 2 m. The number of drops before breaking, as well as the number of pieces after breaking, were recorded. These were used in calculating the impact resistance index (IRI), as shown in Equation E-12.

$$IRI = \frac{N_{drops}}{N_{pieces}} \times 100 \quad \text{E-12}$$

Where N_{drops} is the number of drops before breakage, and N_{pieces} is the number of pieces after breakage. The sample was weighed before dropping, and the broken pieces were weighed afterwards to determine the friability (FR) – Equation E-13 shows the calculation of friability.

$$FR = \frac{m_f}{m_0} \times 100 \quad \text{E-13}$$

Where m_f is the mass of the largest piece, and m_0 is the initial mass of the pellet. Viable briquettes require an IRI of 50% (Richards, 1990). For high-quality briquettes, of similar durability to that of raw coal, an FR of 80% is desired (Adapa *et al.*, 2003; Kaliyan & Morey, 2009; Raghavan & Conkle, 1991).

a) Abrasion resistance

The abrasion resistance procedure is based on work completed by Botha *et al.* (2021). A scaled-down version of the tumbler test initially proposed by Richards (1990) was used. In this test, ~17 g of sample was placed into a stainless-steel drum of dimensions: inside diameter 70 mm; length 51 mm. Thereafter, the sample-filled drum was placed onto roller-shafts which have a variable speed motor turning at 80 rpm. After 197 revolutions, the sample was taken out of the drum and placed onto a +6 mm sieve. The abrasion resistance was then calculated as the mass of sample above 6 mm over the initial sample mass. Equation E-14 shows the calculation for the abrasion resistance of a sample.

$$\text{Abrasion resistance (\%)} = \frac{\text{Final sample mass above 6 mm}}{\text{Initial sample mass}} \times 100 \quad \text{E-14}$$

b) Water resistance

A method utilised by Richards (1990) was employed in this study. A single pellet was weighed before being placed into cold tap water for a time of 30 min. Every 10 min the samples were lightly tapped. Should the pellet have survived the duration of the experiment, it was taken out and dried of surface moisture before being reweighed. The water resistance index was then calculated using Equation E-15.

$$\text{Water resistance (\%)} = 100 - \% \text{ water absorbed} \quad \text{E-15}$$

Additionally, compressive strength tests were conducted on the surviving pellets to compare the standard compressive strength versus the wet compressive strength. Pellets that do not remain fully intact were described according to how much degradation was apparent as well as the time it took before degradation began.

3.4.4 Thermal tests

a) Thermal shock test

To conduct thermal shock tests on the materials, an Elite Thermal Systems Limited tube furnace (Model: TMH16/75/610 3x3216 + 3216i) is utilised. The tube furnace was initially heated to a temperature of 1000 °C under a continuous flow of 0.1 l/min of N₂. Once isothermal, the nitrogen flow rate was increased to 1 l/min. A test sample was weighed and loaded into a quartz boat before being placed into the tube furnace. The quartz boat, loaded with the test sample, remained in the tube furnace for a total time of 10 minutes. After 10 minutes had passed, the quartz boat was slowly moved away from the source of heat while remaining in the N₂ atmosphere. After approximately 15 minutes, the sample was sufficiently cooled to enter atmospheric conditions without combusting. The cooled sample was placed onto a sieve stack to sieve into size fractions of +10 mm, -10+5 mm, -5+2.36 mm, -2.36+1 mm, and -1 mm. Particles in each size range were then counted and weighed. If the test sample remains relatively unchanged, the degree of thermal shock is considered low or none. Table 11 displays how the degree of thermal shock was classified for each material.

Table 11: The scale used in determining the degree of thermal shock.

Particle weight +10 mm after thermal shock test (%)	Degree of thermal shock
98 ≤ 100	None
80 ≤ 98	Low
60 ≤ 80	Medium
< 60	High

b) TGA

The CO₂ reactivity of the samples was investigated. To conduct reactivity tests on the samples, an in-house designed TGA was utilised. An Elite Thermal Systems Ltd. vertical tube furnace is hung from a variable-height pulley system. The tube furnace was first heated to a maximum temperature of 960 °C under a constant flow of 2 nL/min CO₂. The CO₂ is regulated by a Brooks model 0254 mass flow controller. Once the tube furnace was isothermal, a pellet was placed into a quartz holder which is situated on a Radwag precision PS 750/C/2 balance. For the anthracite samples, a single particle of similar mass to the biochar briquettes was chosen.

The tube furnace is lowered into place over the quartz holder and the reaction is allowed to run to completion – the point at which no further mass loss can be observed. This method was reported by Coetzee *et al.* (2013). To study the conversion of the pellets over time, Coetzee *et al.* (2013) used Equation E-16.

$$X = \frac{M_0 - M_t}{M_0 - M_{ash}} \quad \text{E-16}$$

Where X is the conversion of carbon, M_0 is the initial sample weight before undergoing the test, M_t is the weight of the sample at any time t , and M_{ash} is the weight of the ash that remains after the reaction is complete. To ascertain the reaction rate of a sample, Equation E-17 and Equation E-18 are used. Equation E-17 and Equation E-18 ascertain the reactivity of the sample at 50% and 90% carbon conversion, respectively.

$$R_{0.5} = \frac{0.5}{t_{X=0.5}} \quad \text{E-17}$$

Where $R_{0.5}$ is the reactivity at 50% carbon conversion and $t_{X=0.5}$ is the time at which $X = 0.5$.

$$R_{0.9} = \frac{0.9}{t_{X=0.9}} \quad \text{E-18}$$

Where $R_{0.9}$ is the reactivity at 90% carbon conversion and $t_{X=0.9}$ is the time at which $X = 0.9$.

c) Sessile drop test

The sessile drop test is performed using a specialised rig designed and made at Sintef situated in the Norwegian University of Science and Technology. Figure 6 presents a schematic of the sessile drop furnace, as shown by Canaguier and Tangstad (2021). A carbon substrate (diameter ~10 mm) was placed in the holding cup at the end of the graphite arm. On top of the carbon substrate, a slag drop (diameter ~4 mm) was then placed. The loaded graphite arm was slowly positioned into the graphite tube before the entire rig was sealed. A vacuum pump was initially utilised to ensure no air remained in the furnace. Once the vessel was at 0.299 mbar, the vacuum inlet was closed, and the Ar gas inlet was opened to allow a flow of 0.3 l/min. When atmospheric pressure was reached with the Ar gas flowing then the Ar gas outlet was opened. Heating commenced to 900 °C in 3 min, followed by heating to 1500 °C in 12 min, and lastly to 1700 °C at a rate of 5.5 °C/min (36 min), where it was held isothermally for 60 min. The temperature was constantly measured and recorded using a C-type thermocouple. Additionally, pictures were taken throughout the process using a Basler acA1280-60gc camera. A picture was taken every 2 seconds to record the entire process. At

the end of the run, the furnace was allowed to cool below 200 °C before the sample was taken out. Further analyses of the slag sample through X-ray diffraction (XRD) revealed the degree of reduction of FeO into Fe. XRD analysis was performed by an external company, XRD Analytical and Consulting cc. The degree of reduction is assessed using metallisation (%), as shown in equation E-18 (Chuanchai & Wu, 2024).

$$\text{Metallisation (\%)} = \frac{\text{Metallic Fe}}{\text{Total Fe in sample}} \quad \text{E-19}$$

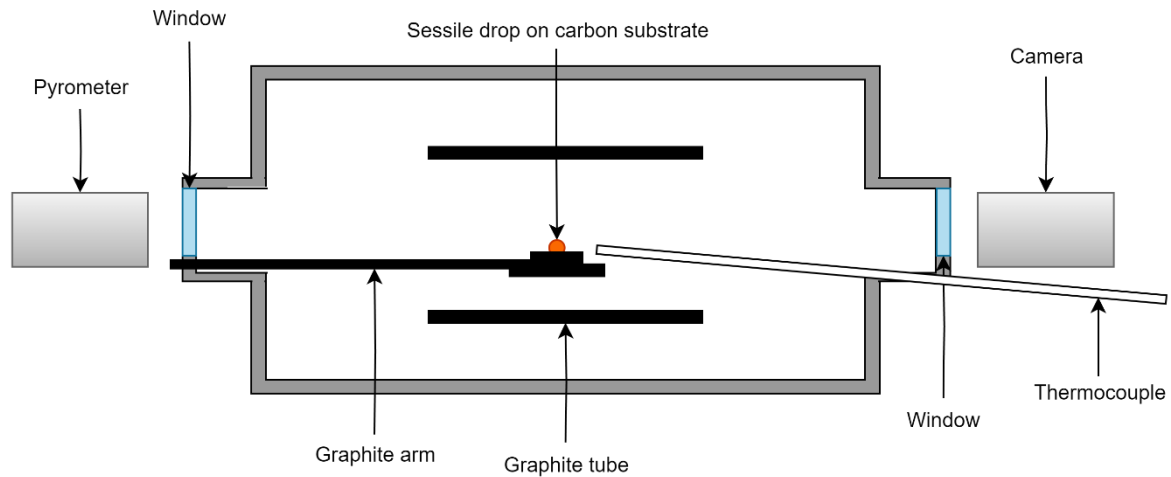


Figure 6: Schematic of the sessile drop furnace (Adapted from Canaguier and Tangstad (2021))

3.5. Lab-scale tests

For lab-scale testing, all biomass samples (PS, SS, and MS) were charred before being pelletised using a Lloyd LRX press. The press was also used to determine the compressive strength of the produced pellets. Along with chemical analyses of the samples, the compressive strength of the pellets was a determinant of which biomass material to study further.

3.5.1 Biochar preparation

To prepare the biochar for pellet creation an Elite Thermal Systems Limited tube furnace (Model: TMH16/75/610 3x3216 + 3216i) was used. Approximately 20 g of biomass was placed into a ceramic boat before being placed into the tube furnace. The tube furnace was then set to heat at 10 °C/min, under a constant flow of nitrogen (100 ml/min), from ambient temperature to the desired temperature. Temperatures of 650 °C, 750 °C, and 850 °C were investigated to determine the effect of temperature on the mechanical stability and carbon content of the pellets. Once at the desired temperature, the sample was held at temperature for a holding

time of 30 min. After 30 min was over, the tube furnace was left to cool under a constant flow of nitrogen. When the sample had cooled sufficiently (below 200 °C) it was taken out of the tube furnace to be used for producing pellets.

3.5.2 Producing pellets

The method followed here is based on research done by Hu *et al.* (2016). For the lab-scale tests, the binder, binder ratio, and water addition were all kept constant. The biochar samples were first crushed to $-500\ \mu\text{m}$ and then mixed with 10% LIG and 35% water. Pellets were produced using the LRXPlus instrument from Lloyd instruments (LRX). One gram of the biochar-binder mixture was placed into a 10 mm die-set after which the die-set was placed onto the LRX. The LRX was set to move downwards at 21 mm/min until the die-set was reached. Once reaching the die-set, the LRX downward speed was increased to 100 mm/min until a load of 4 kN (51 MPa for a 10 mm diameter sample) was exerted on the die-set. It remained at this load for a holding time of 30 s. After the holding time, the LRX reset to its original state and the pellet could be removed. The pellet was allowed to air dry for 1 day before undergoing compressive strength tests. Hu *et al.* (2016) pelletised at a pressure of up to 224 MPa, however, the LRX has a safety limit whereafter power is cut at 4.5 kN.

3.5.3 Determination of the primary biomass

The TGA was utilised for quick and accurate proximate analyses of the biochar samples. Using the proximate analyses of the biochar materials produced at different temperatures, a charring temperature could be chosen by comparing the carbon and ash contents of the materials. Using the TGA for quick, effective proximate analyses has been studied in detail (Jain *et al.*, 2016; Mayoral *et al.*, 2001; Park *et al.*, 2022; Shi *et al.*, 2013). A sample of 10 – 20 mg is placed into the TGA and heated at 10 °C/min under a nitrogen atmosphere. From atmospheric temperatures to $\sim 200\ ^\circ\text{C}$, the moisture content is heated off the samples, after which any mass loss is due to the expulsion of volatile matter content. The max temperature was set at 900 °C. Once at max temperature, the gas switched over from nitrogen to CO_2 . The mass loss observed after the introduction of CO_2 is considered to be the fixed carbon content of the sample. Any mass that remains after the sample has undergone complete combustion is thus the ash content. For more accurate analyses, some of the samples were chosen to be sent to Bureau Veritas for proximate, ultimate, and CV analyses. As previously stated, the compressive strength of the biochar pellets, as well as the carbon content of the materials, are the determining factors for eliminating materials from studying further. The ash content of the samples is also important and was considered when the ash content was significantly greater

than that of the anthracite materials tested. The anthracite materials underwent the same tests to provide a basis for comparison. From the lab-scale tests, a single biomass was chosen to use in the pilot-scale briquetting operation, Section 3.6.

3.6. Pilot-scale briquetting

Using the biomass selected in Section 3.5, briquettes are produced on a larger scale using a K.R. Komarek Inc. B050 roll press. Additionally, molasses and PVA binders are introduced. This section has 2 distinct phases used in completing the study; Phase 1 (Section 3.6.4) and Phase 2 (Section 3.6.5) are clearly explained below.

3.6.1 Biochar preparation

A large quantity of biochar was required to operate the Komarek press, with each run requiring approximately 200 g. In Section 3.5 the biochar was produced in a tube furnace under an inert N₂ atmosphere. While this may have been effective at producing high-quality biochar, the output was minimal, with a maximum output of 30 – 40 g of biochar per day. To produce sufficient biochar for this section, a biochar kiln was utilised.

The biochar kiln is depicted in Figure 7. Wood was first loaded into the furnace and ignited to allow the furnace and chamber, with the 3-pass screw conveyor, to heat up. The system was left to heat the chamber until the temperature remained constant; around 600 °C. Once at this temperature, the feed material, pine sawdust, could be fed into the top of the chamber – where it fell into the topmost screw conveyor. Pine sawdust was fed into the kiln at a feed rate of 2 kg per 2 min (60 kg/hr). Biochar was produced as the sawdust was slowly pushed along the 3 successive screw conveyors, one below the other. Volatile matter content released from the sawdust was channelled to the furnace, which acts as a vacuum pulling the volatile matter content, as well as any air, to combust – further heating the chamber. This increase in heating allows for greater charring temperatures. Multiple variables may be manipulated to control the temperature of the chamber, namely:

- Feed rate of wood into the furnace: A constant supply of wood fed into the furnace ensures the temperature can remain high. It has less of an effect once the volatile matter from the biomass begins to combust.
- Opening of the air intakes of the furnace: Sufficient oxygen allows for the combustion of materials in the furnace, thereby increasing the temperature. Opening the air intake fully allows more oxygen, lowering the temperature of the chamber.

- Opening of the chimney: It may be used to draw in additional air for combustion. Smoke from the chimney indicates too little air and it can be opened more to increase combustion, thereby increasing temperature.
- The feed rate of the raw biomass material: A higher feed rate increases the temperature due to the increase in combustible gases flowing to the furnace. The feed rate should be carefully regulated as high feed rates may lead to temperatures greater than what the equipment is rated for.
- Opening of the flare: Varying the opening of the flare proved to be the most effective method for controlling the temperature of the rig. A closed flare meant all the combustible gases were directed to the furnace, increasing the temperature. To lower the temperature, the flare opening was widened – redirecting the combustible gases into the atmosphere.

Using these variables to control the temperature of the biochar kiln ensured that all material saw temperatures $\sim 850\text{ }^{\circ}\text{C}$; measured using a thermocouple placed at the centre of the rig – labelled TI-01. The speed of the screw conveyors was set such that the material had a residence of 30 min in the chamber before leading into the screw conveyor that fed into the cooling unit. The screw conveyor feeding into the cooling unit pushes hot material up a steep gradient to a hopper where a butterfly valve seals the rig. The biochar cools sufficiently from the stainless-steel components such that it can be held by hand when exiting the cooling unit. The entire rig was constructed from stainless-steel. The approximate dimensions for the entire rig are as follows:

- Furnace: $0.7 \times 1\text{ m}$ with a height of 0.9 m .
- Chamber: $0.7 \times 1.5\text{ m}$ with a height of 2.5 m .
- 3-pass screw conveyors: Each with a diameter of 0.4 m and length of 1.1 m .
- Chimney: Diameter of 0.4 m .
- Flare: Diameter of 0.2 m .
- Cooling unit: $0.5 \times 0.5\text{ m}$ with a height of 0.7 m .

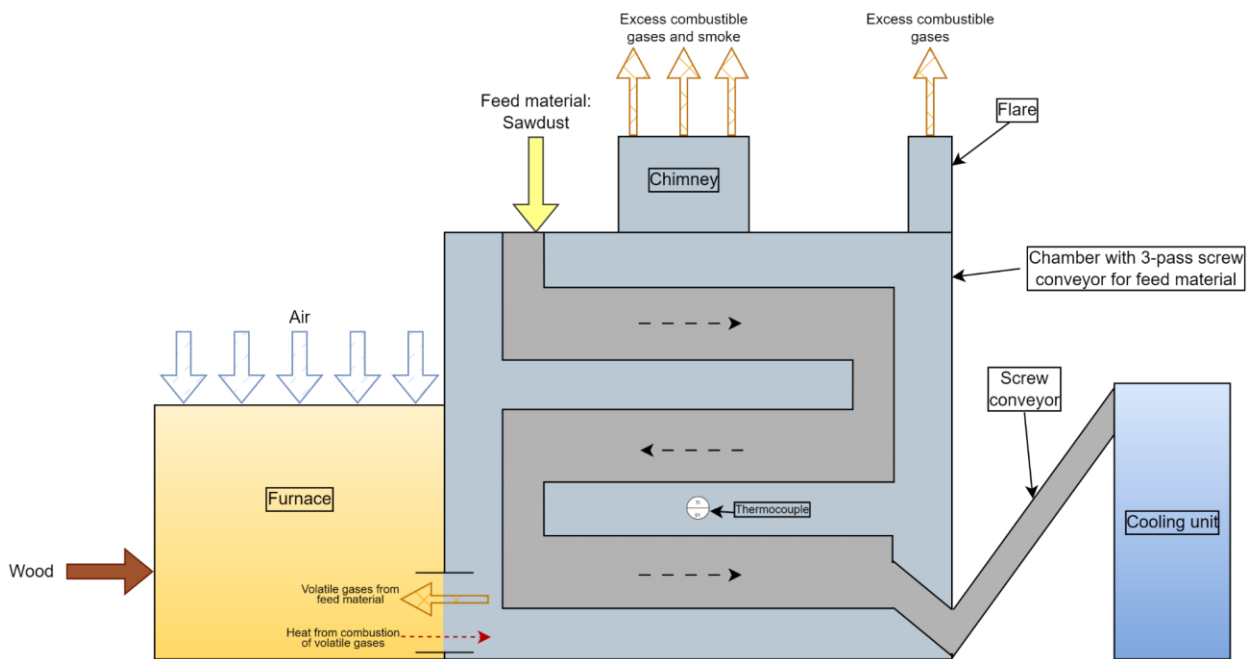


Figure 7: Schematic of the biochar kiln utilised for producing pine sawdust biochar

3.6.2 Binders

Molasses (MOL) and polyvinyl alcohol (PVA) were the primary binders investigated in this study; lignin (LIG) was no longer considered. This is due to how waste lignin is typically sourced. Lignin, when used in binding applications, is normally a waste material from the papermaking industry; therefore, it is an inorganic compound – sodium lignosulphonate. Sodium and sulphur are detrimental to the products of the smelting industry. Guo *et al.* (2018) noted that a high sulphur content negatively influenced the quality of steel. It was found that an increase in the sulphur content of steel lowered the strength and toughness. Sulphur was also found to increase the brittleness and susceptibility of corrosion while lowering the weldability of steel (Schrama *et al.*, 2017). Sodium, meanwhile, is a volatile element which may become gaseous at high temperatures. Due to the high reactivity and corrosion ability, high amounts of sodium in a process may cause damage to smelting furnaces as they may corrode the freeze lining that protects the furnace from the corrosive slag. Both MOL and PVA require dissolution to form a homogenous mixture with the pine sawdust biochar, PC. The method of mixing each binder was as follows.

- Molasses: MOL is easily dissolved in water before being added to PC.
- PVA: This method is based on the PVA mixing method performed in articles by Makgobelele *et al.* (2021) and Rajput and Thorat (2019). To produce a 5 wt% PVA mixture, 5 g of PVA was mixed into 95 ml of water. This mixture was placed onto a

heated stirrer and heated to approximately 98 °C at a heating rate of 2 °C/min and a stirring rate of 100 rpm. After successful dissolution of the PVA, the mixture was allowed to cool below 30 °C before being placed into sealed containers and kept in temperature-controlled rooms. Any addition of PVA to PC is a 5% solution of PVA.

3.6.3 Producing briquettes

The K.R. Komarek Inc. B050 roll press was used to produce pillow-shaped briquettes, with an approximate size of 3.3×1.9×1.2 cm. A schematic of the Komarek is displayed in Figure 6. In addition to varying the binders, the Komarek allows for variation of the screw speed and the roller speed. To determine the screw speed and roller speed, tests were completed using MOL and PVA, in addition to tests without binders. When not using any binders, it was found that a water addition of 15% allowed for briquette formation. Without water added briquettes would not form, and 5%, 10%, and 20% would struggle to process, often getting stuck in the roll press. The process of producing briquettes is:

1. A sample of PC (~200 g) is weighed and placed into the mixing bowl.
2. One of the binders (either MOL or 5 wt% PVA solution) is then added to a beaker (in ratios of 5%, 10%, and 15% of the total char mass) and mixed with 15% water, calculated from the total char mass.
3. The mixer was turned on as the binder mixture was poured into the mixing bowl.
4. The rollers and screws are turned on. It was found that a roller and screw speed of 0.7 and 50 rpm, respectively, worked best for MOL, meanwhile a roller and screw speed of 1.0 and 50 rpm, respectively, worked best for the PVA-bound briquettes.
5. The hatch at the bottom of the mixing bowl is then opened to allow for the biochar-binder mixture to flow into the screw conveyor chamber. The material is pushed through the chamber into the rollers where the material is compressed to form pillow-shaped briquettes.

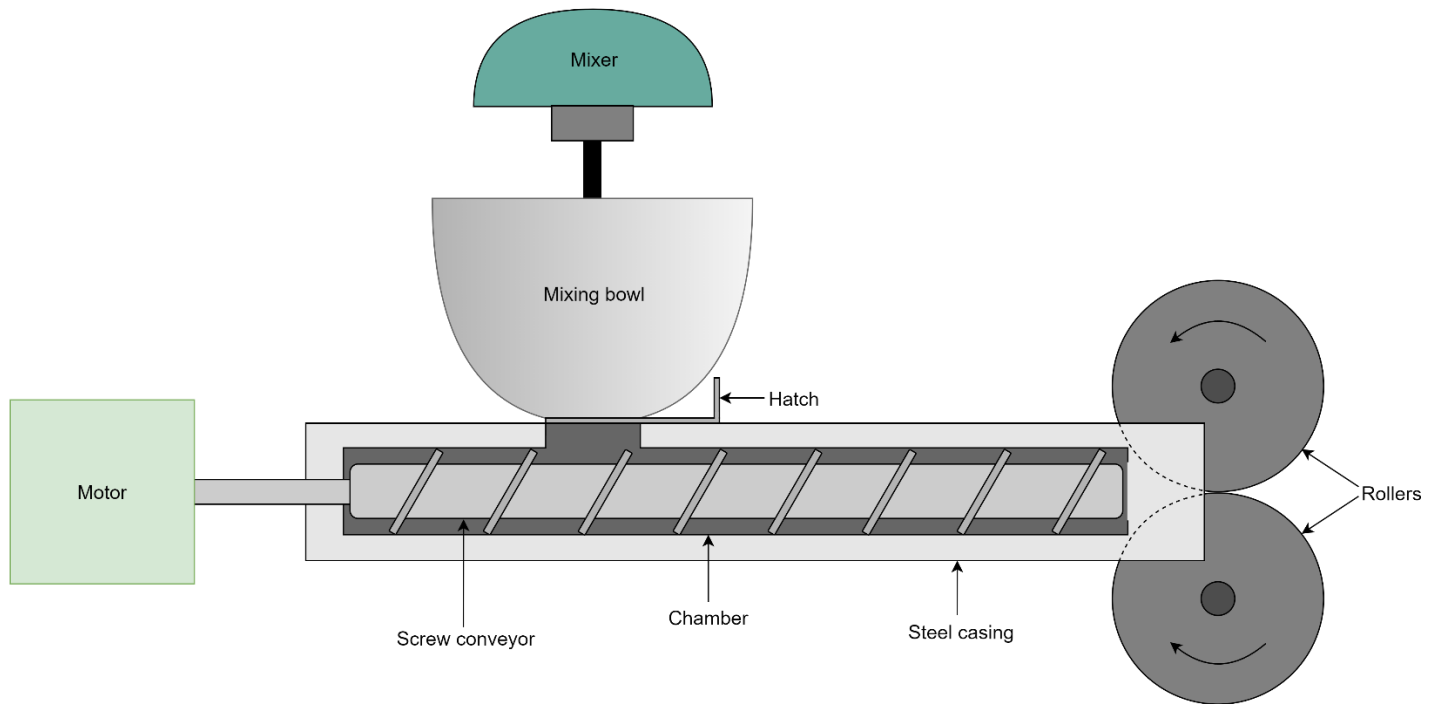


Figure 8: Schematic of the Komarek roll press.

3.6.4 Phase 1: Single binder chosen

To choose a single binder, a variety of mechanical and chemical tests were conducted on each sample. A large quantity of briquettes was produced to determine the effect of curing time for the different samples. The variety of briquettes produced, along with the tests conducted for this phase are displayed in Figure 9. The briquettes produced were mixed with 5%, 10%, and 15% of MOL and the 5% PVA solution. The briquettes were allowed to air-dry in a room with a regulated temperature of 21 °C. At each curing time of 0, 1, 3, 5, 7, and 10 days, the briquettes were mechanically tested, through compressive strength tests, drop shatter tests, and water resistance tests, and the weight loss for each day was examined. After the full 10 days of curing, the briquettes underwent further testing.

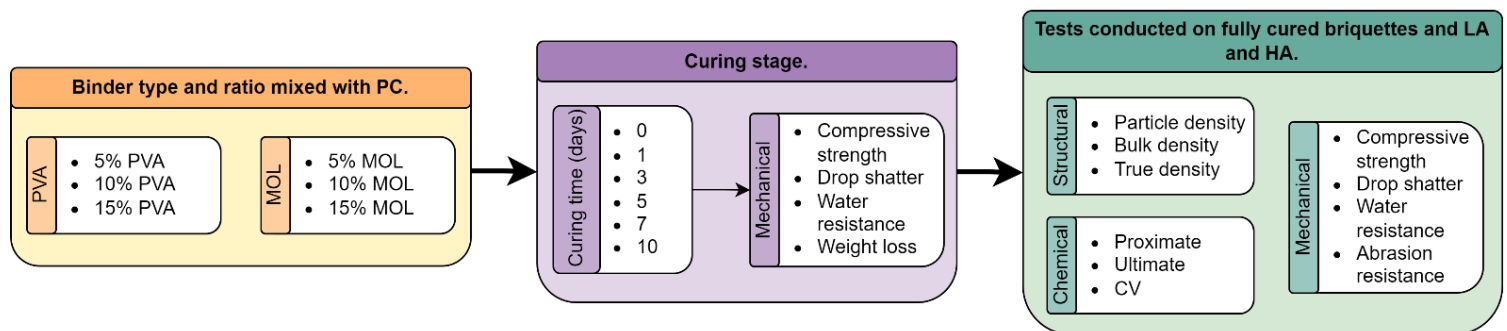


Figure 9: The steps followed in Phase 1, where a binder is eliminated.

Further testing included structural, chemical, and mechanical tests. These tests are displayed in Figure 9 under the heading, “Tests conducted on fully cured briquettes and LA and HA.” Similarly sized anthracite particles from LA and HA were chosen to undergo the same tests. MOL and PVA briquettes were compared with the values determined from the tests conducted on LA and HA, and a single binder was chosen for Phase 2 (Section 3.6.5). Graphs constructed for each test have error bars which represent the standard deviation.

3.6.5 Phase 2: Thermal tests

In this section, briquettes were produced using a single binder with mixing ratios of 5%, 10%, and 15%. Along with the bulk anthracite samples, the briquettes underwent thermal tests, namely, TGA, thermal shock, and sessile drop. The results from the briquettes and anthracite tests were then compared. Once again, any graphs constructed for each test have error bars which represent the standard deviation.

3.6.6 Overview of the experimental method

Figure 10 shows an overview of the experimental method.

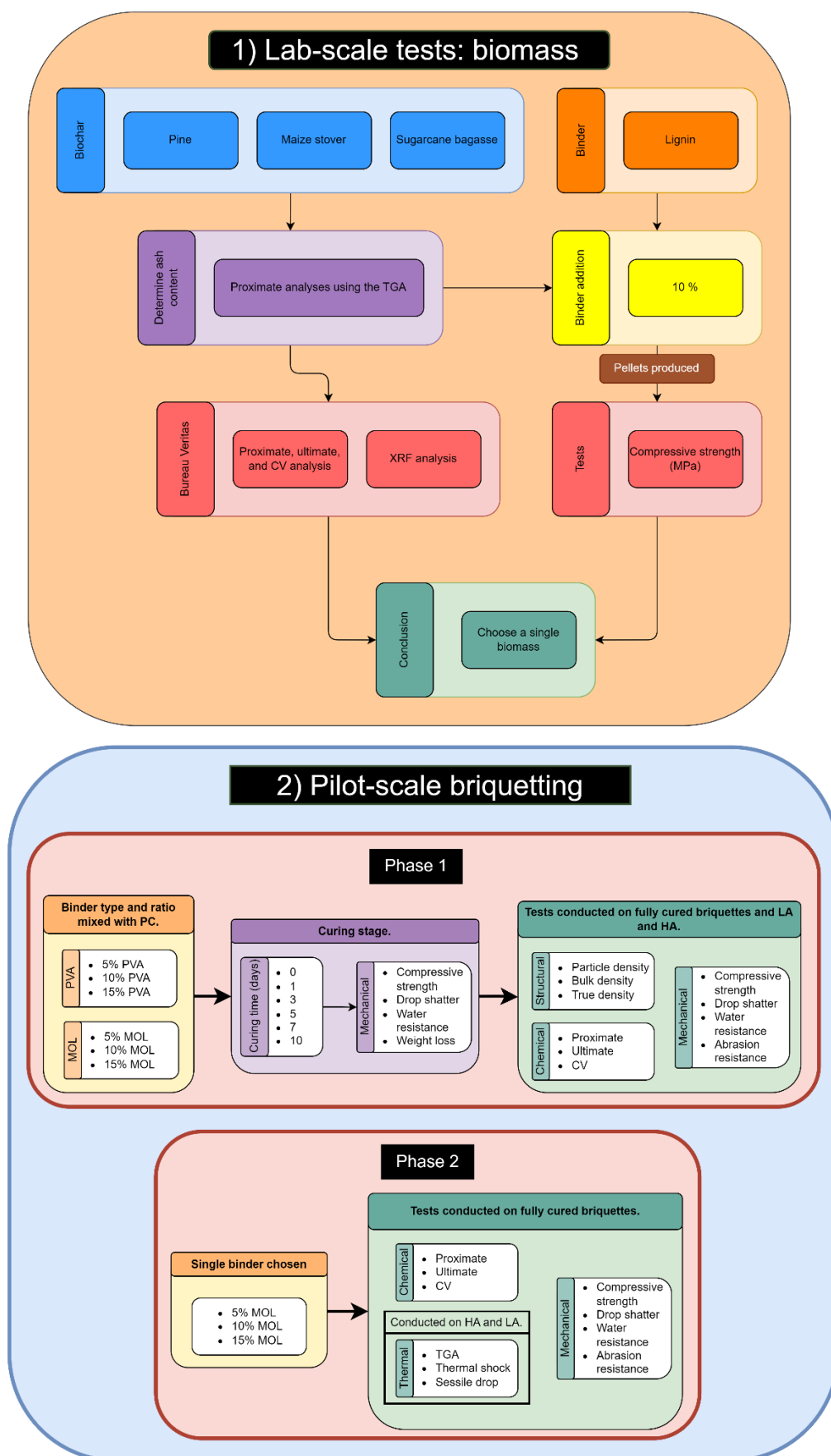


Figure 10: An overview of the experimental method

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Introduction

Chapter 4 presents the results obtained from performing the experiments as detailed in Chapter 3. A discussion of the results is included in each of the subsections. The lab-scale tests are initially discussed before going into depth on the results obtained from the pilot-scale briquetting.

4.2. Lab-scale tests

As stated in Section 3.5.2, this stage was based on research conducted by Hu *et al.* (2016); who had investigated the effect of pyrolysis temperature on the densification of biochar. Pyrolysis temperatures investigated included 250, 350, 450, 550, and 650 °C. At 550 °C the fixed carbon content of the material was 80%, not comparable to that of high-carbon reductants. Only at 650 °C, with a fixed carbon content of 85%, is the biomass-based material similar to that of reductants used in smelting applications. Hu *et al.* (2016) also noted an increase in the strength of pellets the greater the pyrolysis temperature was. Initially, biochar was produced at 650 °C for each biomass sample, maize stover (MS), sugarcane bagasse (SS), and pine sawdust (PS). Using the TGA method for proximate analysis, the ash content of each sample was obtained, and the compressive strength was investigated on pellets made from each biochar; the results are displayed in Table 12.

It was immediately apparent that sugarcane bagasse char (SC) was not suitable, as the material exhibited a high ash content (10%) in addition to low mechanical strength. García-Pérez *et al.* (2002) produced biochar from sugarcane bagasse at 550 °C, resulting in an ash content of 5.5%. An increase in charring temperature results in an increase in the ash content of samples. This is evidenced by Bonelli *et al.* (2007), finding that charring sugarcane bagasse at 600 and 800 °C resulted in ash contents of 10.6% and 12.1% respectively. The compressive strength of SC was much lower than that of pine sawdust char (PC) at 650 °C. There is, however, very little research conducted on the briquetting of sugarcane bagasse char. Most articles that reference the strength of sugarcane bagasse often refer to how cement strength can be improved through the addition of sugarcane bagasse (Krishna *et al.*, 2018; Micheal & Moussa, 2021; Rauf *et al.*, 2017). In cement production, typically sugarcane bagasse ash is

utilised, as it has a high silica content (Rauf *et al.*, 2017). The silica reacts with calcium hydroxide in concrete to form additional calcium silicate hydrate, which fills in micro-voids within the concrete thereby improving the compressive strength of the cement mixture. Another factor that helps in the strength of sugarcane bagasse is the lignin (Ramires *et al.*, 2010), cellulose (Anggono *et al.*, 2017), and hemicellulose (Szczerbowski *et al.*, 2014) content. However, at 650 °C much of these components have decomposed (Varol & Mutlu, 2023). Therefore, neither of these phenomena is present at these temperatures, resulting in a product with low compressive strength.

Similar to SS, MS had a high ash content not suitable as a replacement for high-carbon reductants in use in smelting applications. The MS charred at 650 °C reported an ash content of 15%. Liu *et al.* (2017) and Yang, Sun, *et al.* (2022) produced biochar from maize stover at 700 and 500 °C, respectively, which resulted in ash contents of 14% and 16% respectively. Ngubane and Oyekola (2023) produced biochar at 400 °C, with an ash content of 13%, and then proceeded to produce briquettes using corn starch as a binder at a maximum concentration of 10%. It was found that an increase in the binder concentration and the compression pressure of the briquetting apparatus resulted in a maximum compressive strength of 6.11 MPa. The increased compressive strength is likely due to the greater compaction pressure achieved. A compaction pressure of 40 MPa was achievable for a 50 mm mould. The LRX press in this study may only achieve a compaction pressure of 2.3 MPa for a 50 mm mould.

Table 12: Ash content (%), as determined using TGA proximate analysis, and compressive strength (MPa) of PC, SC, and MC charred at 650 °C for the raw material and the pellets, respectively.

Property	PC, 650 °C	SC, 650 °C	MC, 650 °C
Ash content (%)	2	10	15
Compressive strength (MPa)	5.6 ± 0.6	4.2 ± 0.1	4.2 ± 0.2

PC was further charred at 750 and 850 °C. Along with LA and HA, PS and its charred variants were sent for analysis to Bureau Veritas. The proximate, ultimate, and CV results for these samples are displayed in Table 13. The carbon content of PC at 650 °C was equal to that of the 2 imported anthracite samples, HA and LA. An increase in the pyrolysis temperature increased the fixed carbon content of PC, with a decrease in volatile matter content. The ash content, however, remained relatively the same – due to marginal mass losses in volatile matter content as the temperature increased. The low ash content experienced is in line with

other studies; Investigating pine sawdust charred at 400 °C, Zhang, Jiang, *et al.* (2020) noted a significantly low ash content of 0.56%; Likewise, Yang *et al.* (2014) reported an ash content of 0.52% for pine sawdust biochar produced at 400 °C. The low ash content observed for PS is typical of the plant material (Khelfa *et al.*, 2020), introducing minimal disturbances as a potential reductant in smelting applications. The carbon content and CV seen for HA and LA are in range with what is expected for anthracite (Zohuri *et al.*, 2022).

Table 13: Proximate, ultimate, and CV of HA, LA, PS, and PC at 650, 750, and 850 °C.

Analyses	Samples					
	PS	PC, 650 °C	PC, 750 °C	PC, 850 °C	HA	LA
<i>Proximate analysis (wt.%, a.d.)</i>						
Inherent moisture content (%)	6.2	1.4	1.2	0.9	0.8	2.4
Ash content (%)	0.4	1.4	1.6	1.5	4.7	7.7
Volatile matter content (%)	81.2	8.9	7.9	3.7	6.0	3.7
Fixed carbon content (%) ^c	12.2	88.3	89.3	93.9	88.5	86.2
Gross CV (MJ.kg ⁻¹) ^{a,d.}	17.9	33.9	34.1	33.3	33.8	30.7
<i>Ultimate analysis (wt.%, d.a.f.)</i>						
Carbon content (%)	51.7	91.8	93.7	93.1	90.3	91.6
Hydrogen content (%)	8.9	0.7	0.2	0.0	3.3	1.8
Nitrogen content (%)	0.3	0.5	0.4	0.5	1.4	1.3
Oxygen content (%) ^c	38.8	6.7	5.4	6.1	3.0	4.2
Sulphur content (%)	0.4	0.3	0.3	0.3	0.5	0.3
O:C ratio	0.56	0.05	0.04	0.05	0.02	0.03
H:C ratio	2.06	0.10	0.03	0.00	0.44	0.24

a.d. – Air-dried basis; c – Determined by calculation; d.a.f. – Dry-ash-free basis

Pellets were made from PC charred at 750 and 850 °C. Compressive strength tests conducted on these pellets revealed an increase in the mechanical strength of pellets at greater pyrolysis

temperatures; PC pyrolyzed at 750 and 850 °C had compressive strength values of 7.3 ± 0.3 and 8.0 ± 0.3 MPa, respectively. Producing pellets from corn straw biochar, Xing *et al.* (2018) found that increasing the pyrolysis temperature increased the mechanical properties of pellets. Hu *et al.* (2016) reached a similar conclusion when conducting tests with biochar produced from wood sawdust. It was decided to not investigate charring temperatures higher than that of 850 °C. A temperature higher than 850 °C would increase the cost of production while potentially decreasing the mechanical properties of pellets produced due to the degradation of fibrous and functional groups that help to form matrices with the binders (Ahmed *et al.*, 2021). Additionally, the biochar kiln utilised in this study had an operating max temperature of 850 °C; higher than that for extended periods results may potentially result in the equipment warping.

4.3. Pilot-scale briquetting

Phase 1 (Sub-section 4.3.1) and Phase 2 (Sub-section 4.3.2) of the pilot-scale briquetting process are discussed under their respective subheadings.

4.3.1 Phase 1

a) Effect of curing time

After briquetting, the samples were immediately weighed. Thereafter, each sample was weighed on days 1, 3, 5, 7, and 10. The results of the weight loss for each sample are displayed in Figure 11. Weight loss is incurred due to the addition of water when briquetting samples. As previously stated, the PVA is a 5 wt.% solution of PVA. Hence, the PVA concentration in the sample, “5% PVA,” is 5% of 5%, which results in 0.25% PVA present in the sample. Therefore, at higher additions of PVA, it can be expected that greater mass loss should occur due to the increased water content of the sample. This trend is observed in Figure 11 as the 15% PVA sample reported the lowest end weight out of all the samples. In contrast, any resulting mass loss of MOL samples is due to the addition of 15% water during the briquetting step. This is evident by the similar end weights of each MOL sample. An interesting observation is that no sample reached a weight loss of 15% – equal to the amount of water addition during production.

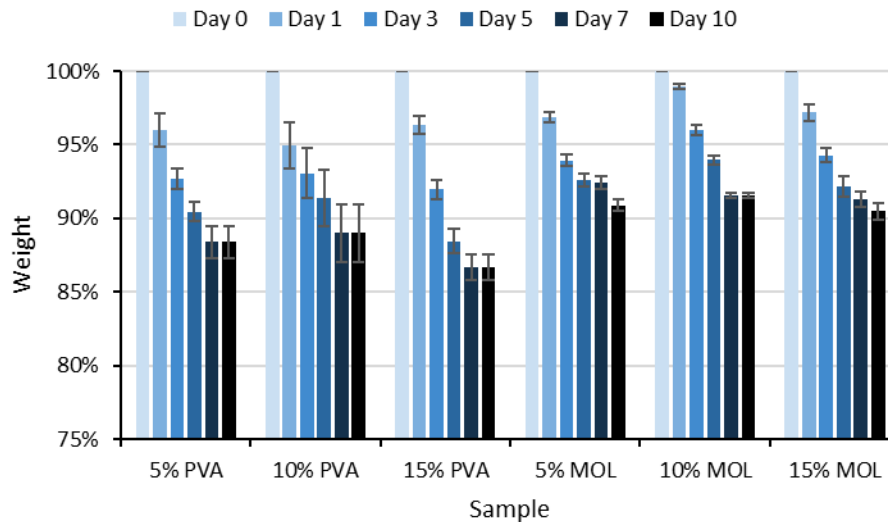


Figure 11: Weight loss results at curing days 0-10 for briquettes produced using various binder additions.

The compressive strength was also measured for 10 days. Figure 12 displays the compressive strength results for each sample for each curing day. Day 0 for all samples is barely visible on the graph as the green strength is poor. Botha *et al.* (2021) and Makgobelele *et al.* (2021) each investigated the effect of curing time on the mechanical properties of run-off-mine coal and charcoal, respectively. The compressive strength was shown to increase substantially within the first few days of curing, before undergoing a consolidation effect to reach equilibrium. Equilibrium was found to be reached at approximately 7 days of curing in both cases. PVA-bounded briquettes reached a stable compressive strength within the first 3-5 days, after which the variability between them lowered – thereby reaching an equilibrium. MOL-bounded briquettes did not appear to reach an equilibrium within the chosen curing time. However, additional compressive strength tests approximately one week later revealed that MOL had reached equilibrium. The variability observed between curing days is likely due to briquette production compression pressure inaccuracies introduced during briquetting.

Strikingly evident is the significantly greater compressive strength of MOL-bounded briquettes compared to PVA-bounded briquettes. PVA at 5% and 10% produced fragile briquettes, leaving powdered remnants wherever placed. Botha *et al.* (2021) produced binder-less briquettes from run-off-mine coal and found a compressive strength of 0.5 MPa. Also using a 5 wt.% PVA solution, a compressive strength of 1.1 MPa was achieved with a PVA solution addition of 0.4%. An increase in the PVA addition for Botha *et al.* (2021), up to 1.2%, did not realise an increase in the compressive strength of the briquettes. However, similar to Makgobelele *et al.* (2021), increasing PVA addition for the pine sawdust biochar briquettes

increased compressive strength. Makgobelele *et al.* (2021) produced pellets from charcoal with up to 5% PVA addition, achieving a maximum compressive strength of 11 MPa. Liu *et al.* (2020) found that briquettes made from coal fines and 0.8% PVA content gave a compressive strength of 7.2 MPa. At 15% PVA addition (5% solution $\times$ 15% addition = 0.75% PVA content), the compressive strength of the pine sawdust biochar briquettes reached an equilibrium of $\sim$ 10 MPa; exceeding the compressive strength of 5% and 10% MOL on its final day. Typically coal fines produce significantly stronger briquettes, however, Liu *et al.* (2020) added dry PVA contents which may not have fully dissolved, forming weaker bonds. It is worth noting that the variability between the strength of PVA briquettes was generally less than the variability seen from MOL briquettes – indicating greater homogeneity across briquettes. Nonetheless, MOL formed mechanically stable briquettes at lower quantities. Anand *et al.* (2023) attempted to produce bio-coke for use in metallurgical smelting. One of the materials investigated was pine sawdust, which was charred at 550 °C before being mixed and placed in a mould in an 80:20 coal:biochar ratio along with 10% molasses and undergoing a further carbonisation step at 900 °C. The resultant compressive strength for the bio-coke was 33 MPa, similar to the compressive strength displayed by 15% MOL. These studies use various standards for determining the compressive strength making it hard to gauge the true effectiveness of each binder, however molasses displays high compressive strength across different variations. Meanwhile, the compressive strength of PVA briquettes appears significantly worse than other studies that utilised markedly less PVA.

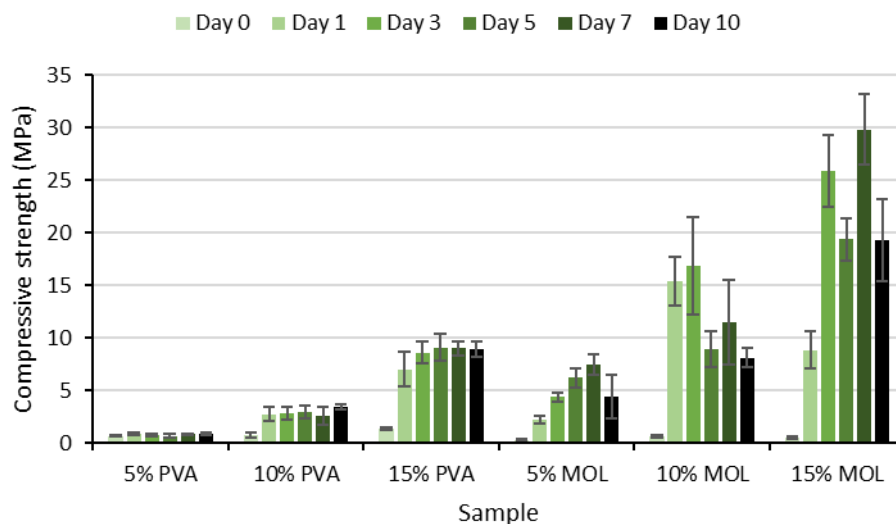


Figure 12: Compressive strength at curing days 0-10 for briquettes produced using various binder additions.

Figure 13 and Figure 14 display the IRI and FR results, respectively. Richards (1990) noted that an IRI of 50 and above is suitable for mechanically stable briquettes. PVA at 5% did not meet this requirement whatsoever, while 10% PVA, according to the standard deviation, had briquettes that may achieve an IRI of 50 after 10 days of curing. A similar result to the compressive strength is seen; 15% PVA had greater mechanical stability in terms of the IRI than that of 5% MOL and 10% MOL additions. Additionally, unlike the compressive strength, 15% PVA had the greatest average IRI of all samples by day 10. It is clear from the graph that increasing binder addition improved the IRI of the samples. These results are in agreement with Liu *et al.* (2020) and Makgobelele *et al.* (2021) where an increase in drop shatter resistance is attributed to an increase in PVA addition. In general, it can be said that the greater the compressive strength of the material, the greater the IRI. A somewhat surprising relationship between MOL samples exists. On the first day of curing, MOL samples showed substantial variation from the average, but it can be seen that proper formation began on days 3 and 5. Looking at the friability (Figure 14), most of the materials met the requirement of 80% set out by Richards (1990); 5% PVA is the only sample to not have reached 80% by day 10. At 10% and 15%, PVA was found to be above the threshold of 80%. The results for PVA are consistent with Liu *et al.* (2020), finding that briquettes produced from PVA exhibit low friability. After 10 days the greatest friability result is achieved from 15% MOL, with 97% mass retained after multiple drops. Zhai *et al.* (2018) found that adding molasses to biochar produced from food waste increased the drop shatter resistance of briquettes, with marginal increases at greater molasses addition; in line with what was found in this study.

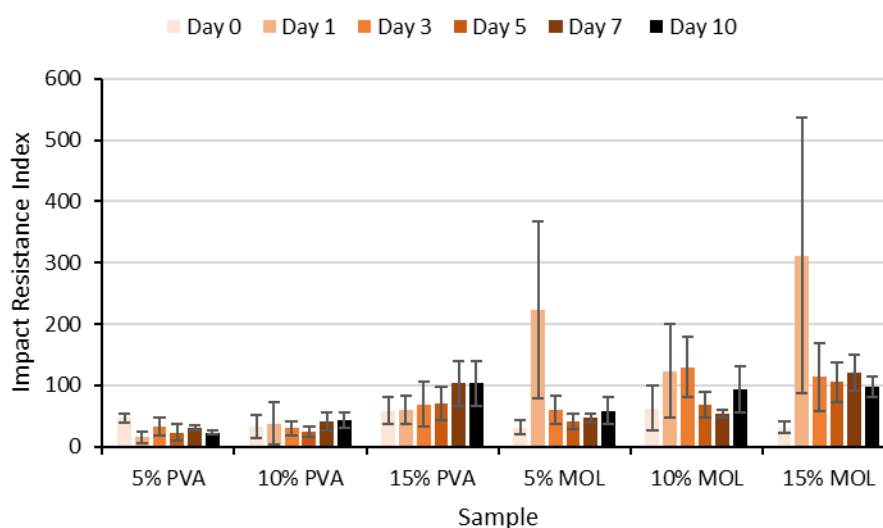


Figure 13: Impact resistance index (IRI) at curing days 0-10 for briquettes produced using various binder additions.

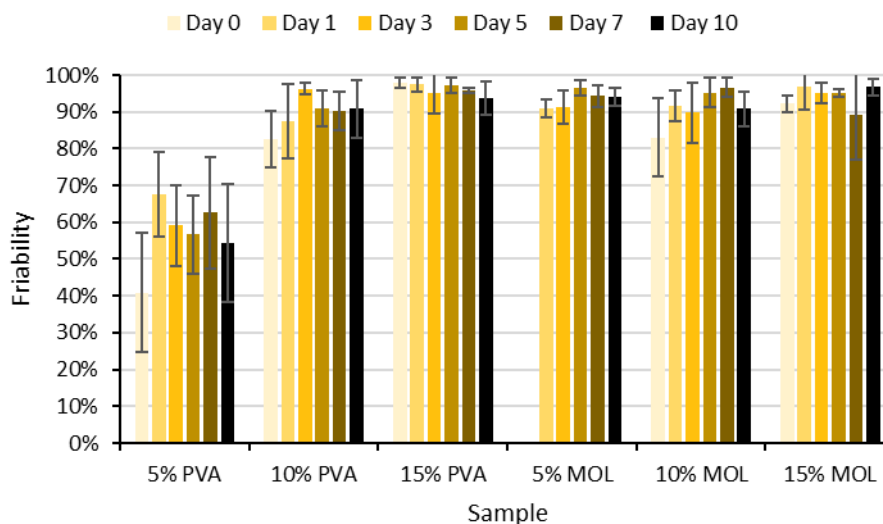


Figure 14: Friability (FR) at curing days 0-10 for briquettes produced using various binder additions.

The last characteristic examined was water resistance. This was conducted on all samples, however, each sample dissolved shortly after having been placed into water. This indicates that the water resistivity of both MOL and PVA-bound briquettes is very poor and open-air storage of these materials would not be possible.

b) Chemical tests on cured briquettes and anthracite

Chemical tests conducted on samples included proximate, ultimate, CV, and XRF analysis. The proximate, ultimate, and CV results are displayed in Table 14. It can be observed that there is a drop in moisture content and volatile matter content from PS to PC, with a resultant increase in fixed carbon content and ash content. The ash content of PS differs from the ash content of PS seen in Table 13. To prepare sufficient biochar, more pine sawdust was collected from the local sawmill. The difference in ash content is therefore most likely due to the pine sawdust coming from different pine plantations in the country. The increase in ash content of the raw material results in an increase in the ash content of the biochar produced at 850 °C; PC in Table 14 has the same volatile matter and moisture content, with higher ash content and lower fixed carbon content, compared to PC in Table 13. Nonetheless, PC has a lower ash content than HA and LA, in addition to having a greater fixed carbon content. The addition of PVA results in slight increases in moisture content and volatile matter content, and an insignificant decrease in fixed carbon content, however, there are no differences in ash content between the variations of PVA addition, indicating that PVA has a low ash content. The moisture introduced during the briquetting stage had dried. The remaining moisture is due to the dissolved PVA, which at 15% PVA is as little as 0.75% PVA in total. The increase in

volatile matter content is due to PVA and may potentially be due to the moisture content bound by PVA that no longer reports to the inherent moisture content. Yang *et al.* (2012) found that PVA would decompose at temperatures above 280 °C, and the most prominent volatile product was water. Hence, it seems likely that additional water may be trapped by the dissolved PVA present in the briquettes. Makgobelele *et al.* (2021), using a 5 wt.% PVA solution found that ash and volatile matter content remained the same with a greater addition of PVA, while the moisture content and fixed carbon content decreased and increased, respectively. However, an increase in the carbon content seems unlikely as the addition of PVA implies the addition of volatile matter content. Unlike PVA, MOL displayed a decrease in fixed carbon content – with increasing ash, moisture, and volatile matter content – at greater binder additions. In decreasing order, molasses primarily consists of volatile matter (60-80%), moisture (20%), fixed carbon (6-16%), and remainder ash content (6-8%) (Anand *et al.*, 2023; Mousa *et al.*, 2019). Therefore, the significant increase in volatile matter content per 5% increase in MOL addition is reasonable, in addition to the sharp decrease in fixed carbon content experienced. MOL briquettes differentiate more substantially from HA and LA, in terms of volatile matter and fixed carbon content than any of the PVA-bound briquettes. However, the Van Krevelen diagram, presented in Figure 15, reveals that all samples are within the anthracite range. In addition to having ash contents similar to HA and LA, the briquettes may all be suitable depending on the tolerances allowed within certain smelting applications.

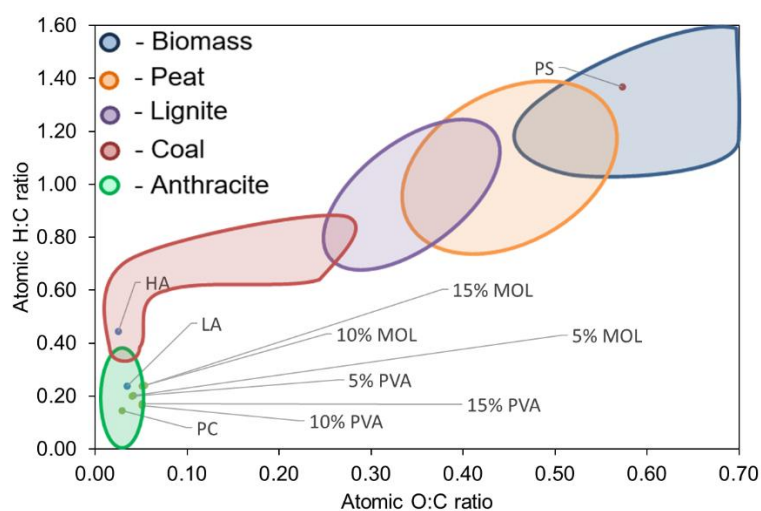


Figure 15: Van Krevelen diagram of HA, LA, PS, PC, and PC with 5%, 10%, and 15% MOL and PVA binder addition.

The XRF analysis is presented in Table 16 with elements that are most prevalent highlighted in yellow. Table 15 presents the tolerances of slag products from an ilmenite smelting operation which may give context as to desirable compositions for products of smelting applications (Pistorius, 2008). The majority of the TiO_2 , Ti_2O_3 , and FeO in ilmenite smelting

are fed into the system through ilmenite (FeTi_2O_3) and rutile (TiO_2). The reductant introduces other elements through the ash content. HA and LA have ash compositions rich in Al_2O_3 , Fe_2O_3 , and SiO_2 . These are values typical of coal samples as reported by Suarez-Fernandez *et al.* (2001) with ranges of 45 – 60 wt% SiO_2 , 20 – 35 wt% Al_2O_3 , and 3 – 15 wt% Fe_2O_3 . The biochar presents high values of CaO , Fe_2O_3 , and SiO_2 , of which Fe and Si are not a problem as these are expected from anthracite reductants. However, when compared with HA and LA, PC has substantially greater quantities of other materials such as P_2O_5 , MnO , and MgO . It is worth noting that SO_3 and P_2O_5 report to the slag phase within an ilmenite smelter. An increase in sulphur and phosphorus could lead to a decrease in the ductility and increased brittleness of metals produced (Saqlain *et al.*, 2018). There is, however, a desulphurisation step that occurs after the metal has been extracted from the smelting furnace, reducing the effect that sulphur has on the process but increasing the operational cost. Manganese content should be closely monitored due to potential side effects from both high and low concentrations. While MnO should largely report to the slag phase, too low concentrations of Mn in the metal phase may promote porosity and cracking of the metal, meanwhile, a high concentration of Mn may decrease ductility and trigger embrittlement (Saqlain *et al.*, 2018). High concentrations of CaO and MgO may have harmful effects in further processing of ilmenite smelting slags as they readily produce salt in chlorination processes (Pistorius, 2008) – potentially rendering biochar alternatives, with high CaO and MgO concentrations, unusable for ilmenite smelting. It is important to note that slag produced from ironmaking and steelmaking typically ends up in landfills (Zhang, Chen, *et al.*, 2020). Due to the low ash content of PC and all the MOL and PVA-bound derivatives, the effect of elements present in the ash may be insignificant. However, the ash content and ash composition did prove to affect the mechanical strength and reactivity of samples, as discussed in sections 4.3.1 d) and 4.3.2 b), respectively.

Table 14: Proximate, ultimate, and CV of HA, LA, PS, PC, and PC with 5%, 10%, and 15% MOL and PVA binder addition.

Analyses	Samples									
	PS	PC	5% PVA	10% PVA	15% PVA	5% MOL	10% MOL	15% MOL	HA	LA
Proximate analysis (wt.%, a.d.)										
Inherent moisture content (%)	4.9	0.8	1.3	1.2	1.3	1.4	1.5	2.0	0.8	2.4
Ash content (%)	1.9	4.2	4.1	3.8	4.0	4.4	4.6	4.9	4.7	7.7
Volatile matter content (%)	80.4	3.6	5.6	5.0	5.1	7.2	9.3	11.2	6.0	3.7
Fixed carbon (%) ^c	12.8	91.4	89.0	90.0	89.6	87.0	84.6	81.9	88.5	86.2
Gross CV (MJ.kg ⁻¹) ^{a.d.}	17.3	32.7	32.7	32.4	32.8	32.0	31.4	30.6	33.8	30.7
Ultimate analysis (wt.%, d.a.f.)										
Carbon content (%)	52.9	94.4	92.8	91.6	91.6	92.4	91.0	90.5	90.3	91.6
Hydrogen content (%)	6.0	1.1	1.6	1.3	1.3	1.6	1.8	1.8	3.3	1.8
Nitrogen content (%)	0.4	0.7	0.5	0.7	0.7	0.7	0.7	0.8	1.4	1.3
Oxygen content (%) ^c	40.4	3.7	5.0	6.2	6.2	5.1	6.2	6.5	3.0	4.2
Sulphur content (%)	0.0	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.5	0.3
Atomic O:C ratio	0.57	0.03	0.04	0.06	0.05	0.04	0.05	0.05	0.02	0.03
Atomic H:C ratio	1.37	0.15	0.20	0.17	0.17	0.20	0.24	0.24	0.44	0.24

a.d. – Air-dried basis; c – Determined by calculation; d.a.f. – Dry-ash-free basis

Table 15: Tolerance of slag product from ilmenite smelting (Adapted from Pistorius (2008))

Element	TiO ₂	Ti ₂ O ₃	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O	V ₂ O ₅
Tolerance (%)	>85.0	<35.0	<12.0	<2.0	<1.5	<0.13	<1.2	<2.0	<0.25	<0.6

Table 16: XRF analysis of the ash content of samples HA, LA, and PS/PC.

Elements (%)	Samples		
	PS / PC	HA	LA
Al ₂ O ₃	7.1	32.9	25.4
CaO	19.0	3.0	4.4
Cr ₂ O ₃	1.4	0.0	0.0
Fe ₂ O ₃	11.3	7.4	8.2
K ₂ O	6.0	3.5	1.8
MgO	4.1	1.0	2.4
MnO	1.5	0.0	0.1
Na ₂ O	0.6	0.0	0.5
P ₂ O ₅	1.8	0.3	0.3
SiO ₂	44.3	48.2	51.8
TiO ₂	0.0	0.1	0.0
V ₂ O ₅	0.1	0.0	0.0
ZrO ₂	0.3	0.1	0.1
BaO	0.1	0.0	0.2
SrO	0.2	0.1	0.0
ZnO	1.3	2.6	3.7
SO ₃	1.0	0.9	0.8

c) Structural tests on cured briquettes and anthracite

Structural tests conducted on the briquettes include bulk, particle, and skeletal density, which are displayed in Figure 16. It can be seen that the briquettes exhibit skeletal densities much

higher than that of the anthracites, HA and LA. Meanwhile, HA and LA display bulk densities significantly greater than any of the briquettes. Jafri *et al.* (2018) state that woody biomass tends to have greater bulk density compared to non-woody counterparts. Nevertheless, a low bulk density is observed for the briquettes, and this may result in logistical issues, both on and off-site of a smelting operation. Smelting plants are equipped to handle dense materials; and feed systems may struggle to feed similar quantities of carbon when handling low bulk density materials such as PC briquettes (Lam *et al.*, 2008). A greater bulk density decreases the packing and shipping costs of materials (Kalyankar *et al.*, 2016). Producing briquettes from pine needles and molasses, Roy and Kundu (2023) suppose that a bulk density of 460 kg/m³ is sufficient for the transportation and storage of biochar materials. This may be true as the global push for environmentally friendly materials requires modernisation and adaptation of industry practices.

The true and particle density have no major effect on the quality of the briquettes; however, certain furnaces have a strong updraft within the furnace and the particles should have enough weight to counteract this draft and land on the slag bath. Additionally, an improvement in the particle density has a positively correlated effect on the bulk density. At temperatures ranging between 200 – 260 °C, Zhai *et al.* (2018) noted an increase in particle density with an increase in pyrolysis temperature as well as binder addition. This is not evident for PVA briquettes, however, there is a slight increase in particle density at greater additions of MOL and a resulting increase in the bulk density. The increase noted for greater MOL addition is due to the density of molasses. Liu *et al.* (2018) produced briquettes from pine sawdust pyrolyzed at 400 – 800 °C and found a decline in particle density from 400 to 500 °C, followed by an increase in particle density until a maximum at 800 °C where the density began to plateau. From Table 13 it can be seen there is a decrease in volatile matter content, with a consequential increase in fixed carbon content at higher pyrolysis temperatures. At 850 °C, the volatile matter content has been heated off, and greater pyrolysis temperatures would have insignificant effects on the fixed carbon content. The loss of volatile matter content leads to an increase in porosity (Claoston *et al.*, 2014; Jindo *et al.*, 2014). It is possible that the porosity allowed for greater binding of MOL as there is greater surface area within the particle. A greater surface area creates more points that binders can adhere to. This leads to an increase in the mechanical strength of particles. Other factors affecting the density of particles are the compression pressure during production and the particle size. Shintawati *et al.* (2024) found that an increase in pyrolysis temperature and a decrease in particle size resulted in biochar briquettes of greater density. Varying both the compaction pressure and particle size, Sunardi *et al.* (2019) observed an increase in the density when increasing compaction pressure while decreasing the particle size.

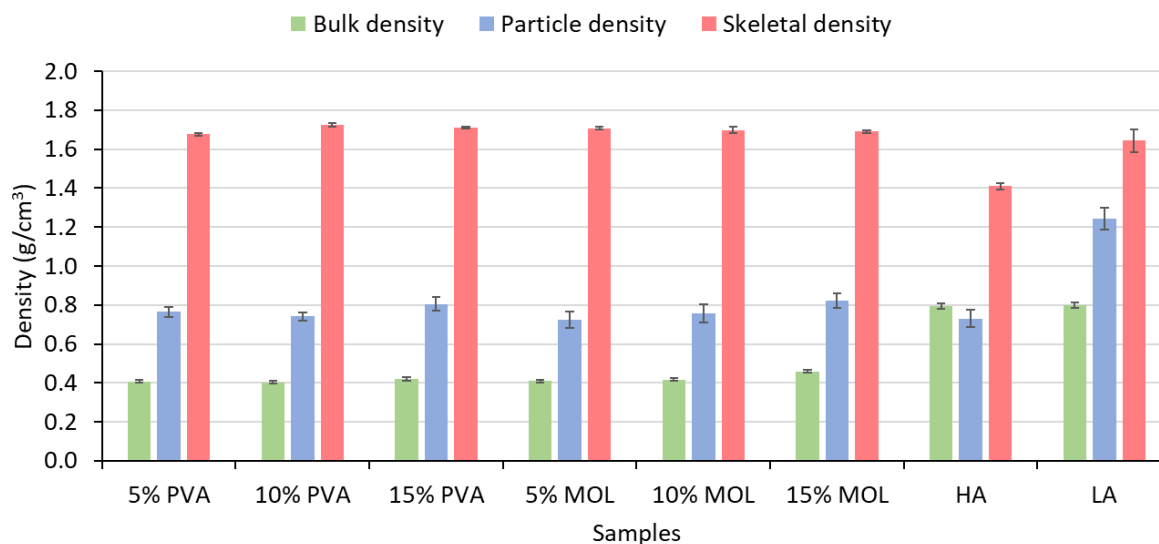


Figure 16: Bulk, particle, and skeletal density of HA, LA, and PC with 5%, 10%, and 15% MOL and PVA binder addition.

d) Mechanical tests on cured briquettes and anthracite

Many of the mechanical tests have been discussed during the curing tests in the section, “Effect of curing time.” However, this section compares the briquettes that have undergone curing against the anthracites, HA and LA. Figure 17 displays the compressive strength results for PVA and MOL-bound briquettes, and anthracite samples HA and LA. The compressive strength indicates the packing ability of materials. A low compressive strength alludes to increased degradation and fines generation when particles are stacked on top of one another (Bai *et al.*, 2015). Reductants are typically stockpiled on large conical heaps, where they must remain intact while under the force of tonnes of material on top.

Briquettes 15% PVA, 10% MOL, and 15% MOL exhibited a compressive strength similar to or greater than that of HA and LA – 15% MOL noticeably having more than double the strength of HA and LA. With the method used for compressive strength, the anthracite materials, unlike the biochar briquettes, did not break cleanly but shattered as layers broke off. Once a clean break was achieved, then this was taken as the compressive strength. Coal rank or maceral composition has little effect on the strength of anthracite materials, with ash content being a better predictor of compressive strength (Agioutantis *et al.*, 2023). LA has a greater ash content than that of HA, and it has a resulting greater compressive strength. Comparing different ranking coals, Zhao *et al.* (2024) found that anthracite displayed the greatest hardness, reduced modulus, and fracture toughness; these are all mechanical parameters. Due to the irregular, asymmetrical nature of anthracite particles, comparing compressive

strength tests with uniformly shaped briquettes may not give an accurate picture of the mechanical properties of anthracite. However, 15% MOL has a compressive strength equivalent to approximately 200 kg/cm². The briquettes weigh a little more than 3 g; this gives context to the scale at which they may be stockpiled without breakage.

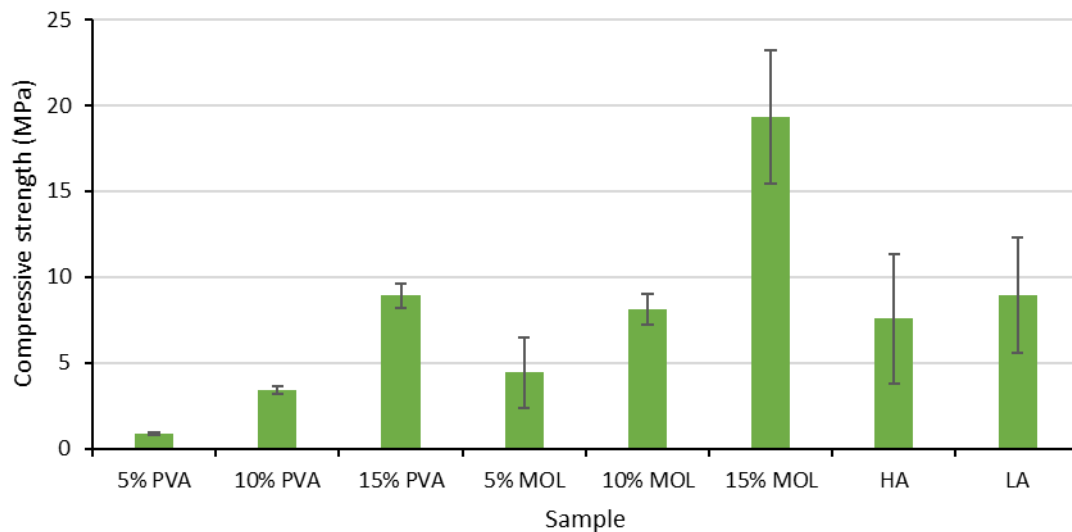


Figure 17: Compressive strength of HA, LA, and PC with 5%, 10%, and 15% MOL and PVA binder addition.

Figure 18 displays the results of the impact resistance index (IRI) tests for PVA and MOL-bound briquettes, and anthracite samples HA and LA. The IRI indicates the ability of a material to handle impact during handling (Dohm *et al.*, 2012). HA shared similar IRI characteristics with 15% MOL and 15% PVA, however it had a larger standard deviation. Meanwhile, the IRI of LA showed a substantial deviation from the average. Considering the standard deviation, HA remains within the desired IRI of 50, but LA does not (Richards, 1990). The worst-performing particle of LA broke into 6 pieces after a single drop, whereas the best-performing particle had yet to break after a maximum of 10 drops. Much the same as the compressive strength, Xie (2015) notes that the ash content of a material affects the drop shatter characteristics. LA has the highest ash content of all materials investigated, resulting in an average IRI much greater than other samples. The high IRI deviations observed for LA and HA are most likely caused by how the material is layered. The asymmetrical shape of the anthracites can cause breakage if the material lands on an edge.

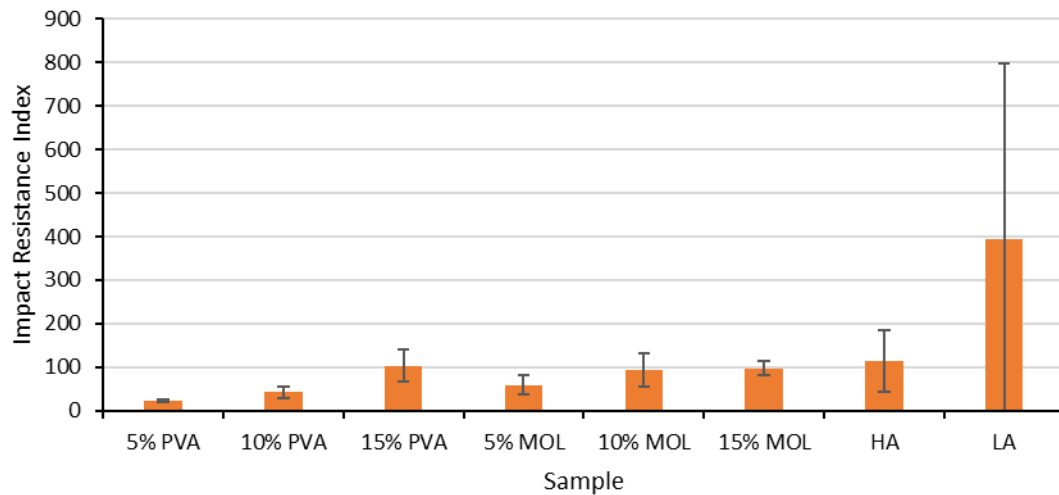


Figure 18: Impact resistance index (IRI) of HA, LA, and PC with 5%, 10%, and 15% MOL and PVA binder addition.

The friability (FR) and abrasion resistance (AR) of each particle are shown in Figure 19 and Figure 20, respectively. These tests work hand-in-hand to assess the durability of materials. The greater the FR and AR, the greater the durability of materials, and therefore the lesser fines are generated. Apart from 5% PVA, all particles passed the minimum requirement of 80% for FR (Kaliyan & Morey, 2009). Across the compressive strength and IRI, the ash content has been the determining factor in the strength of anthracite materials HA and LA. Despite this, LA has one of the lowest reported values for FR. This is a false depiction of the FR of LA, however. The strongest performing in IRI, LA had undergone significantly more drops than other particles. The increased number of drops increased the generation of fine particles which are subsequently lost during the test.

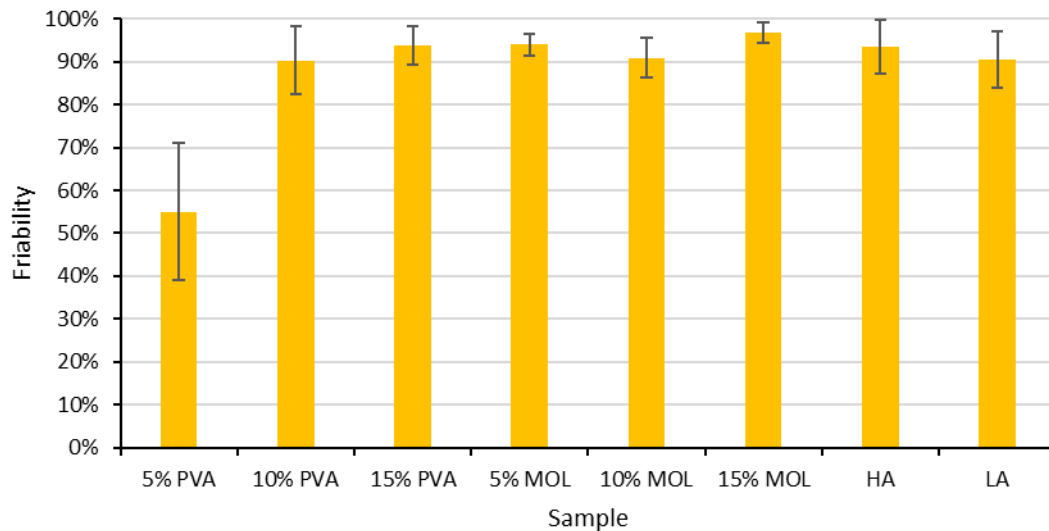


Figure 19: Friability (FR) of HA, LA, and PC with 5%, 10%, and 15% MOL and PVA binder addition.

The minimum of 95% for AR (Richards, 1990) is far stricter than the requirements of IRI and FR. Abrasion resistance is the ability of a material to not be worn away from rubbing or friction (Yuksel, 2018). It is a common test when assessing the durability of anthracite and biochar briquettes (Buravchuk & Guryanova, 2014; Ngene *et al.*, 2024; Wu *et al.*, 2023). These particles do not need to be as resistance as cement, and the test is designed to inspect how the materials behave during handling and transport as they rub against each other. The test takes approximately 2 min and 30 sec to complete. If any samples did not achieve a minimum of 95% then it is likely that the sample will not survive transport and handling on an industrial scale. Samples that do not meet this minimum requirement include 5% PVA and 10% PVA. The average for 5% MOL is above 95%, however, the standard deviation reveals that there may be particles which are below the threshold. Conversely, 10% PVA is below the threshold, but the standard deviation indicates that an AR of above 95% is achieved for some particles. Neither 5% MOL or 10% PVA are suitable. The samples which meet the requirement of 95% include 15% PVA, 10% MOL, 15% MOL, and the anthracites samples, HA and LA.

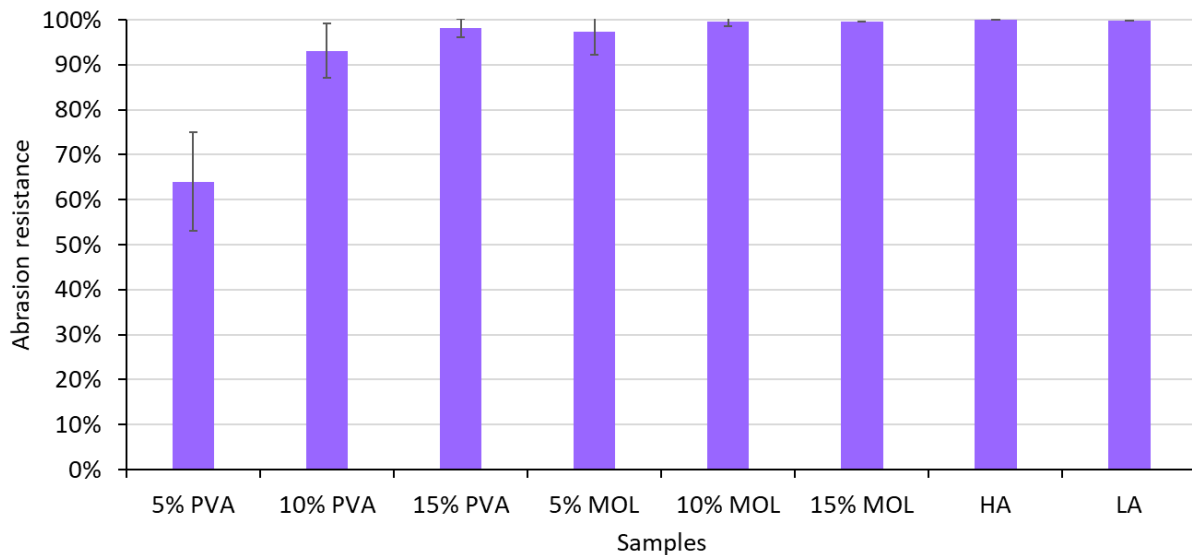


Figure 20: Abrasion resistance (AR) of HA, LA, and PC with 5%, 10%, and 15% MOL and PVA binder addition.

Water resistance tests were conducted on the anthracite samples, revealing HA and LA to not absorb any water and retain their mechanical strength. This is an area that requires massive improvement from the biochar briquettes. With all varieties of MOL being closer in quality to anthracite samples, LA and HA, it was decided to move forward with MOL-bound briquettes for the thermal tests.

4.3.2 Phase 2

Phase 2 of the study includes all thermal tests conducted on MOL briquettes and anthracite materials.

a) Thermal shock

The thermal shock results are displayed in Table 17 and Table 18. Table 17 indicates the number of particles the test began with and the number of particles that remained in each sieve bracket after the test; the size range of -1 mm was noted as no data (N/D) due to the particles being too fine to count. Meanwhile, Table 18 reveals the initial weight of the particles before the test and gives the weight fraction that remained after the test. Thermal shock is an important metric that examines how a particle will behave upon entering a high-temperature environment. Gous (2006) explains that furnaces go up to 1750 °C and materials will often enter from ambient conditions.

Table 17: Thermal shock results displaying the particle count.

Sample name	Number of particles	Particle count					Degree of thermal shock
		-1mm	-2.36+1 mm	-5+2.36 mm	-10+5 mm	+10 mm	
5% MOL	3	N/D	27	4	0	3	Low
10% MOL	3	N/D	16	3	0	3	None
15% MOL	3	N/D	10	2	0	3	None
HA	3	N/D	62	44	31	2	High
LA	3	N/D	46	15	10	3	Low

MOL briquettes performed well in this test, all exhibiting minimal thermal shock. The mass loss observed from the initial to the final weight of HA and LA is likely due to dust and environmental moisture being expelled upon the samples entering the high-temperature environment, in addition to fine generation as the anthracite particles would begin to shatter. Meanwhile, the loss of mass observed for the biochar briquettes is likely due to volatile matter from the binders being driven off. Nieto-Delgado *et al.* (2014) found anthracite to experience thermal shock at 1550 °C in a cupola furnace. This was a much lower temperature, but both would experience thermal shock when introduced into a smelting furnace; HA being the significantly worst-performing material. HA was retrieved from an industrial smelting company that utilised a DC-arc furnace for smelting applications. The company had specifically chosen HA due to how it fractures within the furnace. As Pistorius (2008) describes, the DC arc furnace has a freeze lining which is made up of solidified slag. Due to how HA behaves at high temperatures, it is speculated that HA would add to the freeze lining. This lining protects the furnace from corrosion due to the highly corrosive slag. It is named the freeze lining as the outside of the furnace is water-cooled to allow the slag at over 1700 °C to “freeze” onto the side of the furnace wall. Although none of the MOL briquettes can perform this function, they can replace LA effectively, since LA is purely a high-carbon reductant meant to land in the hot liquid slag and reduce the ilmenite.

Table 18: Thermal shock results displaying the change in particle weight.

Sample name	Initial weight (g)	Weight after (g)	Particle weight (%)					Degree of thermal shock
			-1 mm	-2.36+1 mm	-5+2.36 mm	-10+5 mm	+10 mm	
5% MOL	9.4	8.7	0.3	1.0	1.3	0.0	97.3	Low
10% MOL	9.7	8.9	0.4	0.3	0.5	0.0	98.7	None
15% MOL	10.7	9.0	0.6	0.3	0.5	0.0	98.6	None
HA	10.1	9.1	0.8	2.7	22.9	44.8	28.9	High
LA	10.7	9.9	0.4	0.7	3.2	11.6	84.1	Low

b) TGA

To try to gauge how the samples will behave upon entering the furnace, the CO₂ reactivity is determined. The time taken and reactivity at 50% and 90% conversion is given in Table 19. A graphical representation of the conversion of each sample is given in Figure 21. It is immediately apparent that anthracite samples, HA and LA, have significantly lower reactivities compared to that of the MOL briquettes. High-carbon reductants enter a smelter and begin to react with raw materials to form CO, which may also act as a reductant in certain operations, further reducing the materials to form CO₂. Through the Boudouard reaction, carbon from the reductant reacts with CO₂ to form CO, as shown in reaction R-1. In the case of iron smelting, oxygen is injected into the bottom of the furnace through inlets called tuyères, which reacts with the reductant to form CO, as shown in reaction R-2 (Kreider & Lipinski, 2018). Tabereaux and Peterson (2014) note that above 900 °C, the forward reaction for the Boudouard reaction is highly favourable, with CO virtually being the only product.



Therefore, the high reactivity observed for MOL briquettes may result in the material reacting before landing in the slag bath. Although the CO-rich environment may aid reduction (Pistorius, 2008), LA would likely land in the slag bath, directly reducing any metals. All MOL briquettes exhibit a marginally greater reactivity at 50% conversion (R_{0.5}) than at 90%

conversion ($R_{0.9}$). This indicates that the reaction takes place quicker initially then it does towards the end. This is indicative of surface-limited reactions, whereby a decrease in the surface area results in a decrease in the reaction rate. However, a more likely scenario is an initial mass loss upon entering the heated environment. As discussed in section a) Thermal shock, MOL briquettes suffered none to low thermal shock, but there was mass lost during the test. As seen in Figure 21, a large amount of mass is lost as the sample enters the tube furnace. The conversion graph then becomes more linear, with a decline in the end as all the samples have virtually turned into ash. Meanwhile, both HA and LA undergo a significant loss in mass at the beginning of the test, yet the reactivity values at 50% and 90% conversion suggest a linear relationship. The loss in mass for all MOL samples is likely due to loss in surface moisture content, as well as binder volatile matter being expelled from the sample. On the other hand, HA and LA did not have any binders and yet still incurred a significant mass loss at the beginning of the test. As shown in the thermal shock tests, the anthracite materials form cracks at high temperatures, expelling small particles, and resulting in a rapid mass loss at the beginning of the experiment.

Table 19: The time and reactivity at 50% and 90% conversion.

Sample	$t_{0.5}$ (min)	$t_{0.9}$ (min)	Reactivity (min^{-1}) ($\times 10^4$)	
			$R_{0.5}$	$R_{0.9}$
5% MOL	22.7	54.9	220	164
10% MOL	25.9	64.8	193	139
15% MOL	26.0	64.5	192	140
HA	3450	6240	1.45	1.44
LA	2390	4750	2.10	1.90

Many factors could affect the rate of reaction, such as structural differences, varied gasification kinetics, and potential catalytic effects of ash. Structural differences could include differed surface area to volume ratios, with a low ratio resulting in a decreased reaction rate. However, particles smaller than MOL, with similar mass to MOL briquettes, were utilised for HA and LA; but both anthracite samples displayed slow reactivity. The slow reactivity may be a result of the different pore structures in addition to the minerals present in the ash. Another structural difference that could result in reactivity variances includes the porosity of the materials. Pores are formed from the release of gas and volatile matter content during the pyrolysis of materials

(Park & Seo, 2011). Leng *et al.* (2021) found that woody materials favoured pore development, warranting an increase in porosity from raw to charred wood material. This is particularly noticeable at elevated production temperatures (Hanandeh *et al.*, 2016; Leng *et al.*, 2021). Meanwhile, anthracite has a highly ordered carbon structure, similar to graphite, which results in high thermal stability, but low reactivity (Li *et al.*, 2020). The dense and compact structure of anthracite lowers the number of active sites for gasification reactions. Yang, Liu, *et al.* (2022) confirm this, stating that anthracite requires higher temperatures for ignition and takes longer during combustion and gasification reactions due to its high thermal stability. While articles that investigate biochar porosity (Liao *et al.*, 2021; Qu *et al.*, 2021) report a specific surface area of up to 2700 m²/g, papers that investigate the porosity of anthracite have reported values as high as 1200 m²/g (Albiniak *et al.*, 1996; Maroto-Valer *et al.*, 2005; Zondlo & Velez, 2007). It is unlikely that the porosity alone could have such a profound effect on the reactivity.

It is known that alkali and alkaline earth metals can act as catalysts during gasification or combustion reactions while lowering the activation energy; and that biochar tends to contain high amounts of these elements (Li *et al.*, 2020; Nzihou & Bouesso, 2024). Investigating the effect of mineral content, leads to an expedient equation, the alkali index equation. The alkali index (AI) is defined as the sum of the mass fractions of alkali compounds present in a carbonaceous material divided by the sum of the mass fractions of the acid compounds and then multiplied by the ash content (Lahijani *et al.*, 2015). It is used to quantify the effect that the minerals present in the ash have on the reactivity of the material (Kim *et al.*, 2011; Zhang *et al.*, 2006). The calculation for the alkali index is given in equation E-20 (Sakawa *et al.*, 1982).

$$AI = \text{ash content (\%)} \times \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3} \quad \text{E-20}$$

Calculating the AI for HA, LA, and PC, respectively yields a value of 0.86, 1.73, and 3.34. Once again, the difference in AI between anthracite and MOL is not sufficient to merit the considerable difference in reactivity.

Another factor which affects the reactivity is the fuel ratio. The fuel ratio is described as the mass fraction of the fixed carbon content divided by the volatile matter content (Viswanathan, 2017). A decrease in the volatile matter content of a material results in an increase in fuel ratio, which subsequently leads to a fuel that is more difficult to ignite and slower burning (Miller, 2013). The calculation for the fuel ratio is given in equation E-21 (Meyer *et al.*, 2022)

$$\text{Fuel ratio} = \frac{\text{Fixed carbon content (\%)}}{\text{Volatile matter content (\%)}} \quad \text{E-21}$$

The fuel ratio for HA and LA is 14.8 and 23.4, respectively. Conversely, the fuel ratio for 5%, 10%, and 15% MOL is 12.1, 9.1, and 7.3, respectively. In the same way that the AI and porosity show minimal differences between HA, LA, and MOL briquettes, the fuel ratio of MOL shows minimal improvement in HA and LA. Therefore, it seems likely that the combination of each parameter mentioned results in the large increase in reactivity noted for MOL. There are other factors which may have influenced the reactivity; however, a more in-depth investigation is required and not in the scope of this study.

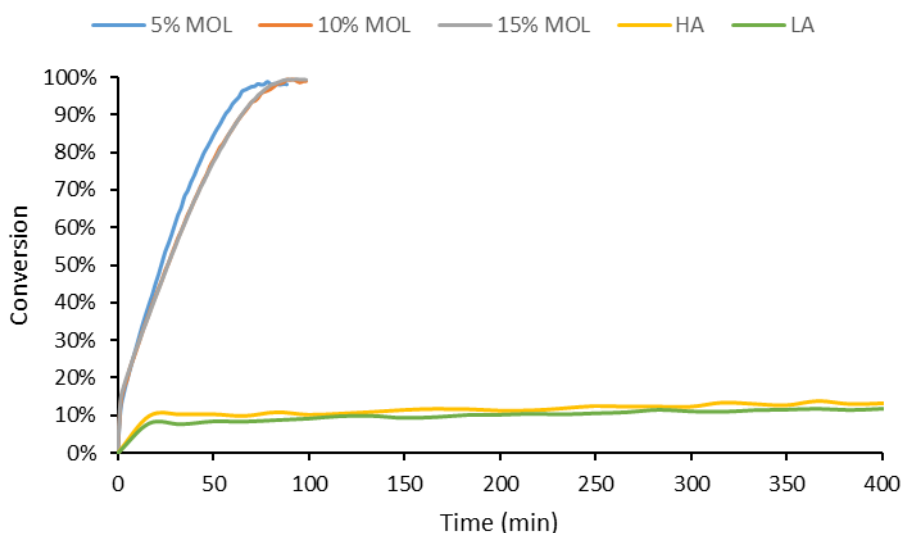


Figure 21: Conversion versus time (min) of HA, LA, and PC with 5%, 10%, and 15% MOL binder addition.

c) Sessile drop

The sessile drop test was performed using slag and reductants produced in this study. A reductant disk of ~10 mm was placed in the holding cup before placing a ~4 mm slag particle atop it. Once positioned in the furnace and sealed, the chamber was flooded with Argon and heating commenced. It took 3 min to achieve 900 °C in the chamber, a further 12 min for 1500 °C, and a final 36 min for a temperature of 1700 °C, which remains isothermal for 2 h. This test examines the effectiveness of reductants by heating a particle on a carbon substrate at elevated temperatures. XRD analysis was conducted on both the raw and reduced slags, providing the composition in terms of tistarite (Ti_2O_3), iron (Fe), anatase (metastable TiO_2), anosovite (Ti_3O_5), pseudobrookite (FeTi_2O_5), rutile (TiO_2), and ilmenite (FeTiO_3). These results are provided in Table 30. Using these results, the total quantity of elements was calculated, to produce Table 20. Additionally, the metallic Fe weight percentage was calculated and utilised to determine the total percentage of metallic iron versus the total iron present in each sample.

Notable differences between the totals of each element for the reduced slags, particularly for Ti and Fe, were observed. These differences are likely due to inconsistencies between different particles of slag. Inspection of the metallic iron percentage between the raw slag and reduced slags indicates the reduction of iron oxides. It was found that 36.2% of all the iron present in the unreduced slag sample was metallic iron. Meanwhile, slags reduced by the MOL-bound and anthracite reductants exhibited a metallic iron content between 86.3% (10% MOL_2) and 97.6% (HA_2), with metallisation similar across all investigated samples.

Gous (2006) notes that slag exiting an ilmenite furnace has a TiO_2 content above 86%. The degree of reduction observed should allow for a slag of similar quality. Due to the significantly greater density of iron, the TiO_2 slag layer is separated from the iron, which sinks to the bottom of the furnace. Safarian *et al.* (2008) investigated how carbon materials affect the reduction of MnO from high-carbon ferromanganese slags in Ar and CO atmospheres. Charcoal was one of the samples investigated, which yielded improved reduction abilities over the coke materials considered. Varying the reaction time, as Safarian *et al.* (2008) did, may reveal that the increased reactivity displayed by MOL results in improved reduction. Chuanchai and Wu (2024) conducted a similar investigation by producing pine wood char at 700 °C and determining its performance in iron ore reduction compared with coke. In agreement with Safarian *et al.* (2008), Chuanchai and Wu (2024) observed a greater reduction capability with biomass-based materials when compared to coke. However, coke outperformed the pine wood char at the study's maximum temperature and holding time of 1300 °C and 25 min. Varying the composition of coke and biochar, they got metallisation values of 86% - 96%, consistent with the values in Table 20. Overall, these results suggest that biochar briquettes with 5% MOL, 10% MOL, and 15% MOL have similar reduction capabilities to the 2 imported anthracite materials, HA and LA, commonly used as reductants in industrial applications.

Table 20: Elemental analysis calculated from XRD analysis revealing the total Ti, Fe, and O present in each slag sample, in addition to the metallic Fe present and the percent of metallic Fe over the total Fe.

Sample	Total of each element (wt.%)			Metallic Fe (wt.%)	Metallisation (%)
	Ti	Fe	O		
Raw slag	48.2	18.0	33.8	6.5	36.2
5% MOL_1	53.1	17.6	29.4	15.4	87.7
5% MOL_2	51.3	19.5	29.1	17.5	89.6
5% MOL_3	46.3	28.8	24.9	27.6	96.0
10% MOL_1	61.7	6.9	31.4	6.2	90.4
10% MOL_2	53.9	16.6	29.6	14.3	86.3
10% MOL_3	53.0	18.2	28.7	16.7	91.9
15% MOL_1	54.4	15.5	30.1	13.5	87.1
15% MOL_2	46.3	28.8	24.9	27.6	96.0
15% MOL_3	59.7	8.8	31.5	7.8	88.2
HA_1	41.6	34.7	23.7	32.3	93.0
HA_2	43.0	33.2	23.9	32.4	97.6
LA_1	49.0	23.5	27.6	21.9	93.1
LA_2	50.5	20.8	28.5	18.9	90.7

4.4. Summary

A summary of some of the results is displayed in Table 21.

Table 21: A summary of the main findings for the most relevant tests and analyses

	5% PVA	10% PVA	15% PVA	5% MOL	10% MOL	15% MOL	HA	LA
Proximate analysis	MC – 1.3	MC – 1.2	MC – 1.3	MC – 1.4	MC – 1.5	MC – 2.0	MC – 0.8	MC – 2.4
	A – 4.1	A – 3.8	A – 4.0	A – 4.4	A – 4.6	A – 4.9	A – 4.7	A – 7.7
	VM – 5.6	VM – 5.0	VM – 5.1	VM – 7.2	VM – 9.3	VM – 11.2	VM – 6.0	VM – 3.7
	FC – 89.0	FC – 90.0	FC – 89.6	FC – 87.0	FC – 84.6	FC – 81.9	FC – 88.5	FC – 86.2
CV (MJ.kg⁻¹)	32.7	32.4	32.8	32.0	31.4	30.6	33.8	30.7
Bulk density (g/cm³)	0.41	0.40	0.42	0.41	0.42	0.46	0.79	0.80
Particle density (g/cm³)	0.76	0.74	0.81	0.72	0.76	0.82	1.24	0.73
True density (g/cm³)	1.68	1.72	1.71	1.71	1.70	1.69	1.64	1.41
Compressive strength (MPa)	0.9	3.4	8.9	4.4	8.1	19.3	7.6	8.9
IRI	23	43	103	59	93	97	115	395
FR (%)	55.0	90.3	93.7	94.0	90.9	96.8	93.4	90.5
AR (%)	64.0	93.1	98.1	97.3	99.5	99.5	99.9	99.8
R_{0.9} (min⁻¹) (×10⁴)	-	-	-	164	139	140	1.44	1.90
Thermal shock	-	-	-	Low	None	None	High	Low
Sessile drop	-	-	-	Effective	Effective	Effective	Effective	Effective

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Mousa *et al.* (2019) describe the challenges associated with using biochar in smelting applications, highlighting issues such as low bulk density, low mechanical strength, and excessively high reactivity in furnace use. The objectives, outlined in sections 5.1.1 to 5.1.5, and the methods used to achieve them, are detailed below.

5.1.1. Determine the primary biomass and charring temperature through a series of pre-screening tests.

Initially, three different biomass sources were investigated: pine sawdust, sugarcane bagasse, and maize stover. An analysis of the ash content and compressive strength of pellets produced from the biochar of these sources revealed pine sawdust to be the best-performing biomass. Pine sawdust exhibited the lowest ash content and the greatest compressive strength. Consequently, pine sawdust was selected for further study. The charring temperature was then determined by performing proximate analysis on samples produced at temperatures of 650, 750, and 850 °C. The proximate analysis provided the fixed carbon content, which served as the main criterion for selecting the charring temperature. The fixed carbon content increased with higher charring temperatures, reaching a maximum of 850 °C. Therefore, 850 °C was chosen due to the high fixed carbon content, low ash content, and increased strength of briquettes produced at this temperature.

5.1.2. Produce a large variety of biochar briquettes and assess the impact of curing time on the mechanical properties.

Biochar briquettes were produced using PVA and MOL at 5%, 10%, and 15% addition. The briquettes were allowed to cure for a maximum of 10 days at 21 °C. On days 0, 1, 3, 5, 7, and 10, several mechanical tests were performed, which included compressive strength, drop shatter, water resistance, and recording of weight loss. A weight loss was observed at each testing interval, indicating that water added during the production of the briquettes was expelled during curing. However, none of the samples reached a 15% weight loss, which was the total amount of water added during production. Compressive strength and drop shatter

results showed a general improvement as curing days progressed. Meanwhile, the briquettes displayed poor water resistance, often disintegrating seconds after submersion.

5.1.3. Determine a single binder based on chemical, structural, and mechanical tests conducted on anthracite and biochar briquettes.

All tests mentioned in Section 5.1.2 were repeated on anthracite samples HA and LA. In addition to the compressive strength tests already conducted, abrasion resistance was performed on all samples. For the structural analysis of the samples, bulk, particle, and true density were investigated. Notably, the bulk density of the biochar briquettes was significantly lower than that of HA and LA. A low bulk density increases the cost of shipping and packaging and may be problematic for feed systems designed to handle heavy loads rather than voluminous loads of proportional carbon content. Chemical tests conducted on the samples included proximate, ultimate, calorific value (CV), and X-ray fluorescence (XRF) analysis. The proximate analyses revealed that biochar samples had similar characteristics to HA and LA. Additionally, similar CV and ultimate analysis results were observed. Conversely, there was a difference in the XRF results for each sample. HA and LA primarily displayed quantities of SiO_2 , Al_2O_3 , and Fe_2O_3 in the ash, whereas biochar briquettes predominantly displayed SiO_2 , SO_3 , Fe_2O_3 , and CaO . It was discovered that MOL briquettes performed better than PVA briquettes per percentage of binder addition. Hence, MOL was chosen as the binder for Section 5.1.4.

5.1.4. Conduct thermal tests on anthracite and biochar briquettes produced using the chosen binder.

Thermal tests conducted on the samples included thermal shock, thermogravimetric analysis (TGA) for reactivity, and sessile drop tests. The poor performance observed for HA during the thermal shock test is intentional, as this material is chosen for its tendency to shatter upon entering a high-temperature environment, which helps maintain the freeze lining within a smelter. However, MOL briquettes performed remarkably well in the thermal shock test, outperforming LA, which showed thermal decrepitation of approximately 84%. In contrast, MOL briquettes did not perform similarly to HA and LA in reactivity tests. There was a substantial difference in reactivity between MOL and the anthracite particles (HA and LA), with MOL briquettes reacting approximately 100 times faster on average. This difference may be attributed to greater porosity, mineral content in the ash, and a lower fuel ratio. The rapid reaction of MOL briquettes may prevent the material from reaching the slag bath to directly reduce metals, as it reacts with the CO and CO_2 -rich atmosphere within a smelting furnace.

This reduced effectiveness as a reductant requires consideration. Should the MOL briquettes land in the slag bath, sessile drop tests confirm that MOL briquettes would be a suitable reductant and replacement for the anthracites, HA and LA, displaying reduction abilities equal to those of the anthracites.

5.1.5. Compare the quality of biochar briquettes to anthracite and evaluate the potential as a replacement fuel.

The quality of biochar briquettes produced is compared with anthracite throughout Chapter 4. Chemical tests revealed that MOL was similar to HA and LA in terms of proximate, ultimate, and calorific value (CV) analyses. Differences were observed in XRF analyses, but these may not pose a problem due to the low ash content of each sample. Structural tests showed that the bulk density of MOL briquettes was approximately half that of HA and LA, potentially leading to logistical issues. Mechanically, the MOL briquettes outperformed HA and LA in almost all areas, except for water resistance. The low water resistance of MOL means outside storage would not be feasible. In thermal shock tests, MOL briquettes displayed practically no thermal degradation but displayed significantly higher reactivity. While MOL excels and even outperforms HA and LA in many areas, it is hindered by low bulk density, extremely poor water resistance, and high reactivity. However, if logistical issues are not problematic and the briquettes are stored in sheltered conditions, the primary concern remains their reactivity. The impact of reactivity on the process requires further testing, but MOL may still prove to be suitable.

5.2. Recommendations

The recommendations are bulleted to improve legibility.

- Increase the concentration of PVA in the binder solution. The PVA demonstrated great potential at higher binding ratios; at 15% PVA, it produced mechanically stable briquettes, and the proximate analysis revealed that the quality remained high despite changes in PVA addition.
- Conduct research into producing water-resistant biochar pellets (using waterproofing agents). The briquettes in this study showed poor water resistance.
- Determine the factors that influence the reactivity of the samples and to what extent these factors influence the reactivity, including the effect of porosity and surface area.
- Investigate the reactivity of materials. The reactivity of the biochar materials was significantly greater than that of the anthracite materials. This may limit the use of

biochar within smelting furnaces. If reactivity presents a problem, then co-blending with anthracite may be an alternative. Other studies have successfully investigated the co-blending of coal and biomass-based materials.

- It would be worthwhile to consider what it would cost to produce this material for a client and what volumes would be practical. Both capital expenditures (CapEx) and operating expenses (OpEx) requirements could be addressed.

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ANNEXURE A: EQUIPMENT AND SAMPLES

Annexure A contains the equipment list and sample list with accompanying pictures.

A.1. Equipment list

The equipment list with pictures is provided in Table 22.

Table 22: Pictures of some of the main equipment used in this study.

Equipment	Photo
Elite Thermal Systems Limited tube furnace (Model: TMH16/75/610 3x3216 + 3216i)	
Micromeritics AccuPyc II 1340 Gas Pycnometer	

**TA Instruments SDT-Q600
thermogravimetric analyser**



Drum roller built at NWU Engineering



LRXPlus instrument from Lloyd Instruments



Head used for compressive strength testing



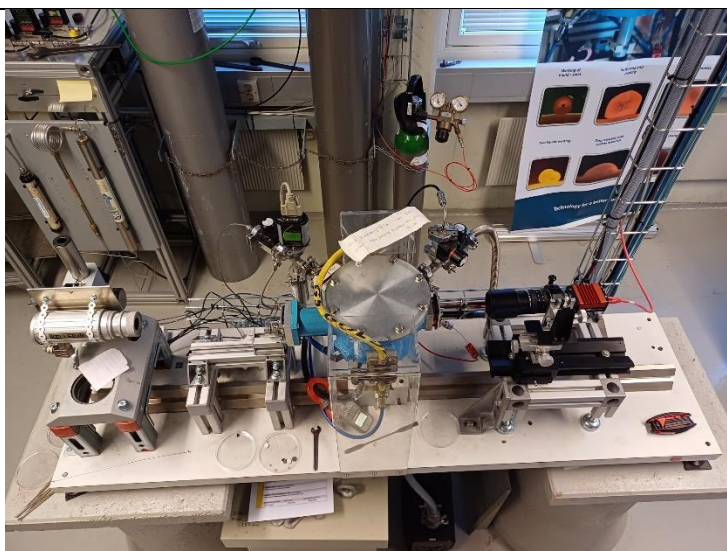
**Vertical Elite Thermal Systems
Limited tube furnace (Model:
TMH16/75/610 3x3216 + 3216i)**



K.R. Komarek Inc. B050 roll press



Sessile drop rig



Slag on 15% MOL disk.



Slag on HA disk.



15% MOL after reduction.



A.2. Samples

The pictures of the samples are provided in Table 23.

Table 23: Pictures of the samples

Pine sawdust as received	
Sugarcane bagasse as received	

Sugarcane bagasse washed



Maize stover as received



Biochar



Briquettes produced using biochar (Size
of 3.3×1.9×1.2 cm)



HA



LA



15% MOL after thermal shock tests.



Briquettes in water after ~10 seconds.



ANNEXURE B: EXPERIMENTAL DATA

Annexure B contains the data used for compiling the graphs presented in the study. The chemical analyses are not included as these were performed by Bureau Veritas and those results have been placed into this dissertation.

B.1. Structural tests

The bulk, particle, and skeletal density are displayed in Table 24.

Table 24: Bulk, particle, and skeletal density (g/cm³) of the samples.

Sample	Bulk density (g/cm ³)	Particle density (g/cm ³)	Skeletal density (g/cm ³)
5% PVA	0.41 ± 0.01	0.76 ± 0.03	1.68 ± 0.01
10% PVA	0.40 ± 0.01	0.74 ± 0.02	1.72 ± 0.01
15% PVA	0.42 ± 0.01	0.81 ± 0.04	1.71 ± 0.00
5% MOL	0.41 ± 0.01	0.72 ± 0.04	1.71 ± 0.01
10% MOL	0.42 ± 0.01	0.76 ± 0.05	1.70 ± 0.01
15% MOL	0.46 ± 0.01	0.82 ± 0.04	1.69 ± 0.01
HA	0.79 ± 0.01	1.24 ± 0.05	1.64 ± 0.06
LA	0.80 ± 0.01	0.73 ± 0.04	1.41 ± 0.02

B.2. Mechanical tests

B.2.1. Weight loss

The weight loss of the briquettes is shown in Table 25.

Table 25: Weight loss (%) of the samples.

Sample	Weight loss (%)					
	Curing time (d)					
	0	1	3	5	7	10
5% PVA	100.0	96.0 ± 1.1	92.7 ± 0.7	90.5 ± 0.6	88.4 ± 1.1	88.4 ± 1.1
10% PVA	100.0	95.0 ± 1.6	93.1 ± 1.7	91.4 ± 1.9	89.0 ± 1.9	89.0 ± 1.9
15% PVA	100.0	96.3 ± 0.6	92.0 ± 0.6	88.5 ± 0.8	86.7 ± 0.9	86.7 ± 0.9
5% MOL	100.0	96.9 ± 0.3	93.9 ± 0.4	92.6 ± 0.4	92.4 ± 0.4	90.9 ± 0.4
10% MOL	100.0	99.0 ± 0.2	96.0 ± 0.3	93.9 ± 0.3	91.6 ± 0.2	91.6 ± 0.2
15% MOL	100.0	97.2 ± 0.5	94.3 ± 0.5	92.2 ± 0.7	91.3 ± 0.5	90.5 ± 0.6

B.2.2. Compressive strength

The compressive strength results are shown in Table 26, whereby day 10 represents fully cured briquettes and the anthracite, HA and LA, values are given at day 10.

Table 26: Compressive strength (MPa) of the samples.

Sample	Compressive strength (MPa)					
	Curing time (d)					
	0	1	3	5	7	10
5% PVA	0.7 ± 0.1	0.9 ± 0.1	0.8 ± 0.1	0.7 ± 0.1	0.9 ± 0.1	0.9 ± 0.1
10% PVA	0.8 ± 0.3	2.8 ± 0.7	2.9 ± 0.6	3.0 ± 0.7	2.6 ± 0.8	3.4 ± 0.2
15% PVA	1.4 ± 0.1	7.0 ± 1.7	8.6 ± 1.0	9.1 ± 1.3	9.0 ± 0.7	8.9 ± 0.7
5% MOL	0.3 ± 0.1	2.2 ± 0.4	4.4 ± 0.4	6.2 ± 0.9	7.5 ± 1.0	4.4 ± 2.0
10% MOL	0.7 ± 0.1	15.4 ± 2.4	16.9 ± 4.6	9.0 ± 1.8	11.5 ± 4.1	8.1 ± 0.9
15% MOL	0.5 ± 0.2	8.9 ± 1.7	25.9 ± 3.4	19.4 ± 2.0	29.9 ± 3.3	19.3 ± 3.9
HA	-	-	-	-	-	7.6 ± 3.8
LA	-	-	-	-	-	8.9 ± 3.4

B.2.3. Drop shatter

The impact resistance index and friability results are shown in Table 27 and Table 28, whereby day 10 represents fully cured briquettes and the anthracite, HA and LA, values are given on day 10.

Table 27: Impact resistance index of the samples.

Impact resistance index						
Sample	Curing time (d)					
	0	1	3	5	7	10
5% PVA	47 ± 7	15 ± 9	33 ± 14	23 ± 14	30 ± 4	23 ± 2
10% PVA	33 ± 19	37 ± 35	30 ± 11	24 ± 8	42 ± 15	43 ± 13
15% PVA	59 ± 22	60 ± 23	69 ± 36	70 ± 27	103 ± 37	103 ± 37
5% MOL	31 ± 11	223 ± 144	60 ± 23	41 ± 12	47 ± 7	59 ± 22
10% MOL	63 ± 36	123 ± 76	130 ± 50	68 ± 21	53 ± 7	93 ± 37
15% MOL	32 ± 10	312 ± 224	113 ± 55	105 ± 32	120 ± 29	97 ± 17
HA	-	-	-	-	-	115 ± 70
LA	-	-	-	-	-	395 ± 403

Table 28: Friability (%) of the samples.

Sample	Friability (%)					
	Curing time (d)					
	0	1	3	5	7	10
5% PVA	40.9 ± 16.2	67.5 ± 11.5	59.1 ± 11.0	56.6 ± 10.6	62.6 ± 15.2	54.3 ± 16.0
10% PVA	82.6 ± 7.7	87.5 ± 10.0	96.4 ± 1.4	90.9 ± 5.0	90.3 ± 5.1	90.9 ± 7.8
15% PVA	97.9 ± 1.5	97.5 ± 1.9	95.1 ± 5.6	97.2 ± 2.1	95.9 ± 0.6	93.7 ± 4.5
5% MOL	0.0	91.0 ± 2.4	91.3 ± 4.6	96.5 ± 2.1	94.4 ± 2.9	94.0 ± 2.5
10% MOL	83.0 ± 10.6	91.6 ± 4.2	89.8 ± 8.1	95.2 ± 4.0	96.6 ± 2.6	90.9 ± 4.6
15% MOL	92.2 ± 2.4	96.7 ± 6.2	95.1 ± 2.9	95.0 ± 1.0	89.4 ± 12.3	96.8 ± 2.3
HA	-	-	-	-	-	93.4 ± 6.3
LA	-	-	-	-	-	90.5 ± 6.4

B.2.4. Abrasion resistance

The abrasion resistance (%) is displayed in Table 29.

Table 29: Abrasion resistance (%) of the samples.

Sample	5% PVA	10% PVA	15% PVA	5% MOL	10% MOL	15% MOL	HA	LA
Abrasion resistance (%)	64.0 ± 11.0	93.1 ± 6.0	98.1 ± 2.0	97.3 ± 5.0	99.5 ± 1.0	99.5 ± 0.0	99.9 ± 0.0	99.8 ± 0.0

B.3. Thermal tests

B.3.1. TGA

The full results for TGA are extensive so the graphs are split to see the MOL briquettes and anthracite materials easier, as shown in Figure 22.

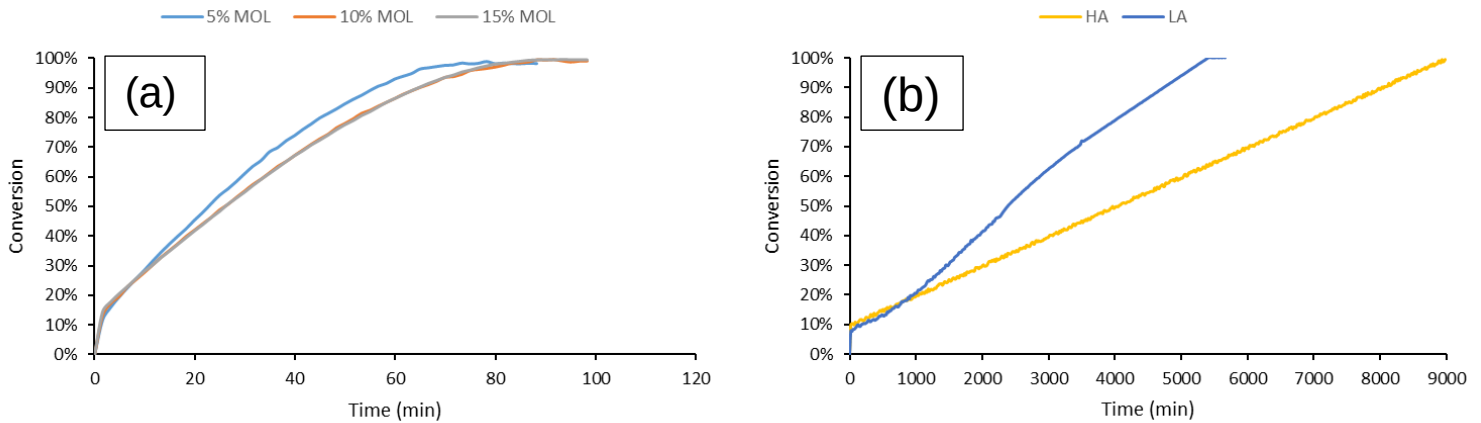


Figure 22: The conversion graphs for (a) 5%, 10%, and 15% MOL, and (b) HA and LA.

B.3.2. Sessile drop

The XRD analysis of the reduced and unreduced slag samples is presented in Table 30.

Table 30: XRD analysis of the reduced slag and raw slag samples.

Sample	Compound (wt.%)						
	Tistarite (Ti ₂ O ₃)	Iron (Fe)	Anatase (TiO ₂)	Anosovite (Ti ₃ O ₅)	Pseudo- brookite (FeTi ₂ O ₅)	Rutile (TiO ₂)	Ilmenite (FeTiO ₃)
Raw slag	2.8	6.5	12.1	18.8	43.4	13.7	2.7
5% MOL_1	32.9	15.4	1.1	42.8	1.6	1.4	4.8
5% MOL_2	11.1	17.5	0.1	63.8	4	0.5	2.9
5% MOL_3	35.6	27.6	0*	33.1	1	0.2	2.5
10% MOL_1	90.2	6.2	1	0*	0.9	0.5	1.2
10% MOL_2	38.9	14.3	0.4	38.3	2.4	1.1	4.6
10% MOL_3	40.6	16.7	0*	36.3	1.1	1.9	3.3
15% MOL_1	31.8	13.5	2.1	46	1.7	0.6	4.3
15% MOL_2	35.6	27.6	0*	33.1	1	0.2	2.5
15% MOL_3	63.4	7.8	1.1	23.4	2.2	0.8	1.4
HA_1	17.5	32.3	0.6	40.7	2.3	1.5	5.1
HA_2	15.8	32.4	1	47.2	2	0.8	0.9
LA_1	18.3	21.9	2	50.5	3.7	1.7	2
LA_2	11	18.9	0*	64.5	0.6	0*	4.9

*0 = not detected above the detection limit of 0.5 – 3 wt.%

ANNEXURE C: REPEATABILITY

This section aims to provide proof of the repeatability noted in the tests throughout the study.

C.1. Particle density

When calculating the particle density, 5 tests were performed for each sample. This required many steps and so there is more chance of human error. However, performing each test thoroughly resulted in the density of each run being similar, as can be seen in Figure 23.

1	4.602056 4.079753	
	Density of sand	
	W _{dp} 260.89 g	Weight of sand and container
	W _p 67.88 g	Weight of container
	V _p 118.94 cm ³	Volume of container
2	Density of sand	
	W _{dp} 261.33 g	Weight of sand and container
	W _p 67.88 g	Weight of container
	V _p 118.94 cm ³	Volume of container
	P _d 1.626450311 g/cm ³	Density of sand
3	Density of sand	
	W _{dp} 262.09 g	Weight of sand and container
	W _p 67.88 g	Weight of container
	V _p 118.94 cm ³	Volume of container
	P _d 1.632840087 g/cm ³	Density of sand
4	Weight of sand displaced	
	W _{cd} 260.89 g	Weight of container filled with sand
	W _{cds} 257.02 g	Weight of container filled with sand and sample
	W _s 3.59 g	Weight of sample
	W _d 7.46 g	Weight of sand displaced
5	Volume of sample = volume of sand displaced	
	V _s 4.597131755 cm ³	
	Density of sample	
	P _s 0.780921712 g/cm ³	
	Density of sand	
6	Weight of sand displaced	
	W _{cd} 261.33 g	Weight of container filled with sand
	W _{cds} 258.22 g	Weight of container filled with sand and sample
	W _s 3.42 g	Weight of sample
	W _d 6.53 g	Weight of sand displaced
7	Volume of sample = volume of sand displaced	
	V _s 4.014878263 cm ³	
	Density of sample	
	P _s 0.851831556 g/cm ³	
	Density of sand	
8	Weight of sand displaced	
	W _{cd} 262.09 g	Weight of container filled with sand
	W _{cds} 258.19 g	Weight of container filled with sand and sample
	W _s 3.77 g	Weight of sample
	W _d 7.67 g	Weight of sand displaced
9	Volume of sample = volume of sand displaced	
	V _s 4.697336903 cm ³	
	Density of sample	
	P _s 0.802582416 g/cm ³	
	Density of sand	
10	Weight of sand displaced	
	W _{cd} 263.55 g	Weight of container filled with sand
	W _{cds} 260.34 g	Weight of container filled with sand and sample
	W _s 3.66 g	Weight of sample
	W _d 6.87 g	Weight of sand displaced
11	Volume of sample = volume of sand displaced	
	V _s 4.175999387 cm ³	
	Density of sample	
	P _s 0.87643691 g/cm ³	
	Density of sand	
12	Weight of sand displaced	
	W _{cd} 266.34 g	Weight of container filled with sand
	W _{cds} 262.67 g	Weight of container filled with sand and sample
	W _s 3.37 g	Weight of sample
	W _d 7.04 g	Weight of sand displaced
13	Volume of sample = volume of sand displaced	
	V _s 4.219175653 cm ³	
	Density of sample	
	P _s 0.798734226 g/cm ³	
	Density of sand	

Figure 23: The particle density calculation for 15% MOL

C.2. Compressive strength

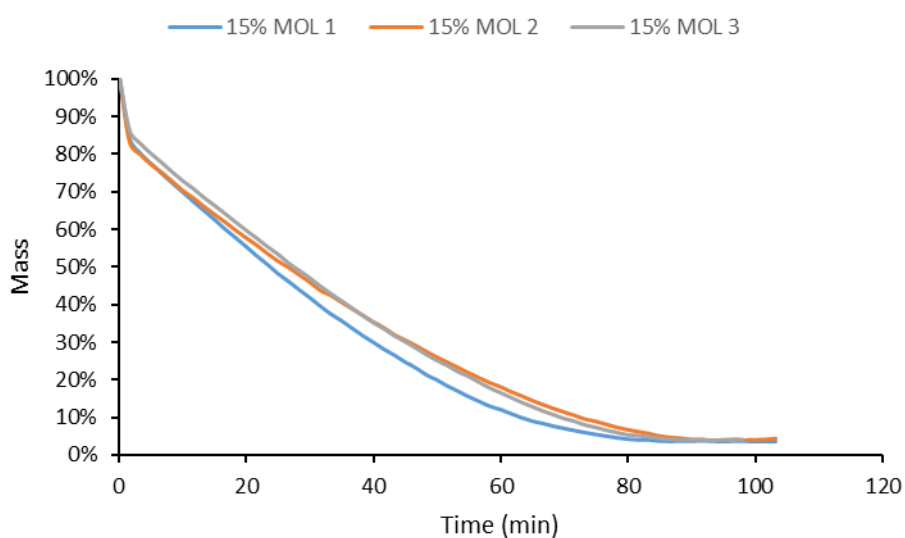
During the curing tests, 5 briquettes were tested on each day for each test. However, the compressive strength of the anthracite materials proved to have a large variance. Reported below are the 20 compressive strength tests done on HA and LA.

Table 31: Compressive strength results for HA and LA.

Sample		Compressive strength (MPa)								
HA	11.8	7.3	11.4	14.4	11.7	6.7	5.2	8.7	5.3	12.8
	3.9	6.5	9.5	7.9	5.2	10.9	16.4	8.9	8.7	4.2
LA	3.1	10.2	11	6.8	14.9	9.7	12.8	4.7	8.4	2.6
	3.4	8.0	3.4	3.0	12.0	5.6	12.0	4.8	4.6	10.3

C.3. TGA

Multiple runs were conducted for each sample on the TGA. If the results were all similar then a single run is taken to construct the graph for the results chapter and the reactivity values are taken from that single as the results are all similar and these are comprised of large datasets, making it hard to combine them. Shown in Figure 24 are the mass loss curves for 3 runs of 15% MOL.

**Figure 24:** Mass loss curves for 3 runs of 15% MOL.