

Evaluation of binders in briquetting of coal fines for application in combustion processes

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Dissertation submitted in fulfilment of the requirements for the degree *Master of Engineering in Chemical Engineering* at the Potchefstroom Campus of the North-West University

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Graduation ceremony: May 2019

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ACKNOWLEDGEMENTS

“Plan for what is difficult while it is still easy, do what is great while it is still small” ~ Sun Tzu

To everyone who assisted me in the journey of this project, I would like to thank you, for every moment of inspiration and for every word of encouragement.

A special thanks to my family for believing in me and setting me up to succeed.

Ms. Sanet Botes and Ms. Rene Bekker. You made things happen.

My study leaders (Ms. Nthabiseng Leokaoke, Prof. J.R. Bunt, and Prof H.W.J.P Neomagus), and colleague (Mr. Martin M. Modise). Thank you for making this project possible, and for the long hours you invested.

The staff at BASF (Mr. Willy Cilengi, Ms. Julie Mortimer, Ms. Datrium Mhlanga, Ms. Ncebakazi Majeke, Ms. Kagiso Tshenye, and Mr. Elie Mitshiabo). Thank you for the warm-hearted welcome to your facility.

North-West University Statistical Consulting Services (Mr. Shawn Liebenberg and Prof. Suria Ellis). Thank you for assisting me so patiently in my modelling and design.

Dr. Frikkie H. Conradie, thank you for your abounding insights into so many things.

Mr. Jan Kroeze, Mr. Adrian Brock, Mr. Elias Mofokeng, and Mr. Warren Brauns. We could not have asked for more skilled and equipped technical assistance. Thank you.

NECSA for allowing use of their facilities for scanning and tomography.

Hannes Krapohl, Julius Aldum, Pieter Broersma, and Gerhard de Beer, thank you for your assistance in this project. I wish you well in your journeys ahead.

Mr. L.C. Mgano thank you for motivating me like an army general.

Last, but not least, to my Father in Heaven it is all in His hands.

DECLARATION

I, Daleen Liza Botha declare herewith that the dissertation entitled, *Evaluation of binders in the briquetting of coal fines for application in combustion processes*, which I herewith submit to the North-West University is in compliance with the requirements set out for the degree: Master of Engineering in Chemical Engineering is my own work, has been text-edited in accordance with the requirements and has not already been submitted to any other university.



20 November 2018

DL Botha

Date

This report is confidential due to the intellectual property contained within. This report has also been proofread and language edited by Dr. D. Powell, Prof. J. R. Bunt, and Ms. N.T. Leokaoke. Some of the results formed part of a conference proceeding, namely, *Fossil Fuel Foundation conference 21 November 2018: Can coal clean up its act?*

ABSTRACT

Fine coal (-1 mm top size) is a global problem in terms of handling and pollution. It is expected that at least 6 percent of run-of-mine coal will be fines, and this does not include the fines generated in mining, beneficiation, and transportation processes. Fines can be processed through various means, which include recirculation with lump coal products to increase product quality. Alternatively, the coal can be sent to agglomeration processes; these include extrusion (pelletizing), spherical agglomeration, and briquetting. When considering briquetting, binders may be required if the coal has low caking properties, which is the case for some South-African bituminous coals. The briquettes can be used as a feedstock in thermal processes such as steam generation for electricity production or in fuel gas synthesis plants. In this study briquettes were manufactured with the aim of alleviating the handle-ability problems associated with coal fines, and then using these briquettes in combustion processes for steam generation. South African bituminous medium rank C coal was used, and its low vitrinite content necessitated the use of a binder. The binder used was of a novel composition consisting of two polymeric components (components A and B) with an added cross-linker to start the reaction (component XL). The study comprised of four phases namely, general mechanical testing (using an FED), an investigation into the optimal concentration and poly-acrylic binder composition, reactivity testing, and finally modelling of the binder formulation to the inherent properties of the coal used, which alluded to the behaviour of a briquette as a result of the maceral and mineral composition of the coal used. It was found that the poly-acrylic (PA) binder bound briquettes were comparably strong relative to briquettes formed using a polyvinyl alcohol (PVA) binder. The briquettes formed using a binder yielded compressive strengths that were twice as strong as the binderless briquettes. None of the briquettes were able to reach lump coal compressive strengths, but achieved the recommended 350 kPa set out by Richards (1990) for transportation requirements. The binderless briquetteing process produced briquettes that had a fines production tendency of 5 ± 2 percent, which was close to the 5 percent recommended value by Richards (1990). The briquettes formed using a binder achieved fines-generation potentials below 5 percent at a 0.4 and 1.2 weight percent addition. None of the briquettes were found to be water resistant at these binder additions, however, when the concentration of the poly-acrylic binder was increased to 5 weight percent, the resulting briquettes yielded an average wet compressive strength of 318 kPa. The addition of binder did not hinder the combustion value of the briquettes. Therefore, the PA formulation could provide an alternative to PVA in the fines briquetting process, yielding briquettes that are stronger than binderless briquettes; that are transportable, and combustible. The resulting briquettes will have to be stored in dry conditions, and in terms of initial financial feasibility will be comparable to PVA.

Keywords: polyvinyl alcohol, organic binders, briquettes, coal fines, bituminous

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CHAPTER 1 INTRODUCTION

1.1 Background and Motivation

Coal continues to be one of the most widely used fuel sources, due to its affordability and reliability (Spencer, 2016). The coal mining industry has discovered new ways to improve the safety and efficiency of the mines with the use of machinery (Le Roux et al., 2015, Vogt, 2016, Singh, 2017). The mechanization process has been known to yield a great percentage of coal fines and ultra-fines (which are particles that have a 1 mm top size) (Karmakar, 2005). These fines have been reported to constitute between 6-12 percent of the run-of mine (ROM) and represents approximately 1 billion tonnes stored after 150 years (Venter and Naude, 2015, Mangena et al., 2004, ESI-Africa, 2014). Over the years, fine (-1 mm top size) and ultra-fine (- 150 μ m top size) coal have accumulated in tailings ponds to approximately 10 million tonnes per year (Reddick et al., 2007). This also leads to significant losses in terms of production, land occupancy, and profit. Difficulties associated with accumulation also include adverse environmental impacts of which soil, water, and air pollution are well known (Hardman and Lind, 2003). To remedy the situation studies have shown that the fine coal can be converted into a profitable product by using agglomeration techniques, yielding calorific values of approximately 16 MJ/kg, with the use of organic binders, while reducing the handling and moisture build up challenges, associated with fines (England, 2013, Bunt et al., 2018).

Coal fines and ultra-fines are generally found in the form of a slurry in the coal mining industry (Boger, 2009). The sustainability of coal as a fuel resource is dependent on how well the industry can convert this waste into both a saleable and employment generating product. Without processing the coal fines and ultra-fines into agglomerates for use in thermal and other processes, their accumulation and waste will only continue to increase exacerbating the environmental challenges previously stated. Although the Integrated Resource Plan (IRP) for 2030 proposes a reduction in the consumption of coal for electricity generation (contributing 29.7% to the energy mix), the demand is significant enough to motivate the expansion South Africa's coal reserves (Modise and Mahotas, 2011).

Figure 1-1 is a depiction of a sustainability chart in which coal fines can be seen as a sustainable resource in that, for the time they are available, the fines and ultra-fines (as waste) can be utilised, creating job opportunities, relieving environmental burdens related to storage, and producing economic benefits.

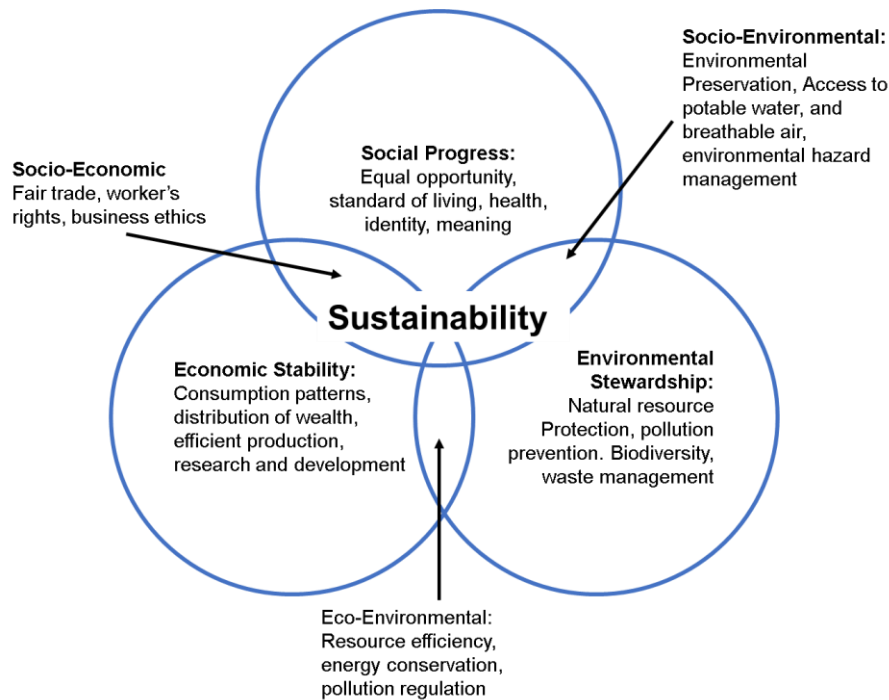


Figure 1-1: The sustainability cycle adapted from Inside.Mines (2017)

1.2 Accumulation of coal fines

Before the increase in value of fine coal in the late 1900's coal fines were removed from the run of mine as waste, usually by screening and then deposited into tailings dams by means of settling cones and thickeners. Mechanised mining as well as the use of crushers caused a steep increase in the amount of coal fines accumulated into tailings dams (Klima et al., 2012, Vogt, 2016). It is estimated that there is approximately 30 billion tonnes of coal fines world-wide (Mzamo, 2017). Figure 1-2 is a depiction of reclamation operations of coal fines at Oaky Creek in Queensland Australia aimed at alleviating the accumulation of coal fines.



Figure 1-2: Reclamation operations for coal fines conducted in Oaky Creek Australia, taken from HALL Contracting Ltd. (2017)

The greatest difficulty is not the reclamation of the fines, but the transportation thereof (Le Roux et al., 2015). Dust pollution can occur from open freight railways carrying coal. The coal fines on the freight wagons or railcars are raised by the wind and are scattered to the surrounding area polluting the air (Jaffe et al., 2014). Figure 1-3 is a depiction of coal dust being blown over the landscape of neighbouring areas.



Figure 1-3: Coal fines dust pollution from a railcar taken from Geochem (2016)

The reclaimed slurry-ponds can be rehabilitated into wet-lands which are more beneficial to the environment (Taylor and Middleton, 2004). Operational slurry ponds and waste piles also contain chemicals and sulfur associated with coal and in the event that these ponds are overfilled, damaged, or catastrophically altered; the neighbouring water sources could become compromised (Schücking, 2013). Figure 1-4 is a depiction of the types of pollution associated with coal and coal fines (CATF, 2001).

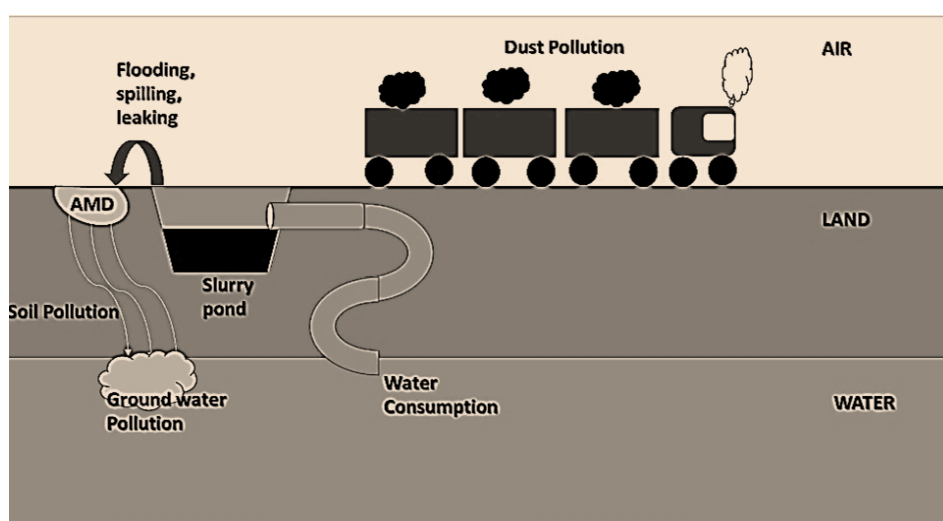


Figure 1-4: Air, water and land pollution by coal adapted from CATF (2001)

The polluting nature of coal can be minimised by utilising the fine wastes through agglomeration. In the case of a slurry-pond fine disposal method, the processes of reclamation of these fines could cause the land used by the slurry pond, over several years, to be reduced. Then the necessity for additional slurry ponds is overcome (Garling, 2015). The treatment of fine coal was initially considered costly and inefficient compared to other parts of the coal preparation process and previous coal beneficiation technologies, which depend on size reduction, increased the mineral content of the coal as the particles decrease in size. Furthermore, the moisture content of fine coal has a negative effect on its marketability, due to the strict moisture limitations in the use of coal (Yoon et al., 2000). These factors are the cause of coal fines being dumped as refuse or sold as-is at a fraction of the price of lump coal (England, 2013). Fines generation due to mining in lower quality or thinning seams cause the ROM and fines to become higher in inorganic materials, which causes the ROM to be unsaleable. The process of washing the fine coal will not necessarily create a saleable product (Klima et al., 2012). It is the purpose of this project to propose a remedy for this fines product by briquetting the as-received fines with low additions of binder to produce a profitable product, depending on the quality of the coal fines. It is also financially more profitable to sell the fines-briquette than to involve the fines in a closed-circuit process (where fines are added back to the washed coarse coal product), since briquettes could relate to some of the lump coal markets. Furthermore, the specifications of coal usage have become more demanding over the years, and beneficiation prior to briquetting could enhance product quality (Klima et al., 2012).

For the product to be feasible it needs to be saleable at a profit and the income must cover both the reclamation processes as well as the briquetting-plant operation costs. If the fines resource quality is high and the reclamation operations are feasible at a mine the briquetting process can enhance productivity by creating a saleable product that is easier to transport than moist fines and more attractive to the market (Garling, 2015). It is important to consider the intended use of the briquettes. Figure 1-5 is a depiction of a reclamation process in a slurry dam and the sheer amount of fines that can be found in such dams. In the figure the slurry pump pontoon was relevelled and safety procedures were to follow to enable accessible walkways (Garling, 2015).



Figure 1-5: Coal tailings reclamation operation Wollondilly New South Wales Australia, taken from Garling (2015)

1.3 Previously studied techniques of dealing with fines

The cleaning of coal fines to produce a saleable product involves costly processes including spiral beneficiation, reflux classifiers, froth flotation, spherical agglomeration, and dense medium beneficiation. The financial loss incurred, due to the expensive preparation and low demand, caused the fine and ultrafine coal to be regarded as waste in the coal industry (Klima et al., 2012). Agglomeration techniques provides the promise that the coal fines could be sold at a value that resembles that of prime coal (England, 2013). These techniques include briquetting both with and without binders at ambient or high temperatures, pelletizing, and spherical agglomeration (Zhang et al., 2018). Briquetting is a pressure compaction process where loose fines are cohered to one another with the goal of creating a product that can undergo all the handling and storing methods associated with coal processing and utilisation (England, 2013).

1.4 Briquetting

Briquetting incorporates the use of a briquetting press to aggregate the coal particles into a more compact whole. The new compacted coal can now be potentially used as a viable fuel product (England, 2013). The process of binderless briquetting relies on the use of coals that have high caking properties (England, 2012). The free swelling index (that represents plasticity) of the coal has an influence on this compaction, and the moisture content of the coal also influences this (Mangena et al., 2004). In general, since briquettes are compacted, they will not adhere to the

surface of the transport vessel or easily spontaneously combust, and can be stored for a very long time compared to fines (Ali, 2013). This means that briquettes are generally easier to transport than fines. Furthermore, the moisture content in the fines increases the compressive strength of the briquette up to an optimal point (Mangena and du Cann, 2007). The moisture that causes a handling problem in the fines could be a positive contributor to the mechanical strength of the briquette. The laboratory scale briquetting process mainly consists of screening the fines, drying the coal, mixing the coal with an appropriate binder, feeding the mixture to the briquetting device and pressing at the appropriate pressure, drying the briquettes, and finally storing or testing the manufactured briquettes (Venter and Naude, 2015).

Bituminous coals make up most of the coal reserves in South Africa and contribute the most to our export market (Jeffrey, 2005). Caking bituminous coals that are oxidised in slurry dams could lose their fluidity and plasticity over time (Seki et al., 1990). Plasticity is an important contributor to the briquetting of coal fines (Tait, 1976). Binders are used to further enhance the binding strength of the fines and increase the mechanical strength of the coal. The use of the correct binder is integral to the process and the following criteria for binders are used (England, 2013):

1. Binders should produce briquettes of high mechanical strength.
2. The briquettes should be waterproof.
3. The binder should not decrease the calorific value of the coal to such an extent that is detrimental to its use.
4. The briquettes produced from the binder should be economically feasible for use.
5. The briquettes should decrease or not increase adverse environmental effects produced by the coal.

Industrially, binders are currently being added in concentrations up to 5 weight percent and constitute approximately 60 percent of the operating costs related to briquetting coal fines (Venter and Naude, 2015). To alleviate the problem of coal fines, by creating a valuable composite fuel source, briquetting is proposed. Furthermore, the high proportion of binder adds significantly to the expensive nature of the process, therefore it is desirable that the binder used is effective at lower concentrations. Polyvinyl alcohol (PVA) could be used as a binder in the concentration range of 0.1 – 0.9 weight percent (Venter and Naude, 2015). However, PVA has additional requirements with regards to its dissolution in water (Scafer et al., 1989), and needs to be dissolved at 90°C and could require stabilisation in the form of freezing to -20°C and subsequent thawing (Molyneux, 2018). The need exists for a binder that is easily dissolved in water without the addition of heat, which can be added in concentrations comparable to PVA. To this end a

patent exists for poly-acrylic binders which were developed in order to provide lower binder concentration options and ease of preparation (Michailovski and Cilengi, 2016).

1.5 Aim and objectives

It was the aim of this project to evaluate the technical suitability of a binder solution made from polymer constituents in terms of mechanical and combustion performance for fine coal briquetting.

To this end the following objectives were to be considered:

- Determine an optimum binder formulation from mechanical strength measurements.
- Do a comparative study on the combustion, and mechanical strength performance of the optimum binder formulation, PVA, and the binderless briquettes.
- Suggest a predictive model for the mechanical strength of the briquette based on the formulation and evaluate the contributions of components A and B

1.6 Project Scope

The variables to be studied include: dry strength, green strength, shatter resistance, tumbler strength, water resistance, and combustibility. The outcome of the mechanical tests will reveal optimum binder formulation and amount. The particle size distribution (PSD) of the coal will be held constant and will only be constrained at the top size (-1.18 mm). The moisture content will be tested to find an optimum and this moisture content will be held constant for briquette manufacture. The coal will be characterised through the following analyses: Proximate Analysis, Ultimate Analysis, Petrographic Analysis, Mineralogical Analysis, X-Ray diffraction (XRD), X-ray fluorescence (XRF), and determination of the surface functional groups by Fourier-Transform Infrared Spectroscopy (FTIR).

1.7 Layout

The dissertation is written such that Chapter 1 has provided an indication of briquetting as a solution to the problem of fine coal. Chapter 2 provides an understanding of the developments made to alleviate these problems. It will also give insight into agglomeration as a fines alleviation method along with elaborating on briquetting. Briquetting will be broken down further in this chapter to include briquettes produced with organic polymers as a binder and also binderless briquettes. The possible uses of the briquettes formed using polymeric binders will be considered, and finally their requirements reviewed. Chapter 3 gives a description on how the coal was prepared, agglomerated, and tested. It will also provide the results of the characterisation of the coal so that the briquetting can be evaluated in terms of petrography, mineralogy, proximate analysis, and calorific value. Chapter 4 provides the mechanical strength results, while Chapter 5

provides the combustion performance results. Chapter 6 concludes the study and recommends improvements. The dissertation layout for the briquetting of coal fines with the development of a novel poly-acrylic (PA) binder comparative to polyvinyl alcohol (PVA) and binderless briquettes is shown in Figure 1-6.

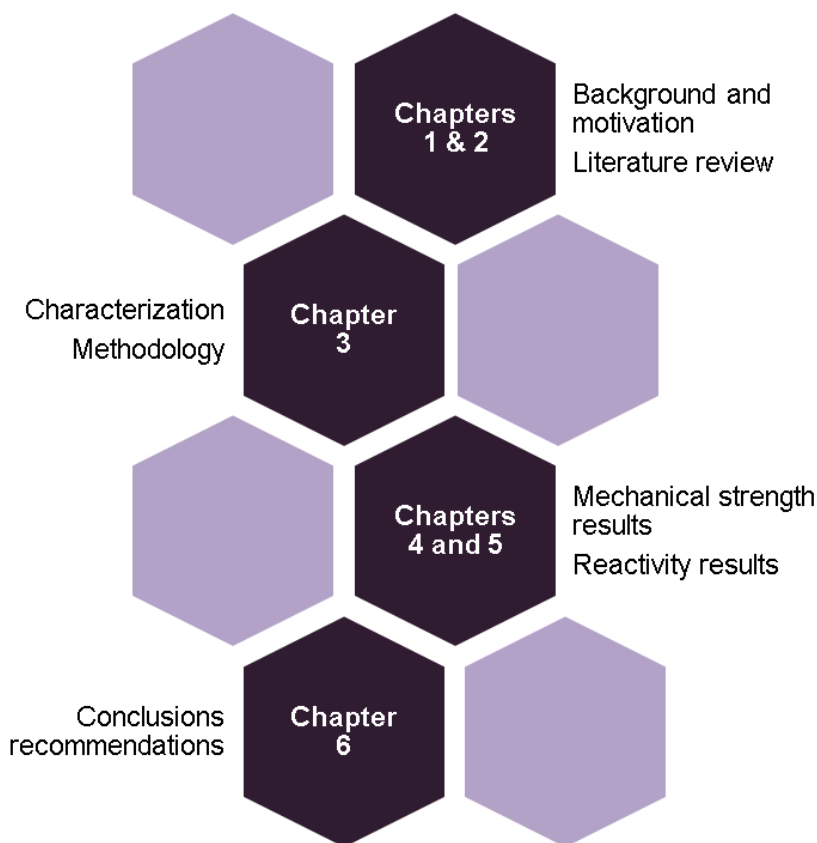


Figure 1-6: Dissertation layout for the briquetting of coal fines with the development of a novel poly-acrylic (PA) binder comparative to polyvinyl alcohol (PVA) and binderless briquettes

CHAPTER 2 LITERATURE SURVEY

The literature survey will evaluate current developments in fine coal processing (section 2.1). The process of agglomeration will then be further elaborated upon (section 2.2), and briquetting will be further described as the chosen agglomeration method (section 2.3). Different binders have previously been studied for the briquetting of coal fines, these will be discussed in further detail (section 2.4), under which two polymeric binders polyvinyl alcohol (section 2.4.1) and a poly-acrylic binder (section 2.4.2), will be evaluated for the briquetting of coal fines. The mechanisms through which binding occurs will be reviewed (section 2.5), and the effects of certain coal properties on briquetting, will be further studied (section 2.6). The industrial application of coal briquettes will be considered (section 2.7), after which combustion of the coal briquettes will be defined (section 2.8). A brief overview of briquetting plants in South-Africa will be given (section 2.9), and finally an initial estimation of economic considerations will be discussed (section 2.10).

2.1 Developments in fine coal processing

The increase in mechanisation in the mining of coal has led to a rise in the loss of product due to an increase in fines generation (England, 2012). Studies have shown that these fines have relatively high heating values and can still be used in combustion (Bunt et al., 2018, Wagner, 2008). Raw fines were traditionally discarded in ground surface tailings dams and underground workings (England, 2013, Modiri, 2016). The quality of the fine discard is similar to the run of mine coal (Le Roux et al., 2015).

Developments in the dewatering of fines include classifying cyclones, vacuum and pressure filters, fine coal centrifuges, and fine screens. Further developments include thickening, settling, and filtration chemicals. Modern centrifuges can treat up to 100 tonnes per hour of fine material, and can result in a free moisture content of 12 – 18 weight percent, while ultra-fine coal can be dewatered to 20 weight percent free moisture content (Klima et al., 2012). The cost of drying the fine to ultra-fine coals outweighs their value as a fuel source and these coals may need to be further processed (Muzenda, 2014).

Processing techniques include agglomeration and the adding back of upgraded fines to the washed coarse coal, so that the quality improves (England, 2013, Le Roux et al., 2015). Regarding the agglomeration of fine coal, standards for laboratory scale evaluation of agglomerates need to be developed, where industrial scale standards cannot be applied (England, 2013).

2.2 Agglomeration of fine coal

For fine coal to be viably transported, it should be agglomerated in regularly sized compacts that have been formed economically (Mangena et al., 2004). Agglomeration is a collection of processes in which particles are combined to resemble lump coal in terms of handle-ability. Agglomeration methods include oil agglomeration, pelletizing, and briquetting (Nkolele, 2004).

The oil agglomeration process involves the addition of oil to a slurry in an attempt to beneficiate the coal and bring hydrophobic coal particles together while repelling moisture (England, 2013). This process can also be seen as coagulation or rapid shear coagulation (Masuda et al., 2007).

Pelletising can be achieved by pan pelletising, extrusion, and drum pelletising. Pan pelletising involves a rimmed sloped disc that produces pellets at low pressure, with resultant lower resistance to weathering. For this reason, binders are recommended during pan pelletising. Extrusion processes also make use of binders and consist of rollers that force material into cylindrical masses that are cut into more handle-able sizes. For this method weather resistance is achieved by heat treatment. Drum pelletising, like pan pelletising, makes use of inclination along with a rotary drum to move material and cause agglomeration due to rotary forces. With this method less pellets are formed, and sieves are used to remove fines from the product. Resultantly coarse material (above 6 mm) is found in the pellet product (England, 2013).

Briquetting is a technique achieved by applying pressure to material in order to bind particles. Briquettes can be produced without binders if the coal permits, e.g. if the coal has high vitrinite content thereby having caking propensity. Other methods include hot briquetting, where heat in addition to the pressure is used to achieve binding. For coal fines that are difficult to briquette without additives, binders can be used (England, 2013). Binders that can be used for briquetting are grouped into biomass, organic binders, organic polymers, and resins.

Briquetting is more efficient in terms of weathering resistance, because of the relatively high pressures used in the processes. To have a good indication of product performance, it will therefore be sensible to use briquetting instead of pelletisation, because the briquettes could be compared to binderless samples as a quality measure.

2.3 Briquetting studies

Briquetting is a compaction process that creates a monolithic solid structure that is uniformly dispersed within the shape of the briquette. The first briquetting process included operations of drying, crushing (where larger particles were present) and lastly screening the coal. Then the coal was mixed with a percentage of molten binder (asphalt). The mixture was fed to a roll type briquetting press, after which the briquettes were cooled on a conveyor; before loading into railcars or diverting to a stockpile. More than 6 Mt of briquettes were produced in the United States before oil and natural gas prices lowered and eroded the market (Klima et al., 2012).

2.3.1 Binderless briquetting as an agglomeration method for fine coal

In this study bituminous coal from slurry dam derived from a colliery in the Middelburg, Mpumalanga Province, was used. Binderless briquetting of South African bituminous coals have been studied with specific focus on the Witbank coalfield (Mangena et al., 2004). These bituminous coals were studied with regard to their chemical, physical, organic, and mineralogical nature. The variables considered in compacting these briquettes included: feed moisture, particle size distribution, and pressure. The tests conducted on these briquettes include compressive strength, water resistance, and abrasion resistance tests. It was possible to correlate the mechanical tests' results with the properties of the coal and the briquetting conditions. The coals used in this study were found to be suitable for binderless briquetting. The successful outcome of binderless briquetting was found to be subject to reactive maceral content (such as vitrinite and liptinite), plasticity (which was tested by the free swelling and hardgrove grind-ability indices), as well as mineral matter content with the kaolinite content being of specific interest; all of which contribute to binding. Binderless briquetting is a preferred method for briquetting, since it is independent of binder addition and heat resistant briquetting equipment. It has been shown that binderless briquetting can be done for some Witbank coals depending on their natural binding properties. Whether these briquettes would retain their integrity with outdoor storage and transportation, during raining season, was questioned, since binderless briquettes could be more porous than dense and glossy, they tend not to be water resistant (Mangena and du Cann, 2007).

2.3.2 Binders for the briquetting of fine coal

Binders should enhance the quality of the briquette by increasing the green strength, adding to the water resistance, and by being environmentally friendly and economically viable. This should be achieved without compromising the applicability and quality of the briquettes. Binders that have been used in the past include: cow dung, coal tar pitch, bitumen, lignosulfonates, molasses, and starch. The moisture content of the feed, which is total moisture, in most cases where binders are used, should be approximately 10 weight percent (England, 2013). This ensures that the quality of the briquette is not compromised by excess free moisture. Binders for the briquetting of coal fines are continually being developed to ensure that the briquetting process has greater economic viability. This is due to the high contribution of the binder to the operating costs of briquetting. Binders that have recently (within 5 years prior to this study) been investigated include: waste plastic materials, starch, co-polymer binders, coal tar pitch and molasses blends, and organic polymer binders.

Briquetting with municipal solid waste plastic is an attractive option, as it incorporates the use of traditionally discard materials to create a saleable product. Massaro et al. (2014) used LDPE (low density polyethylene) as a binder for the production of stoker coal briquettes. Quality testing of these briquettes were done by mechanical tests: compressive strength and abrasion resistance. The binder was added in concentrations of 5 – 15 weight percent LDPE. This binder requires ambient air drying of approximately 48 hours and additional hour of curing time at 100°C (Massaro et al., 2014). This binder resulted in durable briquettes at 10 weight percent binder addition, as shown in Figure 2-1.

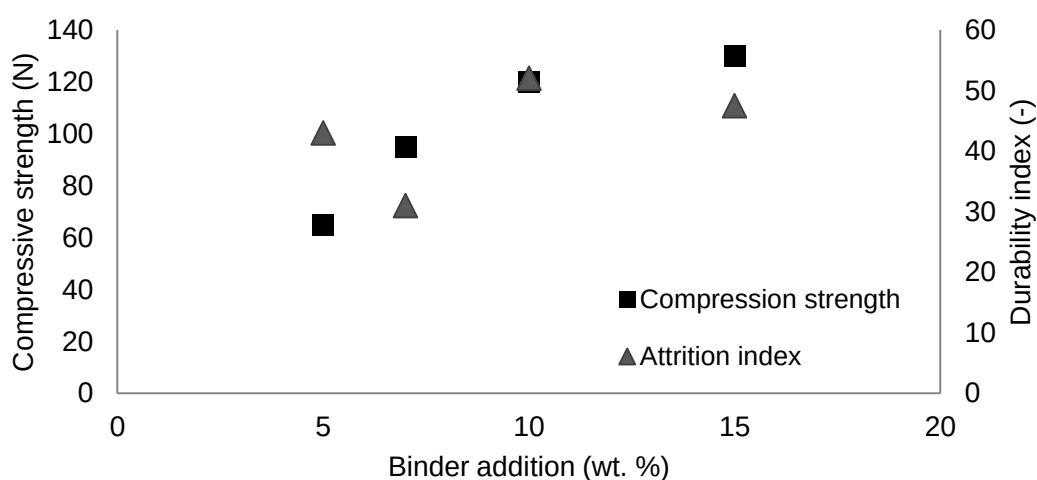


Figure 2-1: Briquette compressive strength and durability of bituminous coal fines bound with LDPE (adapted from Massaro, et al. (2014))

From Figure 2-1 it is observed that as binder addition increases, the briquette compressive strength increases. In addition to this the attrition index, which measures durability, also increases. Therefore, the more LDPE binder added, the stronger the briquettes and the more resistant they are to producing fines.

Water resistance is observed to be a recurring problem in the quality of fine coal briquettes. To this end Deniz (2016) tested a co-polymer (Mowlith-VDM) for the briquetting of bituminous coal fines. This binder is a non-plasticized, aqueous poly-acrylic polymer. For this binder an optimal of 8 weight percent was recommended at a curing temperature of 100°C, for 15 minutes, using coal with a particle size distribution below 3 mm. This binder was found suitable for the production of durable, water resistant coal briquettes (Deniz, 2016).

According to Deniz (2016) molasses was found to be a non-water resistant binder. Nonetheless, Zhong, et al. (2017) tested a mixture of coal tar pitch and molasses. The briquettes were intended for use in the COREX iron making process. The success of the durability of the briquette was attributed to the significant increase in strength after addition of molasses, along with the cost effectiveness thereof (Zhong et al., 2017).

In a study by Zanjani, et al. (2013), beet pulp was found to increase water resistance and compressive strength. The binder is considered to be environmentally friendly and cost effective (Zanjani et al., 2013).

2.4 Organic polymer binders for the briquetting of fine material

Organic binders describe the group of binders that include biomass, tar pitch and petroleum bitumen, lignosulfonates, and polymer binders. Organic binders are preferred due to their advantageous effect on compressive strength and impact resistance; without increasing the ash-yield as much as inorganic binders do. The decomposition of the organic binder along with their inability to withstand thermal shock are considered its biggest draw-backs. Organic polymer binders that are industrially significant include polyvinyl alcohol and, the more expensive, starch. Organic polymer binders are favourable for cold briquetting processes (Zhang et al., 2018).

2.4.1 Polyvinyl Alcohol

Polyvinyl alcohol is a hydrophilic polymer alcohol derived from acetates. Its structure is obtained by polymerising vinyl alcohol. It has applications in pharmaceuticals, sponges, as well as in the cosmetics industry. Figure 2-2 is a depiction of the chemical structure of polyvinyl alcohol. The

monomer is made up of two carbon double bonds and an alcohol group and has the IUPAC name poly-(1-hydroxyethylene).

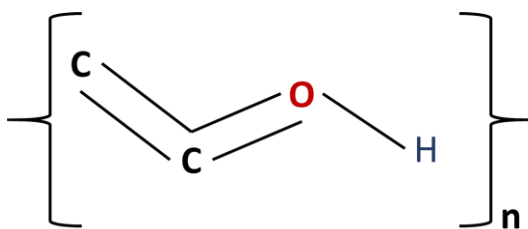


Figure 2-2: Polyvinyl alcohol chemical structure, adapted from Pubchem (2018)

This OH group within the polyvinyl alcohol allows it to enter into a hydrogen bond. This bond is used to bring adjacent coal particles closer together. Because of the strong nature of the hydrogen bonds of carbon based materials and alcohol groups, it can be expected that PVA based coal briquettes should have greater mechanical strength when compared to their binderless counterpart (Hadzi, 2013).

Polyvinyl alcohol is prepared by adding 5weight percent of the powder to cold water slowly. The faster the PVA is added, the higher the probability of lump formation. The polymer can then be solubilized between 90 – 98°C. The prepared binder is then added in appropriate concentrations to the coal. The formulation will be discussed in Chapter 3.

2.4.2 Poly-acrylic binder

This binder is made up of one homo- or copolymer of a (meth)-acrylic-acid ($C_4H_6O_2$) and an alkyl-(meth)-acrylate-styrene-copolymer ($C_{18}H_{18}N_2O$). It was developed to produce briquettes with good mechanical stability and strength, aiming to be a less energy intensive alternative to PVA. This is due to the heat addition necessary for solubilizing PVA powder (Michailovski and Cilengi, 2016). The binder is in a hydrogel form and its components are combined through a phenol formaldehyde resin cross-linker. Other components added to this binder include an anti-foaming agent so that mixing is not compromised. The meth-acrylic acid component is considered to increase the strength of the briquette by forming a film around the particles. The alkyl methacrylate styrene copolymer is considered to be the primary green strength additive.

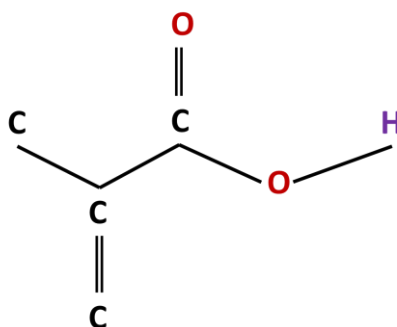


Figure 2-3: Methacrylic acid (C₄H₆O₂) chemical structure, adapted from Pubchem (2018)

Figure 2-3 and Figure 2-4 show the two main components. These two polymers are crosslinked using phenol formaldehyde.

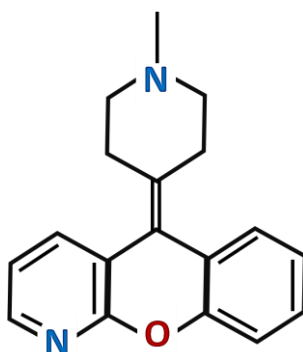


Figure 2-4: Alkyl (meth) acrylate styrene copolymer (azanator) (C₁₈H₁₈N₂O) chemical structure, adapted from Pubchem (2018)

Figure 2-5 is a depiction of a phenol formaldehyde molecule, which is used as the cross-linker between the two hydrogel polymers.

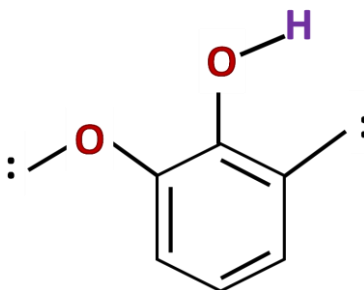


Figure 2-5: 2-methoxy-6-methylphenol chemical structure, adapted from Pubchem (2018)

Cross linkers are used in a group of polymers referred to as hydrogels. These are polymers with high moisture contents that can be cross-linked via physical processes or chemical additives. By

crosslinking, an extension is added and the single polymer chains now become a network. This inhibits the movement of a single chain polymer. This in turn changes the viscosity, and later, the phase of the polymer. The advantages of crosslinked polymers are that they are generally mechanically strong and weather resistant. The greatest disadvantage of cross-linked polymers is that their processing has to be fixed, since they are infusible and insoluble. This is especially seen in polyacrylamides, where the gel without cross-linking is water soluble, but the cross-linked hydrogel is not (Maitra and Shukla, 2014). The preparation of this binder will be discussed in Chapter 3.

The binder was patented and tested mechanically, subjecting briquettes to a drop shatter test at a 2 m height, and an uniaxial compressive strength test (Michailovski and Cilengi, 2016). The briquettes produced from the binder were found to be three times as strong compared to briquettes produced from polyvinyl alcohol (PVA). The patent reported the green strength to be 29.42 N for the poly-acrylic binder, whereas it was 9.81 N for PVA. After two days the briquettes made from the poly-acrylic binder were still twice as strong as the PVA bound briquettes with dry compressive strengths of 68.65 N and 39.23 N respectively. The briquettes were found to produce lower fines (1.36 percent) than PVA (2.85 percent) during an industrial scale tumbler test and could withstand more drops (5) than the PVA bound briquettes (3)

2.5 Mechanisms for the briquetting of coal fines

According to Zhang et al. (2018), the mechanisms for the briquetting of coal fines can be divided into categories, which are of binderless briquetting and briquetting with the aid of a binder during cold briquetting. These hypotheses applicable to most coals are shown in Table 2-1.

Table 2-1: Summary of the mechanism hypotheses for most coals adapted from Zhang et al. (2018)

Mechanism	Coal type	Elaboration
Capillary*	Lignite	The many capillaries in lignite contain moisture. This moisture is drained to the surface once the external briquetting force is applied. This moisture then fills the spaces between coal particles and acts as the binding mechanism between them.

Adhesion*	Most coals	Coal particles are held together by capillary and Van der Waals forces. These forces influence the mechanical strength of the briquette positively. Coals with no capillary water have lower compressive strength. The key player in this binding method is the coal properties and contact area of the coals. Surface water does not influence this.
Dense water*	Most, wet coals	A cation membrane is created by the disorder of the water molecule, brought on by the slightly negative charge of a hydrated calcium or sodium ion. This forms a layer or membrane to which coal particles are drawn and through which they are bonded.
Soaking and bridging**	Most coals	In this mechanism, the level of coverage of the coal with the binder (soaking) is a key component in the binding of the coal particles. As the binder covers the entire surface of the coal, including the pores, a solid bridge between particles is formed. Viscous and organic solvents are used in this case.
Mechanical/ Chemical**	Most	This mechanism is a combination of the physical external force exerted on the briquette, relative slip caused by attraction and repulsion of binder to water, along with ionic, covalent, and capillary forces.
Minimal contact angle, max. bonding power**	Most	This hypothesis relates the level of coalification to the wettability and subsequently the bonding of the briquette. This is done through the contact angle between coal and binder. The smaller the contact angle, the greater the wettability leading to a stronger briquette. This depends strongly on the rank of the coal.

*Mechanisms that describe binderless briquetting

** Mechanisms that describe cold briquetting techniques with binder.

For the briquetting of coals with or without binder, and applying mechanical forces, the most widely known mechanisms for binding are considered to be adhesion, due to Van der Waals and capillary forces, as well as the resulting bonds from a mechanical force.

2.6 Coal as a feedstock for briquetting

Coal is a fossil fuel that the world has become reliant on. In South Africa there are about 19 coalfields, situated in KwaZulu-Natal, Mpumalanga, Limpopo, and Free State Provinces. To a lesser extent, coal is also mined in the Gauteng, North-West, and Eastern Cape Provinces. The main mining activities occur in the Witbank-Middelburg, Ermelo, and the Standerton-Secunda areas in Mpumalanga (Jeffrey, 2005). The coal fines used in this study were generated at a colliery in the Middelburg area, which is part of the Witbank coalfield of the Ecca group from the Karoo super group. In this coalfield there are 5 seams. Most of the economically important coals are mined from the 2 seam which is approximately 4.5 – 20 m in thickness. The 3 seam is regarded as a high quality seam coal, but not economical for mining purposes, it is generally too thin to mine, and is typically not present on most of the mines. The 4 seam comprises of upper, middle, and lower layers. These layers have a greater impurity content, particularly the upper layer, but remain economically viable to mine. The lower grade coals from this seam are used by Eskom for steam generation (Jeffrey, 2005). South Africa uses vast amounts of coal for steam generation and satisfy four main markets including global export. The domestic markets include synthetic fuels, energy supply, heat generation, and industrial use. Each of these markets requires different grades of coal that need to meet certain thermal and sizing requirements. These factors are dependent on the petrography and formation of the coal (Steyn and Minnet, 2010).

Coal formation or coalification occurred millions of years ago, when climatic conditions favoured abundant plant growth. Fallen trees and other vegetation would pile together and cause a compaction of rotting material (England, 2012). The resulting coal would form from vast peat piles with a raw material to product ratio of 4:1 (Woodruff et al., 2017). The rank of coal depends on how long the peat has been subjected to coalification. Coal rank ranges from the highest, being the oldest and most altered due to pressure and temperature, namely anthracite, to the lowest rank, lignite, which is not found in South Africa. In the middle would be the bituminous coals, which is the predominant coal type in South African coals with some anthracite found in Kwa-Zulu Natal. The reactive material in coal is a heterogeneous mixture of organic components that differ in terms of chemical and physical properties, and are called macerals (Nkolele, 2004). The different types of macerals and their occurrence are shown in Table 2-2.

Table 2-2: Maceral classification table adapted from Klima, et al. (2012)

Maceral Group	Maceral	Source	Chemistry
Vitrinite	Telinite	Gel like structures	Moderate hydrogen and volatile content
	Collinite	formed from hydrated plant material	
Liptinite	Resinite	Resins	Increasing hydrogen, volatile, and aliphatic content
	Sporinite	Spore exines	
	Cutinite	Cuticles	
	Alginite	Algae	
Inertinite	Micrinite	Plant materials	Decreasing hydrogen and volatile content and increasing aromatic content
	Fusinite	Woody tissues	
	Semi-fusinite	Woody tissues	
	Sclerotinite	Resistant remains	

Vitrinite is used to classify the rank of the coal through mean random vitrinite reflectance during petrographic analysis, because it is the most abundant maceral in coals of humic nature (Lahaye and Prado, 2012). To determine the rank of South African coals a standard is used as is shown in Table 2-3 (SABS, 2004). Vitrinite random reflectance is used to classify medium (bituminous) to high rank (anthracite) coal. South African coals are to a greater extent bituminous, anthracite, and to a much lesser extent lignite.

Table 2-3: Coal classification table adapted from SANS10320:2004

Vitrinite random reflectance range	Classification
$0.5 \text{ percent} \leq \overline{R_r} < 2.0 \text{ percent}$	Bituminous coals
$2.0 \text{ percent} \leq \overline{R_r} < 6.0 \text{ percent}$	Anthracites

The random vitrinite reflectance can also be used to classify between the various medium ranks of bituminous coals. Table 2-4 is a summary if the vitrinite random reflectance of different ranks of bituminous coals.

Table 2-4: Bituminous medium ranks classification table adapted from SANS10320:2004

Vitrinite random reflectance range	Classification
$0.5 \text{ percent} \leq \overline{R_r} < 0.6 \text{ percent}$	Medium rank D
$0.6 \text{ percent} \leq \overline{R_r} < 1.0 \text{ percent}$	Medium rank C
$1.0 \text{ percent} \leq \overline{R_r} < 1.4 \text{ percent}$	Medium rank B
$1.4 \text{ percent} \leq \overline{R_r} < 2.0 \text{ percent}$	Medium rank A

Over and above petrographic classification, coals differ in important factors such as heating value (CV), ash fusion temperature, ash yield, and sulfur content. These are evaluated when determining the end use of the coal (Woodruff et al., 2017). Since coal is a sedimentary rock it also consists of minerals. These minerals influence the coal's properties (Popov et al., 2011). The mineralogical material can be inherent (bound within the coal's carbon matrix), which are hard to detect. They are mostly associated with the coal precursory plant material and include magnesium, iron, etc. Alternatively, minerals can occur extraneously, deposited in cracks after peat was formed. The most abundant extraneous minerals are silicon, aluminium, and iron. These appear as silicates and sand, aluminium-silicates, and pyrites respectively (Selvig and Gibson, 1956). The mineral matter in coal is converted to ash after the coal has been combusted.

Coal fine samples from collieries are generally mixtures of lumps and stones as well as fine or powdered coal (Mangena and du Cann, 2007). The coal fines originating from slurry ponds require dewatering into filter cakes, and size reduction of any lumpy clots produced, to ensure a constant quality product of fine coal that meets market requirements of the targeted end use. These fines could absorb approximately 20 weight percent free moisture due to stockpiling, transportation, or wet surroundings (England, 2013)

2.6.1 Effect of petrographic properties on fines briquetting

Mangena et.al. (2004) found that for 5 different ultra-fine coal samples, from the Witbank coalfield, that briquettes could be manufactured at ambient conditions without the aid of a binder. These coals differed in terms of petrography, specifically with respect to the total reactive material as shown in Table 2-5.

Table 2-5: Petrographic properties of different medium rank C coal samples originating from the Witbank coalfield adapted from Mangena et.al. (2004)

Sample	Vitrinite	Liptinite	Reactive inertinite	Inertinite	Total inertinite	Reactive material
SJM1	35	6	14	30	44	55
SJM2	32	4	14	42	56	50
SJM3	33	5	16	38	54	54
SJM4	25	4	15	33	48	44
SJM5	34	4	16	40	56	54

The briquettes made from these coals were tested for compressive strength and the results obtained, showed an increase in compressive strength with a higher vitrinite reflectance. Random vitrinite reflectance is the reflectance of vitrinite of a section of the coal that was polished and placed under unpolarised light (SABS, 2004). The compressive strength increases observed with an increase in vitrinite content is shown in Figure 2-6.

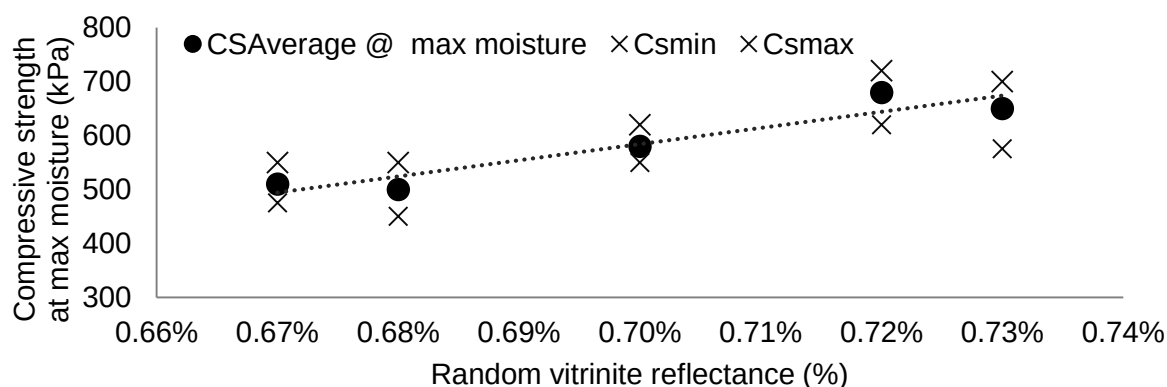


Figure 2-6: Binderless briquette compressive strength vs. random vitrinite reflectance of different samples (adapted from Mangena et al. (2004))

The increasing trend shown in this study is due to the ability of the vitrinite maceral to deform and create stronger bonds by binding to each other (Mangena and du Cann, 2007).

2.6.2 Effect of mineral matter content on coal fines briquetting

The presence of mineral matter, particularly clays, tends to increase the compressive strength of the briquettes for specific moisture conditions. This can be attributed to the plasticity caused, at these conditions, by clays such as kaolinite, while other clays, and specifically illite, tend to decrease the compressive strength (Mangena et al., 2004). The mineral matter will remain as ash after briquette burning, and the amount of ash yield in the briquette will determine its quality

(England, 2012). The mineral matter in coal could therefore be a positive attribute in briquetting, or a negative quality when considering ash yield limitations. Figure 2-7 is a depiction of the effect of mineral matter and clay (specifically kaolinite) content of the coal on the compressive strength of the resultant binderless briquettes.

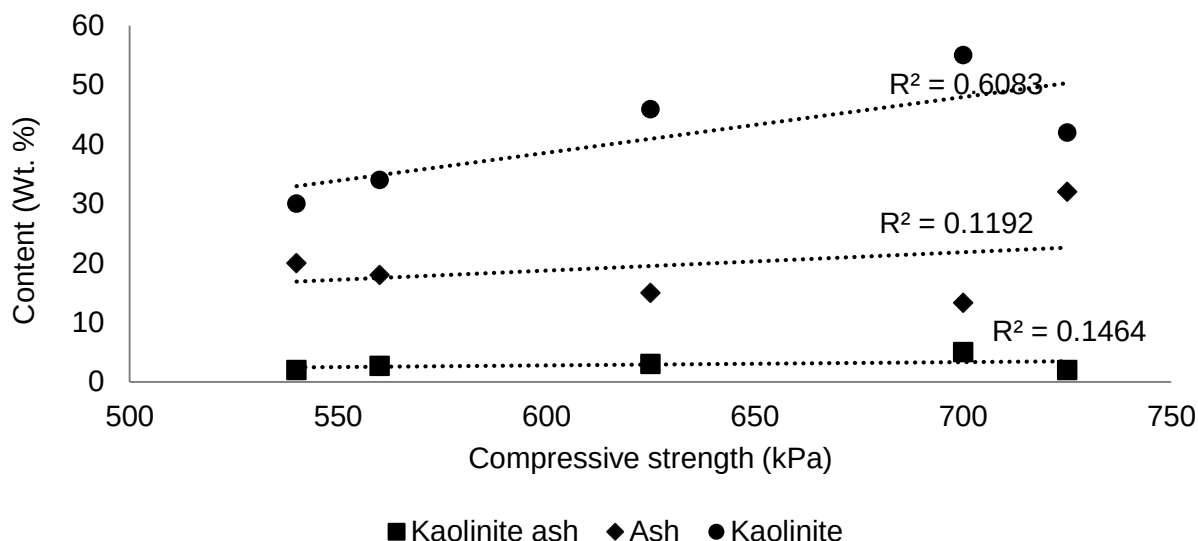


Figure 2-7: Effect of ash yield and kaolinite on compressive strength adapted from Mangena, et al. (2004)

From the increasing nature of the correlation of compressive strength (kPa) to kaolinite content in the coal, along with the higher correlation coefficient, it can be said that the kaolinite content of the coal increases plasticity and therefore compressive strength (Mangena et al., 2004). The ash yield had a lower correlation compared to the clay content. The ratio of kaolinite to ash also shows low correlation such that no relational conclusions could be drawn from the data in terms of ash yield. Mangena proceeded to test for a correlation between water resistance and ash yield and the results are depicted in Figure 2-8.

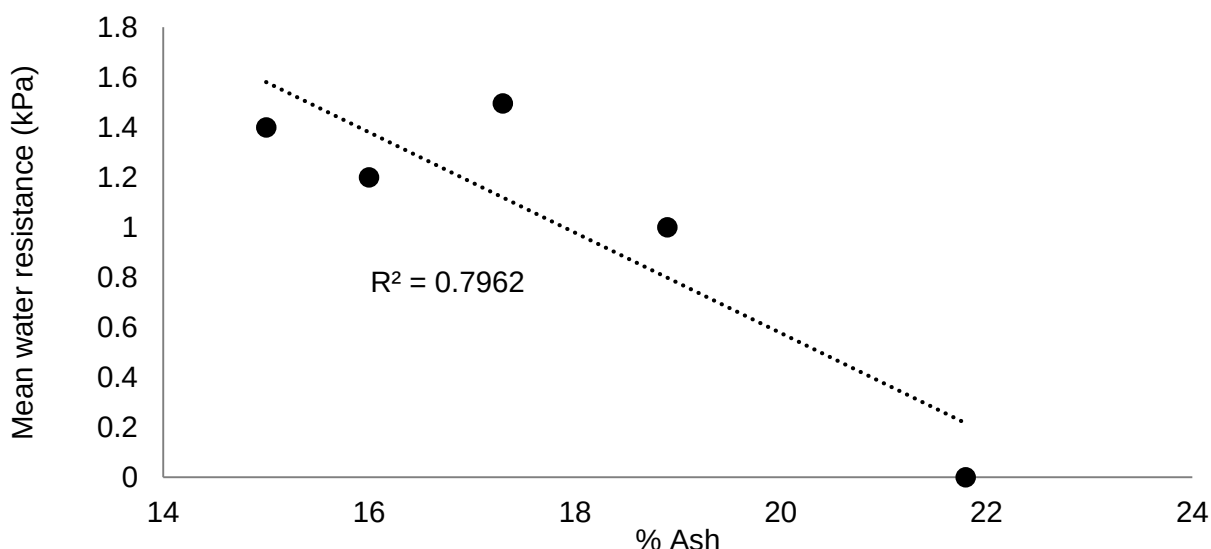


Figure 2-8: Effect of mineral matter (ash yield) on wet compressive strength adapted from Mangena, et al. (2004)

From Figure 2-9 it is shown that a relatively good correlation exists between the ash yield of a sample and its mean water resistance. This is significant, because it shows that if the ash yield is higher, the mean water resistance is much lower and can reach a point where the briquettes are not water resistant. This was done on several different coals which verifies this relationship.

2.6.3 Effect of moisture in fine coal briquetting

Variable free moisture in briquetting results in an optimum curve, i.e. there is a feed moisture content at which the compressive strength of the briquette is the highest, with further increase in moisture reducing the briquette compressive strength (Venter and Naude, 2015, Mangena et al., 2004). The study by Mangena (2004) of 9 bituminous coals as depicted in Figure 2-9 showed the latter half of the moisture curve, where, in some cases, the air dried coal was already at the optimum and any moisture addition resulted in lower wet compressive strength (which is the compressive strength after water immersion). This could have been due to the varying ability of coal fines to absorb moisture.

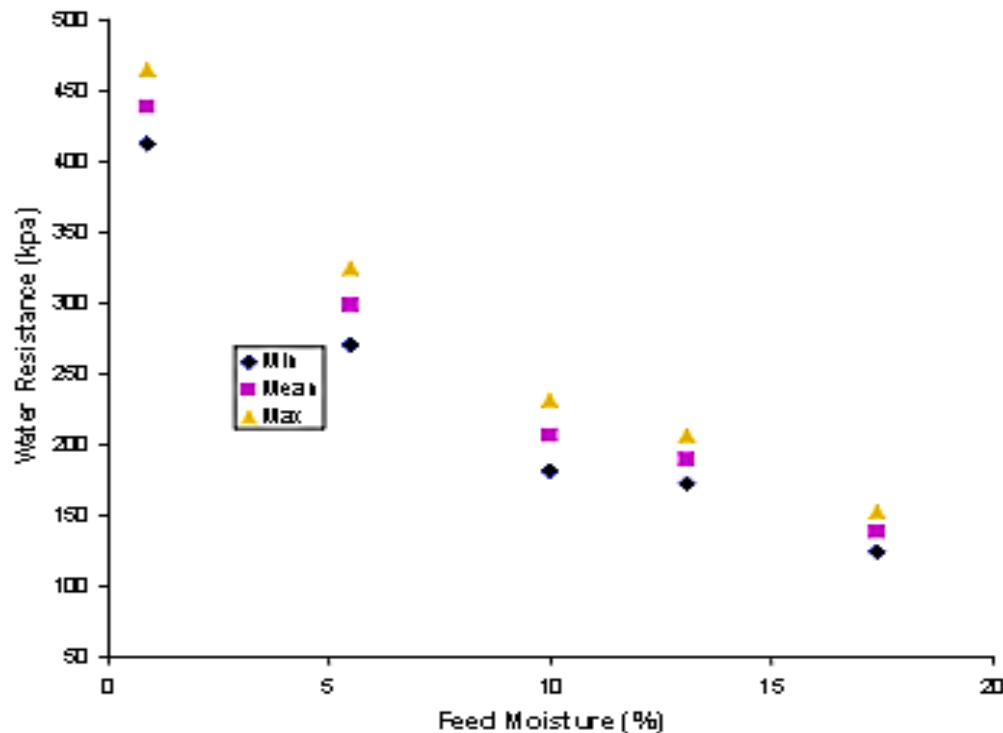


Figure 2-9: Effect of feed moisture on wet compressive strength adapted from Mangena, et al. (2004)

Venter & Naude (2015) suggested that, for laboratory scale testing, the briquettes can be dried either in a room or outside in the sun. Their study was aimed at evaluating the conditions of briquetting to obtain the strongest briquette, using a starch based and a polymer based binder (PVA). The study concluded that the briquettes could obtain maximum strength sooner by drying in the sun, but since the briquettes were not found to be water resitant, sun drying was a moderately risky endeavor. They also found the optimum moisture content for these briquettes was in the region of 12 percent, and that from 18 percent total moisture content the briquettes became too soft to analyse. Figure 2-10 is an illustration of the compressive strength results obtained by Venter & Naude (2015) for varying moisture content. From this figure it is noted that the total moisture content of the coal fines has an increasing effect on the strength of the briquette, and from Mangena (2007) it is known that the coal moisture percentage can lead to a certain optimal value and then decrease. It is therefore necessary to view the moisture content of the coal fines and briquettes as an important variable when evaluating compressive strength.

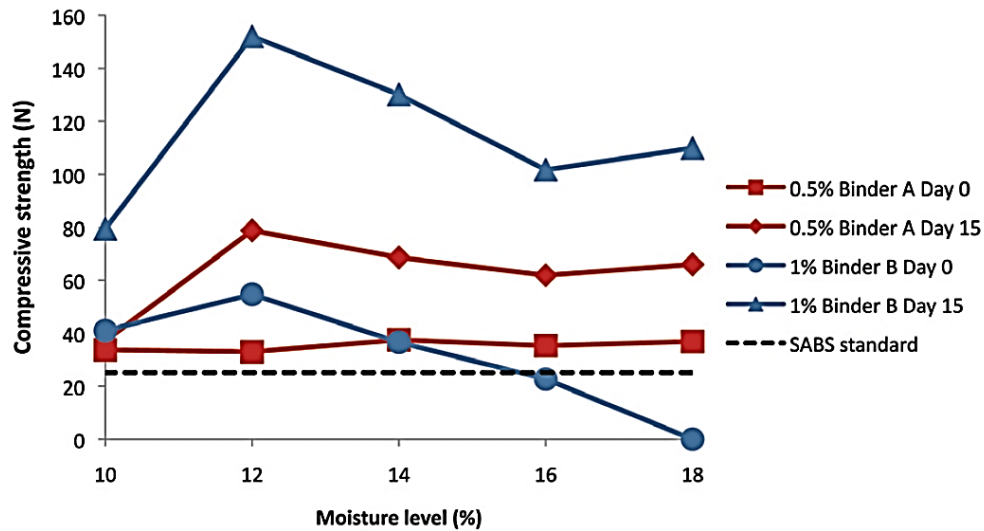


Figure 2-10: Evaluation of the effect of varying moisture content, and binder type (binder A as PVA and binder B as starch) on briquette compressive strength, taken from Venter & Naude (2015)

Figure 2-11 is a depiction of the effect of moisture on compressive strength as conducted on a binderless basis by Mangena et al. (2014)

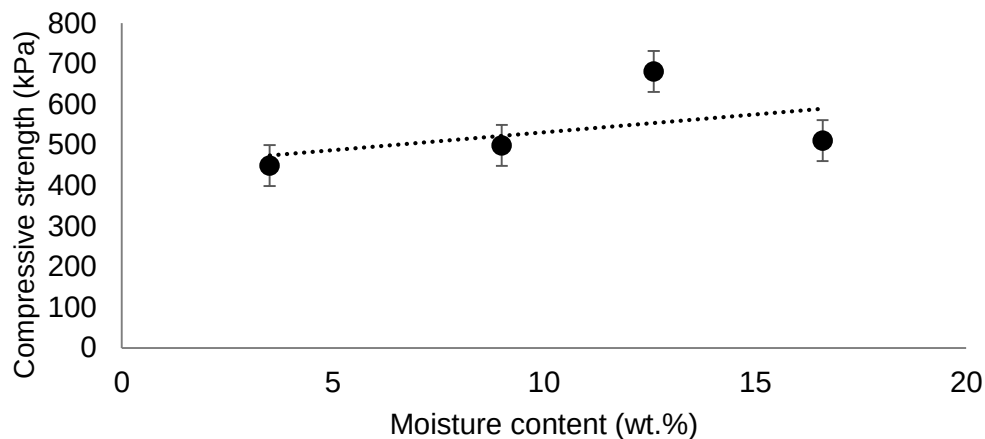


Figure 2-11: Effect of moisture content on compressive strength adapted from Mangena, et al. (2004)

From Figure 2-11 it is noted that the compressive strength increases with approximately 200 kPa compared to the baseline compressive strength of the coal. This moisture is known as the optimum moisture and is unique to the coal used. It can differ for coals from different regions and seams. For this coal the optimum moisture is around 12 weight percent.

2.7 Industrial application of coal briquettes

The respective coal markets in South Africa have different requirements for the coals they use. These requirements are control measures implemented to ensure the optimum quality product reaches each market. There are four main markets that acquires coal in bulk volumes and they include the export market, Eskom, SASOL, and the domestic market (Steyn and Minnet, 2010). Figure 2-12 is a depiction of these markets and an estimate of their share of their respective market demand.

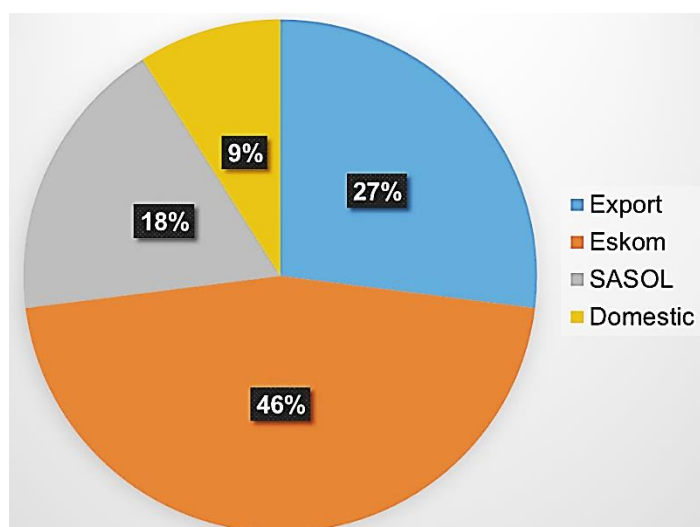


Figure 2-12: The four main South African coal markets and sales demand, adapted from Steyn & Minnet, 2010

Eskom is a major producer of electricity in Africa. The 13 coal fired power stations in its ownership rely on coals that are considered high ash yield coals. This is representative of the coal properties in South Africa that generally include higher ash yields.

On an as received basis, Eskom rejects coals with less than 21 MJ/kg calorific value, more than 12 percent total moisture, greater than 33 percent ash yield, less than 20 percent volatile matter, and greater than 1 percent sulfur content. On a mechanistic level the top size of the product should be 40 mm (Steyn and Minnet, 2010). The minimum size requirement is taken to be 8 mm, where this is seen to be the industry standard (Venter and Naude, 2015).

Coal briquettes have widely been studied for industrial combustion applications. One of these studies include a comparison between raw coal and coal briquettes from the same batch of Chinese coal (Zhang et al., 2001). In this study the behaviour of briquettes was compared to lumps of raw coal in a steam generating boiler. They manufactured briquettes for small and

middle-sized boilers. The boiler was a stoker-chain water tube boiler of Taiwanese make (DZL4-1.25-AIII model). This boiler is shown in Figure 2-13.

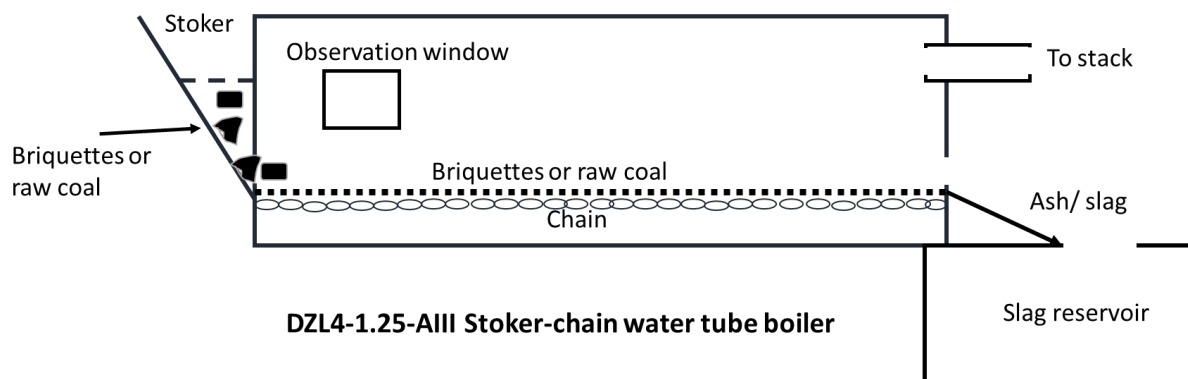


Figure 2-13: An industrial scale boiler for the comparison between combustion of lump coal and briquettes adapted from Zhang et al. (2001)

The raw lump coal was pulverised and mixed with other components (Table 2-6), to make suitable briquettes.

Table 2-6: Components added to industrial boiler briquettes

Component	Weight %
Ca(OH)	14.5
Combustion catalyst	0.4
Water resistance enhancer	0.03
Binder	2

These briquettes were pressed in dimensions of 45 mm length, 35 mm breadth, and 22 mm in thickness. These are quite large in comparison to the briquettes generated in this study. The briquettes were dried in a kiln. The heating values of the briquettes were lower than that of the lump coal by 4 MJ/kg, with the briquettes' calorific value ranging between 23 – 27 MJ/kg. Due to the drying of the briquettes in the kiln the moisture content reduced by 1 percent. Due to the addition of their incombustible components, and possibly the binder, the ash yield and volatile matter increased by 4.3 percent and 13.2 percent respectively. They subsequently found that the hydrated lime reduced the sulfuric emissions, as well as the emissions of carbon monoxide and the PM_{2.5} particulate material, but the particulate material within a 10 µm range was increased.

2.8 Combustion of coal agglomerates and particles

The elementary process of combustion involves three basic stages, including volatile release, due to heating of the coal, burning of the evolved volatile matter, and finally the burn-out of the residual char. The decomposition of volatile matter and char could occur in unison, consecutively, or with some overlapping. The products yielded from the devolatilisation of coal include combustible tars and hydrocarbon gasses. These products react with oxygen in the vicinity of the coal particles, and produce bright flames from the diffusion of the combustion gas. The char particles in which the combustible tar and gas are burnt are often spherical and have numerous pores and cracks. These were produced from volatile evolution and heat stress addition during the pyrolysis stage (Jinsheng, 2009).

Industrially, coals are used in fixed bed firing, fluidized bed firing, and suspension firing. For suspension firing the particle size, which is the most important parameter in combustion, and should be below 100 μm . While, for fixed bed and fluidized bed firing, the particle sizes should be between 5 – 50 mm and 1 – 5 mm lump coals respectively (Lahaye and Prado, 2012).

To test the combustion reactivity of a coal, thermogravimetric analysers (TGA's), fixed bed reactors, entrained particle reactors, and wire-mesh reactors can be used. The results from these analyses can be compared to results from industrial operations. The reactivity of coal is dependent on the rank of the coal, and decreases as the coalification level increases. Reactivity usually implies that the char of the coal is subjected to the above mentioned analyses. The rate of coal reactivity greatly depends on the physical properties of the char, the gas used, as well as the reaction temperature and heating rate. The physical properties of a char are dependent on the conditions of the charring process. It is therefore necessary that these conditions, as well as the conditions of reaction, be constrained to ensure good repeatability. The gases that can be used to evaluate reactivity can vary from CO_2 and steam (gasification) to oxygen or air (combustion), this depends on the intended end-use of the coal. Combustion processes have reaction rates 10^5 times faster than CO_2 gasification processes. The higher heating value of a coal is also an indication of its reactivity, however, how the reaction evolves over time is a better measure than a singular value. Reaction evolution datasets are collected for kinetic modelling to evaluate the process. Of these methods the thermogravimetric analysis is a less expensive method that can be easily altered, and delivers results relatively quickly. These types of experiments have higher temperature limits of between 1400°C and 1600°C and can be operated isothermally or non-isothermally (Speight, 2013).

Richards (1990) highlighted the importance of evaluating the efficiency of the fuel through reactivity. Previous briquetting studies all included some form of reactivity study depending on the intended end-use of their briquettes. Modiri (2016) implemented gasification at temperatures between 875 and 1000°C with intended utilisation in the synthetic fuels industry. Venter & Naude (2015) performed thermogravimetric analysis with air at a maximum temperature of 900°C and plotted residual mass against time. Zhong (2017) performed thermogravimetric analysis with air and nitrogen, by first charring the briquette under nitrogen (viewing the pyrolysis behaviour) and then combusting the char in air at a flow rate of 100 mL/min (0.1 nL/min), and repeated the analyses twice. Char can be reacted in oxygen rich environments at sufficiently high temperatures. The reactions that occur in these environments are gas-solid, and heterogeneous in nature (Jinsheng, 2009). The reactions that occur during the combustion of carbon enriched char are shown in Table 2-7.

Table 2-7: Reactions and heat of reactions during char combustion adapted from Jinsheng (2009)

Reaction	Heat of reaction (kJ)
$C + O_2 = CO_2$	- 392.9
$C + \frac{1}{2}O_2 = CO$	- 111.2
$CO + \frac{1}{2}O_2 = CO_2$	- 281.7
$C + CO_2 = 2CO$	170.5

The combustion of a coal briquette in its uncharred form will, however, provide insights on the onset of ignition and maximum burning rate of the coal briquette. The ignition temperature is considered the lowest temperature at which coal can ignite. This temperature depends on combustion conditions. This temperature is aligned with the temperature at which volatiles are released from the coal. A greater amount of volatiles within the coal leads to lower initial volatile releasing temperature. Ignition temperature and volatile release temperature are also rank dependent as shown in Table 2-8.

Table 2-8: Ignition points and volatile release temperatures of the different types of coal, adapted from Jinsheng (2009)

Coal type	Volatile Matter release (°C)	Ignition Temperature (°C)
Lignite	130 – 170	250 – 450
Bituminous	200 – 300	400 – 500
Anthracite	380 – 400	700 – 800

From the table it is seen that the volatile release and ignition temperatures increase with an increase in coal rank. It is expected that the ignition of bituminous coals should begin when the volatiles and tars are burning at the highest rate, and from the table this should be between 400°C – 500°C.

Other studies also considered the combustion profile of the coal and its char as in Jayaraman (2017) where coal was combusted at different temperatures isothermally, namely, 1050°C, 1100°C, and 1150°C. Air and oxygen at a low flow rate (0.05 nL/min) was used and introduced after pyrolysis in argon at 850°C, 900°C, and 950°C. The thermographs of different runs are depicted in Figure 2-14.

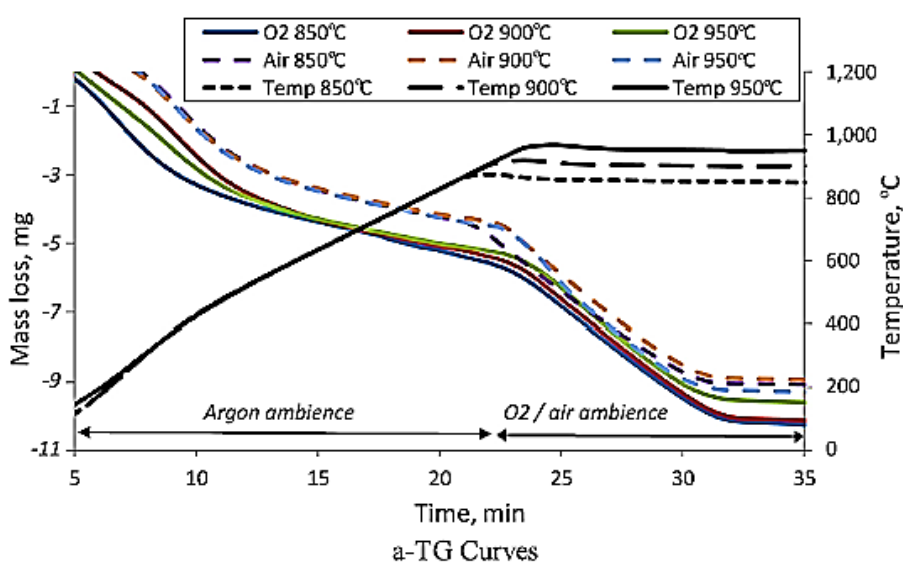


Figure 2-14: Thermogravimetric analysis of 1.4 mm sub-bituminous coal particles taken from Jayaraman (2017)

In Figure 2-14 the pyrolysis regions and combustion regions for sub-bituminous coal particles are depicted. It is clear from this figure that the rate at which the sample is pyrolysed in argon remains constant for all temperatures. There is a difference in the rate of mass loss for combustion in pure oxygen versus air. Air seems to have a better repeatability in these particles for all regions. In this study air would be preferred over oxygen for safety reasons. Figure 2-15 is a thermograph for a 3 mm sub bituminous coal particle combusted in air.

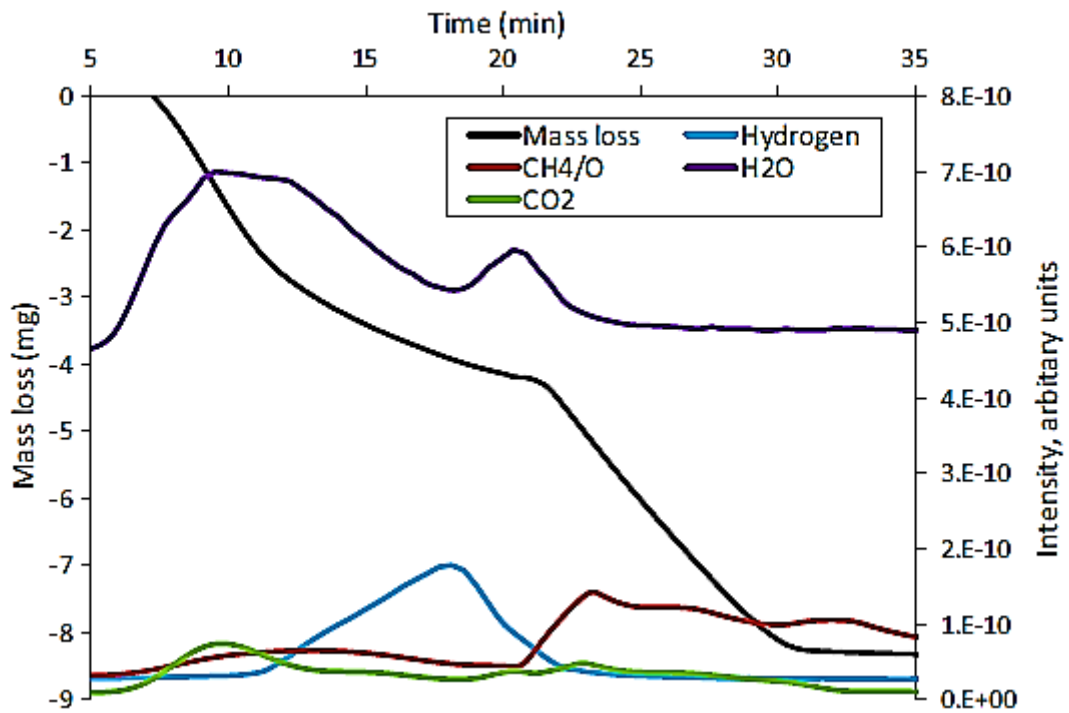


Figure 2-15: Thermogravimetric analysis of a 3 mm sub-bituminous coal particle taken from Jayaraman (2017)

It would be greatly recommended to include kinetic modelling in a study concerning briquette reactivity. Kinetics in combustion can be modelled using the Arrhenius Equation (Jayaraman et al., 2017):

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad \text{Equation 2.1}$$

In Equation 2.1, $k(T)$ represents the rate constant as a function of temperature, A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

Conversion is calculated from Equation 2.2 as follows:

$$x = \frac{m_0 - m}{m_0 - m_{ash}} \quad \text{Equation 2.2}$$

Where x denotes the conversion, m_0 is the original mass, m is the instantaneous mass, and m_{ash} is the residual mass after the completed run. The residual mass should correspond to the proximate analysis value of the ash yield (Venter and Naude, 2015).

To relate the rate constant to carbon conversion and time, three models exist.

- The volumetric model assumes uniform gas distribution in the particle in all possible directions.
- The grain model or shrinking core model, assumes the particle is porous consisting of non-spherical grains.
- The random pore model.

Table 2-9 depicts the kinetic relations for these models, where k_{vm} , k_{GM} and k_{RPM} denote the rate constant for the volumetric model, grain model, and random pore model respectively.

Table 2-9: Models for the prediction of the rate constant adapted from Jayaraman (2017)

Model	Equation	Equation number
Volumetric (Homogenous Relaxation Model)	$\frac{dx}{dt} = k_{vm}(1 - x);$ $\ln(1 - x) = k_{vm} \cdot t$	2.3
Grain/ Shrinking core	$\frac{dx}{dt} = k_{SCM}(1 - x)^{\frac{2}{3}};$ $3[1 - (1 - x)^{\frac{1}{3}}] = k_{SCM} \cdot t$	2.4
Random Pore	$\frac{dx}{dt} = k_{RPM}(1 - x) \sqrt{1 - \psi \ln(1 - x)}$	2.5

The most rigorous model would be the random pore model, which would describe the reactivity of larger briquettes better. The briquettes to be used in this study are approximately 45 mm in length and 22 mm in thickness, and would be expected to have a limit in terms of the extent of reaction, since the core of the briquette may remain unreacted. This property which is associated more with heat transfer should be investigated.

The investigation into combustion kinetics can also be done on a non-isothermal basis. For this the coal is sometimes charred. This is because charring is a way of grading low-rank coals and chars for use in combustion and power generation. This is because 80 percent of the char is converted to energy, but the char has burn-out and ignition challenges (Xu et al., 2014). Char equations exist (as with the isothermal methods) to approximate the activation energy associated with the conversion of the process. According to (Hu et al., 2018) some bridge bonds and structural molecular branch bonds are released when bituminous coals undergo pyrolysis. The combustion of volatile matter is a key function of the ignition temperature. So that chars have higher ignition points than coals.

2.9 Coal briquetting in South Africa

There are coal briquetting plants in South Africa that are currently operational. Some of these include:

1. The Anglo-American Exxaro Mafube Joint Venture coal briquetting plant (Exxaro, 2018).
2. Prodiflex Coal Pty. Ltd duff coal briquetting operations (ProdiflexCoal(Pty)Ltd, 2009).
3. Companies that assist in the management, consultation, and design of coal briquetting plants (ENPROTEC, 2018).
4. Pilot plants including those of Coaltech2020 (Reddick et al., 2007).

Coal briquettes can extend the lifetime of a coal plant as seen by this initiative by Exxaro, where lump coal became increasingly scarce so that fines were utilised. In South Africa the focus of agglomerating fine and ultrafine coals falls on briquetting, because it is considered more financially viable (Reddick et al., 2007). South African coal briquettes are not only seen as viable in South Africa, but also internationally, as 6.5 percent of the total exports for 2017 were coal briquettes or ovoids. This generated an additional R 76 138 million to the South African economy (InvestSA, 2018). For the domestic market it is expected that the financial feasibility for briquetting of coal-fines will increase as the cost of briquetting decreases, while the cost of D-grade coal increases (Reddick et al., 2007).

2.10 Economic considerations in the feasibility of briquettes

The economic feasibility of a coal briquette depends on more than the cost of the raw coal fines. In a scenario where this price can be neglected completely, the impact of processing would bear more weight. Figure 2-16 is a summary of the factors that could influence the economic feasibility of the briquettes, as an initial estimate.

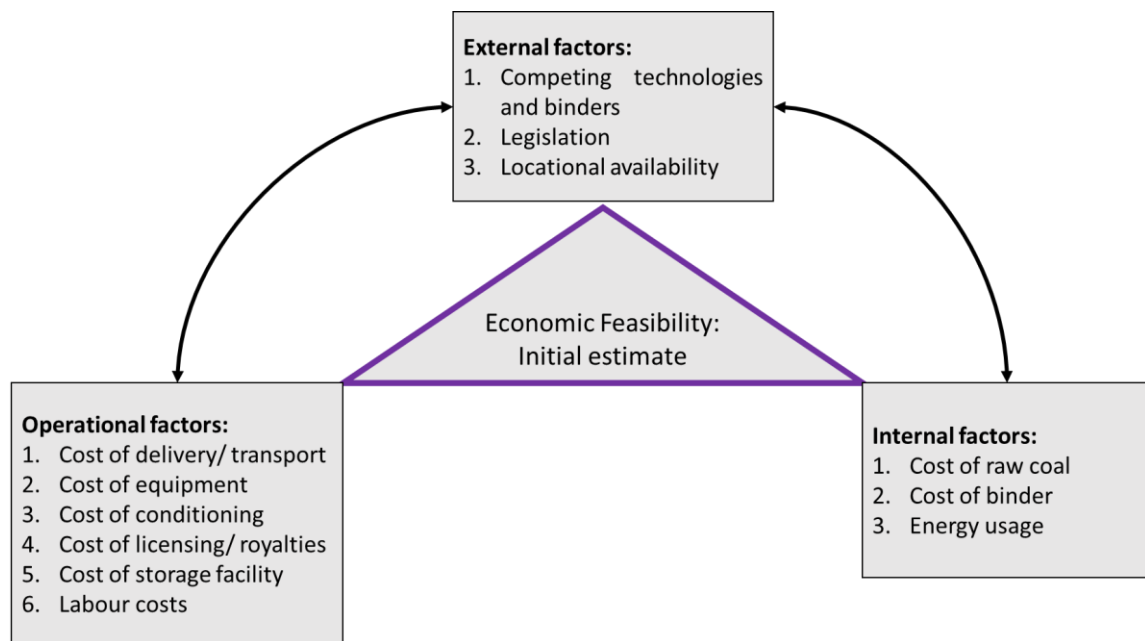


Figure 2-16: Initial estimate of the quantification of the financial feasibility

2.10.1 Competing technology

The raw fines are sometimes back-blended to the washed coal product, and this creates a product that is of acceptable quality to the market where contracts allow (Speight, 2013). It is beneficial for low water consumption and results in much lower fines refuse disposal. These plants are favoured when the coal quality of a certain mine has deteriorated to such an extent that the raw coal product can no longer be sold at a profit (Klima et al., 2012). This produces a competing technology for the briquetting of coal fines.

2.10.2 Competing binders

The most notable competing binder is PVA (polyvinyl alcohol) in the category of organic binders. Other organic binders that could compete include starch and compound binders. PVA will be considered the most important binder in determining comparability (Michailovski and Cilengi, 2016).

2.10.3 Comparative study for economic analysis

To evaluate the economic feasibility of the briquettes bound by the poly-acrylic binders, the price ranges and concentrations used will be compared to that of PVA. The PVA bound briquettes will be considered the base case for the economic analysis, since they represent a product that is already industrially feasible. The cost of PVA per ton at different concentrations are shown in Table 2-10.

Table 2-10: PVA cost per ton for different concentrations, adapted from Venter & Naude (2015)

Cost (R/ton) PVA	0.1 weight %	0.9 weight %
Minimum	20	178
Maximum	28	248

The poly-acrylic binder, as previously discussed, consists of three components. The cost per ton for a concentration between 0.1 – 5 weight percent are provided in Table 2-11.

Table 2-11: Poly-acrylic binder components cost per ton for different concentrations

Cost (R/ton) Component	Weight percent					
	0.1	0.3	0.9	1.25	3	5
A (25 weight %) paste	9	26	79	106	264	440
B (25 weight %) paste	4	13	39	53	131	219
XL (0.03 weight %, 2 weight %) (liquid)	(0,0)	(0,1)	(0, 2)	(0,2)	(0, 5)	(0, 9)
Minimum (XL low)	13	40	119	158	395	659
Maximum (XL high)	13	40	120	160	401	668

From the table it is seen that the cross-linker amount is insignificant compared to the other components. This is especially due to its low concentration. The components were calculated in a standard equimolar ratio with varying cross-linker amount, as an initial comparison to PVA. This comparison is shown in Table 2-12.

Table 2-12: Poly-acrylic binder components cost per ton for different addition amounts, and for a standard concentration

Cost (R/ton) PVA (powder)	PVA	PVA	PA	PA
	0.1 weight %	0.9 weight %	0.1 weight %	0.9 weight %
Minimum	20	178	13	119
Maximum	28	248	13	120

From this initial comparison it is noted that the poly-acrylic binder is generally less expensive than PVA at the same concentration.

2.11 Summary

Coal fines have accumulated for the last 100 years (Venter and Naude, 2015, Garling, 2015). These coal fines can be agglomerated to create a saleable product (England, 2013, Klima et al., 2012). Binderless briquetting is an agglomeration technique that can be used for the effective briquetting of specific bituminous medium rank C coals (Mangena et al., 2004). Most South African coals need to be agglomerated with the aid of a binder, because of the low vitrinite content that aids in briquetting (England, 2013, Venter and Naude, 2015). Briquetting with or without a binder can be described using various mechanisms that can help identify the shortcomings and successes of the fine coal briquetting process (Zhang et al., 2018). The properties of coal that highly influence the quality of briquettes, include the petrography, mineral matter and free moisture content (Mangena and du Cann, 2007, Mangena et al., 2004, Venter and Naude, 2015). Organic polymers can be used to strengthen briquettes without adding significantly to the ash yield (Zhang et al., 2018). PVA is used as an industry standard for producing fuel briquettes (Venter and Naude, 2015, Michailovski and Cilengi, 2016). A poly-acrylic binder was developed to be comparable with PVA to reduce the cost of the binder, by reducing the binder addition required (Michailovski and Cilengi, 2016). The briquettes formed need to conform to certain industrial requirements (Steyn and Minnet, 2010). Reactivity tests are highly important in determining the quality of coal briquettes (Richards, 1990). Combustion in air can be used through thermogravimetric analysis to evaluate the kinetics and thereby the process of combusting briquettes and pulverised briquettes (Speight, 2013). A suitable model needs to be selected to describe these kinetics (Jayaraman et al., 2017). After briquette quality measurements have been concluded, the optimal briquette at the lowest price can be selected for industrial application (Steyn and Minnet, 2010).

CHAPTER 3 EXPERIMENTAL PLAN

3.1 Materials and equipment

Two coal samples from a colliery in Middleburg Mpumalanga, sampled at different times, were used in this study. Both coals were derived from filter cake residues originating from a slurry pond and their characterisation is presented in Section 3.3. The materials used in this study also included the following:

3.1.1 Briquette manufacture

1. Water (from Potchefstroom) for hydration of the sample to 10.85 weight % moisture content was used where drying occurred, to keep moisture constant.
2. Components for the binder were obtained at 99.9 percent purity
3. Anti-foaming agent
4. Demineralised water for the binder manufacture – provided in-house

3.1.2 Briquette testing

1. Potchefstroom tap water for the water resistance test
2. Dry air (< 2ppm water) from Afrox for combustion profiles
3. Oxygen (99.9 percent purity from Afrox) for the bomb calorimeter

3.1.3 Equipment

The equipment used for the briquette manufacture in small scale initial tests was the LRX-plus hydraulic press, and for larger laboratory scale tests the Komarek B050 briquetting press was used. For mixing of the components for the poly-acrylic binder an overhead stirrer was used, and for PVA a hot-plate magnetic stirrer was used. The mixing process of these binders and variables for proper mixing are further described in Section 3.4. The thermogravimetric analysis was done using an in-house vertical tube furnace as discussed in Section 3.9.4. The water immersion and compression test are described in Sections 3.9.1 and 3.9.3 respectively. The abrasion resistance test was a scaled-down model of the Richards (1990) tumbler test and is described in Section 3.9.2. Tomography was done on the briquettes at NECSA at their Hartbeespoort headquarters and is described in Section 3.8.2.

3.2 Sample preparation

The received samples (Coal 1 and Coal 2) each contained a handful of 6 mm and 8 mm top size lump clots respectively, together with a majority of 1.18 mm top size of fine material for each sample. The samples were transferred to a clean, smooth concrete floor for coning and quartering to produce buckets of 29 kg mass (Speight, 2005). The bulk of the representative sample was divided by means of a riffler as depicted in Figure 3-1. The riffler-splitter had the capacity to split the sample into four 1 kg samples. These were then further split using the rotary splitter that could split the sample into 330 g samples which was required for analyses. The general analyses of coal that was conducted in this study included the proximate analysis, ultimate analysis, and calorific value to evaluate the characteristics of the coals.



Figure 3-1: Open type riffler for the reduction of sample bulk

3.3 Coal sample analysis

The coal profile would be used to describe the coal in terms of its overall value. Considering that discard fines are generally perceived to have calorific values between 16 – 19 MJ/kg (Wagner, 2008). X-Ray Fluorescence Spectroscopy (XRF) was done to find a general indication of the mineral matter in the coal, while X-Ray Powder Diffraction (XRD) results indicate the crystalline mineral matter present. The proximate analysis was done to probe the inherent moisture ash yield, along with the volatiles and fixed carbon contents of the coal. The ultimate analysis was done to determine the chemically reactive matter in the coal, namely C, H, O, N, and S. The coal was also sent for petrography analyses to analyse the maceral content in the coal. The final tests included the surface properties of the coal and the binders. The coal samples were sent to an independent laboratory (Bureau Veritas Sunderland) for these analyses.

3.3.1 Proximate analyses

The proximate analysis determines the inherent moisture, volatile matter, ash yield, and fixed carbon (by difference) contents of the coal. Two coal samples were obtained and differed somewhat in terms of inherent moisture (2.2 percent difference), ash yield (6.7 percent difference), and gross calorific value (1.86 MJ/kg). Differences were also observed in terms of fixed carbon (2.6 percent), and total sulfur (0.1 percent). The difference in ash yield reduces the quality of the coal and therefore the coal briquettes, however, both coals would still be acceptable to pulverised fuel boilers as agglomerates by inference from Chapter 2 Section 2.7. The proximate analyses, and gross calorific values are given in Table 3-1.

Table 3-1: Proximate analyses and gross calorific values of coal samples from a colliery near Middelburg

Variable	Standard used	Coal 1	Coal 2
Inherent moisture (%) (Air dry basis)	ISO 13909-4:2001	6.2	4.1
Ash yield (dry basis) (%)	ISO 1171:2010	22.1	28.9
Volatile Matter (dry-ash free) (%)	ISO 562:2010	33.0	32.0
Fixed carbon (dry-ash free) (%)	By difference	67.0	68.0
Total Sulfur (%)	ISO 19579:2006	0.8	0.7
Gross calorific value (MJ/kg)	ISO 1928:2009	22.5	20.6

Table 3-1 was used to evaluate the difference in the volatile matter and fixed carbon contents for the two coals. Volatile matter is liberated while coal is heated by convection or radiation and exists as a volatile-cloud. This directly influences the ignition temperature, the more prevalent the volatile matter, the higher the ignition temperature (Katalambula et al., 1997). For the coals in question, on a dry ash free basis, the volatile matter weight % is similar with a 1 percent difference (33 percent and 32 percent for Coal 1 and Coal 2 respectively). The fixed carbon is also very similar on this basis with a 1 percent difference (67 and 68 percent for coal 1 and 2 respectively).

The coal samples were compared to samples in the same coalfield that were previously investigated in a study by Mangena et al. (2004). The results from this study were tabulated against the results in the study by Mangena et al. (2004) and are presented in Table 3-2.

Table 3-2: Proximate analysis of coal samples from a colliery near Middelburg compared to Mangena et al. (2004) on an air dried basis

Name	H ₂ O (%)	Ash (%)	GCV (MJ/kg)
Coal 1	6.4	22.8	22.5
Coal 2	4.2	28.9	20.6
SJM5	2.6	15.3	27.5
SJM3	2.8	17.7	25.9
SJM2	3.1	18.9	25.1
SJM1	3.6	21.8	23.8
SJM4	2.2	31.8	21.1

From Table 3-2 it can be observed that the coal samples used in this study have higher inherent moisture contents than for the coals used in the study by Mangena et al. (2004), i.e. approximately 2 and 4 percent respectively. The ash yield of the coals are in the same range, and gross calorific values are similar to the coals used by Mangena et al. (2004). The differences in Coal 1 and Coal 2 were ascribed to the coals being mined at different times.

3.3.2 Ultimate analysis

The ultimate analysis of a coal sample is the quantification of elemental carbon, hydrogen, nitrogen, and total sulfur, through the use of two specialised detection instruments for carbon/hydrogen/nitrogen and total sulfur respectively. Oxygen is calculated by difference after subtraction of CHNS, H₂O and ash on an air dry basis (Speight, 2005). The organic material in the coal is what reacts during combustion. Table 3 3 is a summary of the elemental compounds in the coal on a dry ash-free basis.

Table 3-3: Ultimate analysis of coal samples from a colliery near Middelburg, on a dry, ash-free basis

Element/ Analysis	Coal 1	Coal 2
C (%)	83.2	77.8
H (%)	4.02	4.30
N (%)	2.08	1.93
O (%)	9.56	14.9
Sulfur (%)	1.11	1.04

The carbon and hydrogen in Coal 1 makes up 87.3 weight percent of the organic material; whereas it makes up 82.0 weight percent of the organic material in Coal 2.

3.3.3 X-Ray Powder Diffraction (XRD) and X-Ray Fluorescence Spectroscopy (XRF) analyses

Similar to the Proximate and Ultimate analysis, the XRF data was obtained from Bureau Veritas in accordance with the standard ASTM D4326XRF by fusion bed. The sample was converted to ash and subjected to X-ray fluorescence. This was done to determine the major metallic elements in the coal. A comparison between the two coals was drawn and presented in Table 3-4.

Table 3-4: XRF analyses of coal samples on loss on ignition basis

Oxide	Coal 1	Coal 2
SiO ₂	42	56
Al ₂ O ₃	29	27
CaO	11	2.4
SO ₃	6	2.1
Fe ₂ O ₃	5.4	7.6
MgO	2.1	1.1
TiO ₂	1.6	1.6
P ₂ O ₅	0.9	0.3
K ₂ O	0.5	0.9
BaO	0.2	0.1
SrO	0.2	0.1
MnO	0.1	0.1
ZrO ₂	0.1	0.1
Na ₂ O	0.1	0

The XRF data can be used to predict the combustion behaviour of the coal (Speight, 2005). From the data in Table 3-4 it can be observed that the coals have similar SiO₂, Al₂O₃, Fe₂O₃, and TiO₂ contents. Conversely, a great difference is observed in CaO, MgO, and SO₃ contents. All minerals below 1 weight percent was not considered to have a significant impact on the overall make-up of the ash and consequently, the briquetting of the coal. The XRD analysis was performed on the coal samples to evaluate the clay content in the coals. The samples were prepared for XRD using a backloading preparation method. The diffractometer used was a PANalytical AERIS diffractometer. The diffractometer had a PIXcel detector and fixed Fe slits filtered by Co-K α radiation. The phase-determination software used was X'Pert Highscore plus software. The

weight percentages were estimated using the Rietveld method. The XRD analysis had a detection limit of 0.5 – 3 weight percent and amorphous phases were not taken into account. This analysis was performed, since Mangena (2005) found correlations in strength to certain clays in the coal. He found that high levels of kaolinite could ultimately lead to stronger binderless briquettes. Whereas high levels of illite could lead to weak briquettes. The XRD analyses of the coals are presented in Table 3-5.

Table 3-5: XRD analysis of Coal 1 and Coal 2

Mineral group	Mineral	Coal 1	Coal 2
Accessory minerals	Quartz	2.0	9.1
	Gypsum	1.7	1.3
	Magnetite	0.3	0.4
Feldspars	Plagioclase	Not detected	0.0
	Microcline	2.3	Not detected
Carbonate minerals	Siderite	10.9	0.3
	Dolomite	0.8	0.1
	Calcite	1.3	Not detected
Clay minerals (Kaolin)	Kaolinite	10.9	17.0
Sulphides	Pyrite	0.3	Not detected
Shales	Muscovite	Not detected	0.7
Total organic carbon	Organic C	79.8	71.0

The coal contained little to no shales with the most prevalent (in micro amounts) being muscovite. Shales are normally the most abundant extraneous minerals in coal (Speight, 2005). Whereas the clays (kaolin) as kaolinite was present in lower quantities, which has a reducing effect on the briquette-ability of the coal compared to higher kaolinite contents (Mangena et al., 2004). The second coal sample, however had a much higher kaolinite content, hence it is expected that it would produce stronger binderless briquettes.

3.3.4 Petrographic analyses

The petrographic analyses were done by Bureau Veritas through crushing the samples below a sample size of -850 µm and setting the crushed sample in an epoxy resin mixture. The surface of the set mixture was polished and analysed under oil immersion at a magnification of x50. The maceral analysis was done according to ISO 7404 part 3, while the vitrinite reflectance was

conducted according to ISO 7404 part 5, and the rank determination was done according to ISO 11760-Classification of Coals. The petrographic analyses were indicative of a medium rank c, moderate volatile, and bituminous coal for both coal samples. The petrographic images for Coal 1 and Coal 2 are shown in Figure 3-2 and Figure 3-3 respectively.

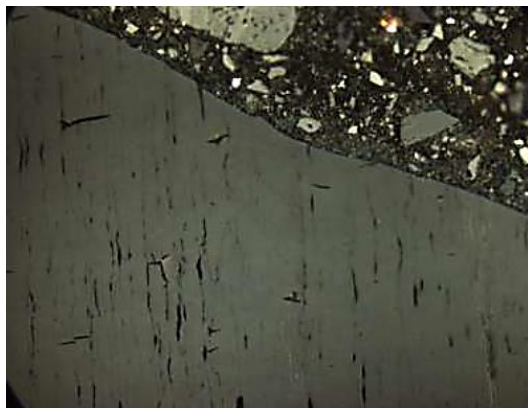


Figure 3-2: Petrographic photo of Coal 1 at a magnification of x50 under oil immersion

From Figure 3-2 the appearance of shiny vitrinite particles was observed, while the particle of coal under evaluation showed no significant deformation.

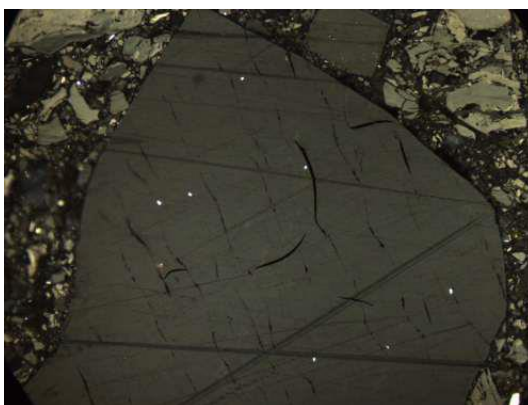


Figure 3-3: Petrographic photo of Coal 2 at a magnification of x50 under oil immersion

From Figure 3-3 it is seen that there are clay overlays and plant cuticles the surface of the vitrinite maceral particle, which are not as pronounced on the surface of Coal 2. This is indicative pseudo vitrinite that formed in situ in the seam and have different surface properties than vitrinite. The clay-rich properties of this coal are expected to aid in the production of very strong briquettes. The results summary as obtained from Bureau Veritas, for both coals are shown in Table 3-6.

Table 3-6: Petrographic analyses of Coal 1 and Coal 2

Parameter	Coal 1	Coal 2
$R_o V_{Max}$	0.70	0.60
$R_o V_{Random}$	0.70	0.60
Standard Deviation (%)	0.70	0.10
Rank category	Medium C	Medium C
V-Class distribution (Max)	5 – 9	4 – 8
Total Vitrinite	23.8	26.4
Total Liptinite	3.2	1.0
Total Reactives	54.9	56.1
Total Inerts	45.1	44.0
Total Mineral Matter	11.9	15.5
Vitrinite Classification	Low	Low

From Table 3-6 the parameters $R_o V_{max}$ and $R_o V_{Random}$ are used to determine the rank (maturity) of the coal. Both coals were found to be Medium rank C bituminous coals with a low Vitrinite classification. The coals have similar amount of inerts (with a difference of 1.1 percent) between them which include the visible mineral matter. They also have very similar amounts of reactive material, with the second coal having a 2.6 percent higher vitrinite content.

The coals used in this study were compared to the coals used in the study by Mangena et al. (2004), as shown in Table 3-7. It was observed from the table that the coals had reactive macerals in the same range as the coals used in the study by Mangena et al. (2004). The amount of vitrinite in the coals used in this study was comparable to the SJM4 coal from the coals used in the study by Mangena et al. (2004), but 10 percent lower than the other 4 coals used in the study by Mangena et al. (2004). The contribution of reactive inertinite in the case of the coals used in this study was approximately 10 percent higher than for the coals used in the study by Mangena et al. (2004). The coals used in this study therefore had less vitrinite, which was balanced by a higher amount of reactive inertinite compared to the coals used in the study by Mangena et al. (2004).

Table 3-7: Comparison of the petrographic analysis to the coals in a study by Mangena et al. (2004)

Sample	Maceral Distribution (%)				
	Vitrinite	Liptinite	Reactive inertinite	Inert inertinite	Total Reactive macerals
SJM1	35	6	14	30	55
SJM2	32	4	14	42	50
SJM3	33	5	16	38	54
SJM4	25	4	15	33	44
SJM5	34	4	16	40	54
Coal 1	24	3	26	7	53
Coal 2	26	1	29	28	56

The properties and condition of the coal could have an impact on the wettability and binding mechanisms as discussed in Section 2.5. The 2.1 % higher prevalence of moisture in Coal 1 (Table 3-1), its reduced release of oxygen in the ultimate analysis with a difference of 5.4% (Table 3-3), and its higher siderite content with an increase of 10.6% (Table 3-5) could indicate that it is much more oxidised than Coal 2. This could also have an impact on the wettability of the coal and the combustion of the briquettes formed from the coal. However, the focus of this study is on the performance of the binder and less so on the performance of the coal.

3.4 Binder preparation

The binders (poly-acrylic (PA) based binder and polyvinyl alcohol (PVA)), being polymeric in nature, have specialised preparation requirements. The components of the binders could be subject to shearing, or improper mixing. Other erroneous preparation methods, in the case of PVA, could lead to insolubility. These problems were overcome by increasing the heating time for PVA and using lower rotational speeds for the overhead stirrers and mixers.

3.4.1 Polyvinyl alcohol (PVA)

Polyvinyl alcohol was obtained in powder form at 99.9 percent purity with a one-year expiration date. The powder was slowly added to water at room temperature and mixed into a colloidal solution. The mixture was heated via magnetic hot plate stirrer in order to completely solubilise

the PVA polymer. This is because PVA solubilises at temperatures above 90°C (Molyneux, 2018). A homogeneous solution was obtained at a temperature of 92°C and was allowed to homogenise at this temperature for 10 minutes. The mixing time and mixing temperature were fixed to ensure repeatability. The mixture was allowed to cool to ambient temperature, while continually being mixed using the magnetic stirrer. The setup that was used for the PVA manufacture is shown in Figure 3-4.

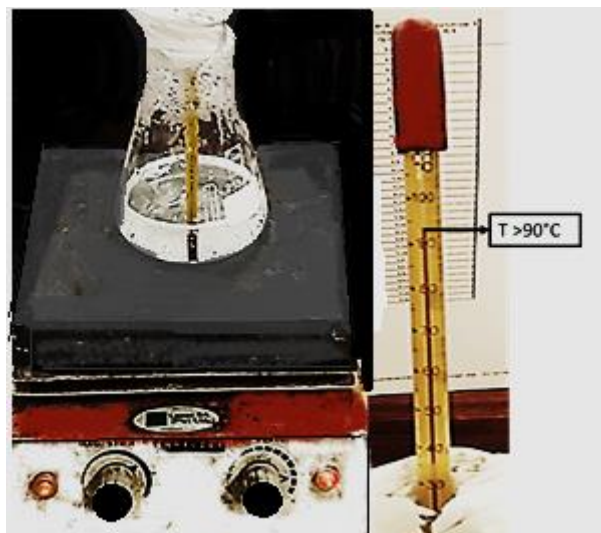


Figure 3-4: PVA preparation setup, hot-plate stirring at 95°C

3.4.2 Poly-acrylic (PA)

The poly-acrylic binder (PA), forms part of the intellectual property of a chemical company and therefore cannot be fully disclosed in this study. The PA binder consists of 4 components: component A, component B, cross-linking additive (XL), and water. Components A and B were obtained in the form of gels. The first phase of binder testing entailed a two thirds to one third relationship between components A and B, with a set amount of XL and water. The second phase of binder testing was subject to a D-optimal design. For this design, varying amounts of component A, component B, XL, and water were specified. This was used to find a model to enable the prediction of the behaviour of each component in the binder mixture, and to find a formulation that would be termed the optimal formulation. The final phase of binder testing included a central composite design. The central composite design focussed especially on components A and B and was used to determine the optimal ratio of the two components with set amounts of XL and water.

Components A and B were prepared by adding equal amounts of water to both components respectively. Each component was mixed with water via overhead stirrer. After the components

were hydrated, Component B was added to the hydrated component A. The mixture was then stirred for ten minutes before the cross-linker was added in drops into the formed vortex. After addition of the cross-linker, the mixture was stirred for a further 10 minutes and kept sealed in an air-tight container. The binder was then added at various concentrations to the coal fines. Beyond 30 minutes after preparation the binder was discarded, at which time a new binder was prepared. This extensive preparation method was followed to reduce the standard error on the mechanical test results of the briquette.

3.5 Preparation of the coal-binder mixture

To prepare the coal-binder mixture 500 g of coal was used. The coal was then moistened to 10.85 weight percent; where drying had occurred, which was close to the as-received total moisture content of the coal this is presented in Annexure A. The moistened coal was uniformly mixed in a Kenwood mixer affixed to the briquetting press to ensure even distribution of the moisture prior to pressing. After a uniform moisture was obtained binder was added in drops to the coal as per the statistical design formulations and concentration limits. The coal binder mixture was then mixed in the Kenwood mixer for a duration of 10 minutes prior to briquetting.

3.6 Mixture analysis

The mixture was analysed via proximate analysis to evaluate the volatile and ash forming properties of the coal-binder mixture.

3.6.1 Proximate analysis

Table 3-8 is a representation of the results obtained for the coal-binder mixtures. The higher moisture content (11 weight percent) represents the as-received sample, while the lower moisture content (7 weight percent) is an air-dried sample. The binder used consisted of a two thirds to one third ratio of component A to B.

Table 3-8: Proximate analysis results of different binder additions of the original and dried sample on a dry basis

Binder addition, [sample total moisture]	% Volatiles	% Ash	% Fixed carbon
1.2 weight %, [7 weight %]	26	25	48
0.8 weight %, [7 weight %]	26	26	48
0.4 weight %, [7 weight %]	26	25	48
1.2 weight %, [11 weight %]	31	24	46

The results indicate that the binder addition had no effect on the total moisture or volatile contents of the dry sample, and no effect was observed in the ash and fixed carbon content. The greatest differences are therefore attributed to the difference in moisture content between the two samples of the 1.2 weight percent concentration level.

3.6.2 FTIR analysis

Even though the mineral matter in coal distorts the peaks of the infrared spectroscopy analysis, the technique can still be used qualitatively to evaluate the components in the coal. These include surface moisture, volatile matter, macerals, and minerals (Speight 2005). The FTIR analysis of the binderless, optimal formulation, and PVA bound briquettes were crushed and analysed after being cured for 21 days. The powder was mixed at a 10 weight percent addition with potassium bromide, which was used as a background. The results are shown in Figure 3-5.

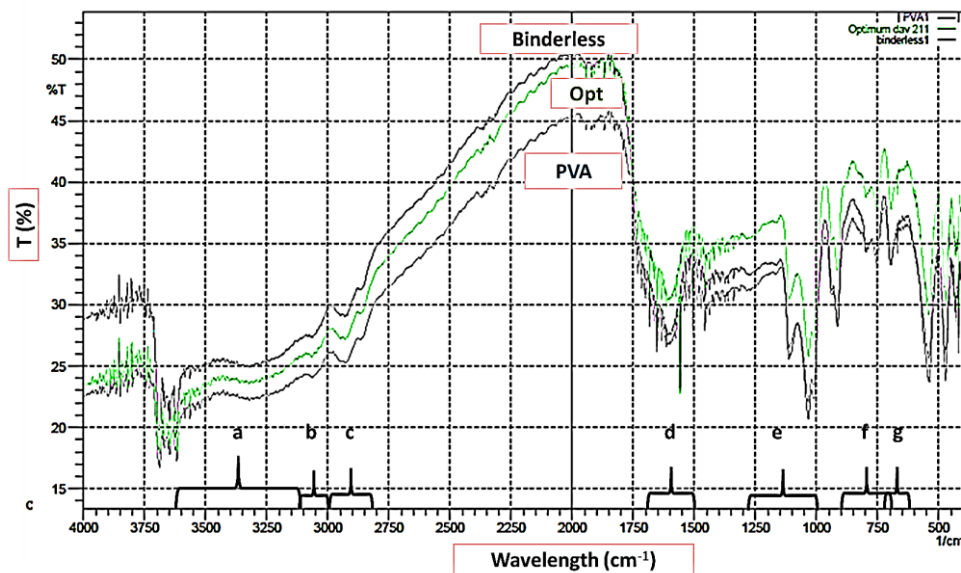


Figure 3-5: FTIR analysis of binderless, optimal formulation and PVA bound briquettes

The regions a – g represent vibrational characterizations, and these have been studied before for bituminous coals (Okolo et al., 2015). These ranges and their chemical functional groups are presented in Table 3-9.

Table 3-9: Characterisation of the surface functional groups per wavelength as adapted from Okolo et al. (2015)

Region	Characteristic group	Wavelength (cm ⁻¹)
a	OH stretching vibration	3600 – 3100
b	Aromatic C-H vibration	3100 – 3000
c	Aromatic C-H vibration	3000 – 2800
d	Aromatic C=C stretching	1680 – 1500
e	Aliphatic OH bending vibrations, skeletal C-C, C-O stretching	1280 – 1000
f	Aromatic C-H vibration	900 – 700
g	Long aromatic alkanes ((CH ₂) _n ; (n>4))	720 – 680

The results indicate insignificant differences in the oxygen functionality region (-OH, C-O, C=O, COOH) which was to be expected, due to the use of one coal in the final briquetting stage in this study. The binder addition only had the potential to raise the moisture content in this case, by 1.2 weight percent. This potential was eliminated once the briquettes were cured under the same ambient, climate controlled conditions, leading to near-equal moisture contents. The fraction of C-H bonding vibrations, and aromaticity regions were also insignificantly affected leading to the same conclusion that the binder at such low concentration insignificantly alters the character of the feed coal. This is corroborated by the proximate analysis of the briquettes, where the moisture, ash, and volatiles of the binderless and binder-bound briquettes showed no difference in comparison. This is due to the low amount of binder added, even at 5 weight percent addition of the poly-acrylic binder no differences were observed and the results are shown in Figure 3-6.

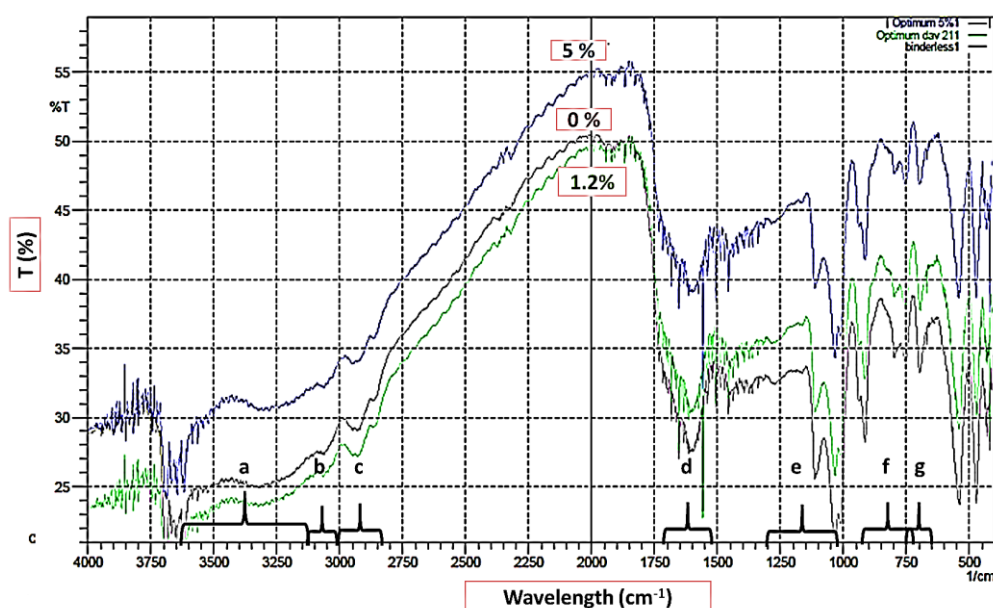


Figure 3-6: FTIR analysis of binderless, and the optimal formulation added in concentrations of 1.2 and 5 weight percent respectively

The briquettes seem to equilibrate after 21 days to the chemical functional groups, chemically similar to the feed coal. This could be due to the film forming nature of the binder that blends in easily with the other C-H and C=C as well as CH_n groups. After the poly-acrylic binder was evaluated at higher concentrations, and no difference was observed, the final analysis was undertaken to evaluate whether the chemically different species are not driven off during curing. This would result in differences between the day 0 and day 21 briquette. The results are shown in Figure 3-7 and the only notable differences were found in the regions shown in Table 3-10.

Table 3-10: Regions of differences in the briquettes after 0 and 21 days under ambient conditions, bound by the poly-acrylic binder at 1.2 weight percent addition.

Wavelength (cm^{-1})	Chemical functional group
4000 – 3750	OH stretching vibration
2450	Between CH_2 and C=O , COOH stretching vibrations
800 - 805	Aromatic nucleus CH bending vibration

All of the above wavelengths have within them a contribution to volatile matter or moisture content. This is congruent with the process of devolatilisation and the drying process during curing.

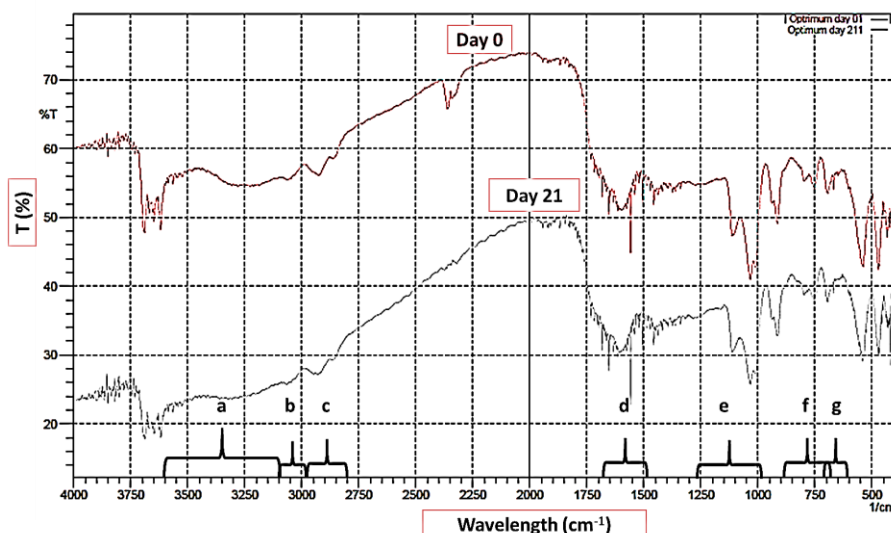


Figure 3-7: FTIR analysis of the optimal formulation briquette added in a concentration of 1.2 weight percent cured for 0 and 21 days respectively under ambient, climate controlled conditions

It is therefore concluded that the contributors to variation in surface functional groups are eliminated during curing. Curing is also, from these results, defined as a process of drying and removing some constituents of the binder as volatiles. It is proposed that the curing of the briquettes by loss of moisture and the unidentified volatile constituents within the C-H bending regions, are integral to the development of a strong briquette.

3.7 Briquetting

The coal-binder mixture or binderless feedstock was cold-briquetted using a Komarek B050 press. The mixture was added to a Kenwood mixer fitted to the press. It was operated at a speed setting of 40 revolutions per minute so that the polymer binder was not sheared. After ten minutes, the feed screw was switched on and operated at 80.0 ± 0.1 rpm. When enough material was fed, the rollers were started operating at 3.8 ± 0.1 rpm. The force applied to the coal from the rollers was set to 30 ± 0.5 kN. These settings were found to produce the most consistent briquettes. All briquettes produced during the course of this study were manufactured using the same settings. The briquettes were then cured under ambient climate controlled conditions at a temperature of 25°C and 40 percent relative humidity.

3.8 Analysis of the briquette

The poly-acrylic binder (PA) bound briquettes were analysed in their compacted form in terms of moisture, volatile matter, and ash yield. To compare how many voids were developed in the PA-bound briquettes, tomography was performed on the PA bound and binderless briquettes.

3.8.1 Proximate analysis

The formulations from the FED that were subjected to proximate analysis are presented in Table 3-11.

Table 3-11: Proximate analysis results of the whole briquettes

Run name	Addition	Weight percent			
		Moisture (Air dry)	Volatiles DB	Ash yield DB	Fixed carbon DB
Binderless	0	4.5	19	36	41
25%A 10% B 1.02% XL	0.4	4.4	20	36	39
25%A 10% B 1.02% XL	1.2	4.2	20	36	39
25%A 10% B 1.02% XL	0.8	4.3	22	35	38
25%A 10% B 0.03% XL	0.4	4.2	18	37	41
25%A 10% B 0.03% XL	1.2	4.1	18	38	41

From Table 3-11 it is evident that the briquettes, that have been left to dry in the climate controlled environment over a period of 14 days, show no significant difference in their proximate analysis properties. However, the ash-yield does differ from the coal-fines and binder mixture as shown in Table 3-8. The fines mixture reports an ash-yield of 25 – 26 percent whilst the whole briquette shows an ash-yield of 36 – 38 percent, and the whole briquettes have a lower amount of volatiles and moisture.

3.8.2 Tomography

Computational tomography or CT-scanning is a method of scanning that makes use of microwaves to produce a 3D scan of an object (Kalender, 2006). Due to the use of microwaves, this scanning type is density dependent. The denser the material the more waves will be absorbed to it, and the greater the difference between what was sent and what passed through (Wellington and Vinegar, 1987). These differences are called grey-values. The grey-values are specific for each density, for instance in coal, the grey value for mineral matter is much lower than that of voids which are essentially air pockets. Macerals however, have low densities that have to be identified as they are similar to voids. These grey values are called voxels and are plotted to assist in the selection of a grey value range. The CT-scan equipment at NECSA was used. The software

to analyse the scan was vgstudiomax30. Figure 3-8 is a depiction of the voxel plot and highlights the section chosen as macerals in the middle so that everything on the left of Interval 2 is a void or air, and everything on the right is mineral matter.

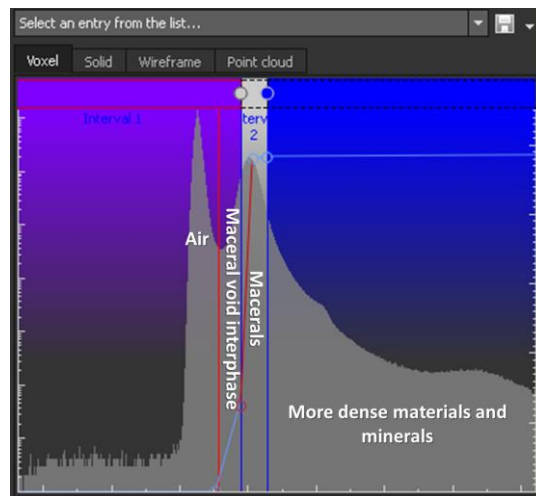


Figure 3-8: Voxel plot as presented in vgstudiomax30

This method determines many variables including pore-distribution, sphericity of pores, mineral matter distribution, and much more. Void volume or porous volume is the volume of air trapped within an object. These voids are dispersed as bubbles. The void volume was difficult to determine, and requires additional testing for briquettes so that a general pore volume could be estimated for briquettes made using the same method.

Tomography was done on briquettes from the poly-acrylic binder, as a way of determining the effect of concentration and composition of the binder. The void volumes and mineral matter were determined for the binder based and binderless briquettes. For this determination a total of four individual briquettes were scanned and a region of interest for each briquette was chosen. The region of interest was chosen between 7 – 8 mm in width, and 15 mm in length, spanning across the whole 10 mm thickness of the briquette. The region of interest was accepted to be large enough to represent both the porous volume and mineral matter throughout the briquette.

3.9 Briquette testing

The briquettes were tested in terms of mechanical strength by means of compressive strength, abrasion resistance, and water resistance. The briquettes were also tested for reactivity using thermogravimetric analysis (TGA).

3.9.1 Compressive strength

The compressive strength of the briquettes was tested using a Chatillon DFX2 force gauge. This gauge measured the maximum force applied to the briquette until it fractured providing a break force value in Newton. The uniaxial force was then converted into a pressure by dividing by the area of contact. The diameter for the tester used, was measured with a calliper to be 1.2 cm. The pressure one briquette could withstand was determined using Equation. 3.9.1 (Richards, 1990).

$$P(MPa) = \frac{F(N)}{A(m^2)} \times 10^{-6} \quad \text{Equation. 3.9.1}$$

The minimum acceptable value for this test as set out by Richards (1990) was 0.35 MPa.

3.9.2 Tumbler testing

A tumbler was designed according to the study by Richards (1990). The Richards tumbler had a diameter of 200mm a length of 270 mm and an inside lifter of 38 mm. A sample size of 1 kg was tumbled, for 100 revolutions at 50 rpm. The residue was screened on a 3mm mesh of which the percent oversize represented the percentage abrasive resistance. The minimum acceptable value for this test was given as 95 percent (Richards, 1990). The dimensions of the setup as used in the study by Richards (1990) were used to design a small scale version of the test, requiring a smaller sample.

Table 3-12: Tumbler design equation list

Equation or conversion	Equation number
$ID_{Richards}: L_{Richards} = \frac{100}{135}$	3.9.1
$ID_{new}: L_{new} = \frac{100}{135}$	3.9.2
$V_{Richards} = \frac{\pi D^2}{4} h = 8.73 \text{ m}^3$	3.9.3
$V_{new} = \frac{\pi r^2}{2} h = 0.149 \text{ m}^3$	3.9.4
$\frac{m_{Richards}}{V_{Richards}} = \frac{1 \text{ kg}}{8.73 \text{ m}^3}$	3.9.5
$\frac{m_{new}}{V_{new}} = \frac{x \text{ kg}}{0.153 \text{ m}^3}$	3.9.6
$N_c = 76.6 (ID^{-0.5})[rpm]; ID [feet]$	3.9.7
$1 \text{ m} = 3.2808399 \text{ feet}$	Conversion 3.9.1
$N = xN_c [rpm]$	3.9.8

For the tumbler a pipe with internal diameter of 52.0 mm was divided into eight pieces according to the ratio calculated in Equation 3.9.2. The length of one tumbler was calculated to be 72.3 mm. There was a lifter placed on the inside of the tumbler. The lifter was equal in length to the down-scaled tumbler. The width and thickness of the lifter, not being specified in Richards (1990), was taken as wide and thick as seemed sensible, 5 mm and 2 mm respectively in this instance.

The tumbler test described in Richards (1990) is similar in principle to an autogenous mill. For this reason, a parameter of critical speed was used to reduce the tumbler size. By taking a percentage (x , as seen in Equation 3.9.8) of the critical speed (N_c) calculated with Equation 3.9.7 in units of rpm; the same percentage could be applied to the miniature tumbler. The percentage of critical speed used by Richards was found to be 53%. The critical speed for the miniature tumbler was calculated as 185.8 rpm. The resulting required speed (N) to mimic the Richards tumbler was found to be 98.5 rpm.

The tumbler test described in Richards (1990) is similar in principle to a ball mill. For this reason, a parameter of critical speed was used to reduce the tumbler size. By taking a percentage(x , as seen in Eqn.3.9.8) of the critical speed (N_c) calculated with Eqn. 3.9.7 in units of rpm; the same percentage could be applied to the miniature tumbler. The percentage of critical speed used by

Richards was found to be 53 percent. The critical speed for the miniature tumbler was calculated as 185.8 rpm. The resulting required speed (N) to mimic the Richards tumbler was found to be 98.5 rpm.

The roller-shafts used in the tumbler were fitted with a Bongifoli variable speed controller. The maximum roller speed setting on the motor was set to be 50/60 units. This led to constraints in the maximum number of revolutions per minute that would be achievable on the motor. The weight of 8 tumblers on the shafts had to be considered a substantial load on the shaft. The maximum frequency of the motor was therefore set to 40 units. This frequency resulted in a revolution speed of 80 rpm. Richards applied a speed of 50 rpm to the tumbler for 100 revolutions, which resulted in minutes of tumbling time. The miniature tumbler would have been operated at 98.5 rpm for two minutes. Correcting for the slower revolution speed, the miniature tumbler was operated at 80 rpm for a duration of 197 revolutions. The resulting fines-briquette mixture was hand sieved on 6.7 mm and 4 mm sieves to determine the amount of coarse particles ($>6.7\text{mm}$), middle sized ($-6.7+4.0\text{mm}$), and fine material (-4.0mm) that was generated during the tumbling process.

3.9.3 Water resistance

For the water resistance test, one briquette was immersed in a container of water for 30 minutes (Richards, 1990). If the briquette could withstand 30 minutes of submersion it was removed and weighed. The difference in the mass before and after water submersion was defined as water retention and presented as a percentage. The briquette was then reintroduced to the water and weighed every hour to obtain the maximum water retention value i.e. where the mass of the briquette no longer changed. After 4 hours the briquette was removed from the water, weighed and tested on a Chatillon force gauge to evaluate the relative change in strength the briquette could endure after water submersion, which is defined as the wet-compressive strength (Modiri, 2016).

3.9.4 Reactivity analysis

The reactivity of the briquettes was tested in an in-house thermogravimetric analyser (TGA). The instrument consists of a Lenton tube reactor, heated via elements surrounding the tube, encased by a ceramic layer that serves as insulation. At the top of the furnace there is a gas-inlet, which allows the dry air to flow, through the sample holder to the bottom. The TGA has a heating rate limit of $10^{\circ}\text{C}/\text{min}$, at which point the risk of damaging the refractories become high, and a maximum temperature of 1400°C . Figure 3-9 is a depiction of the thermogravimetric analyser that was used in the study.

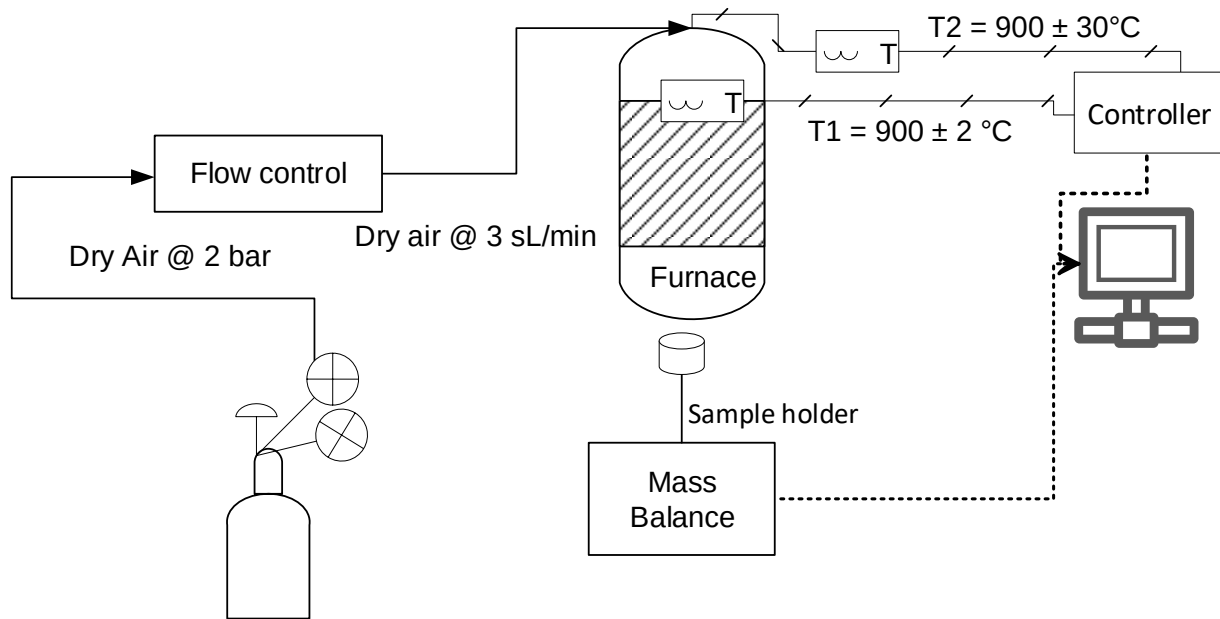


Figure 3-9: Thermogravimetric analyser setup

In the figure, where the gas cylinder is on the left, dry air is pressurised at 2 bar and allowed to flow to the Brooks flow control system. It passes through a mass flow control valve into the tube of the furnace, over a sample the weight of which is recorded by a mass balance. The temperature measured by thermocouple (T) is recorded as a signal. The signal is converted to a mA value and communicated to Visidaq studio® which stores it on a temporary log file on the computer. The mass reduces while the furnace is in operation and the mass is recorded via an Adams data logger. The temperature, mass and time are recorded at 2 s intervals for the duration of the experiment.

The thermogravimetric analyser was operated up to 900°C, since this was the temperature at which mass loss no longer became significant. This was determined from experiments for which the mass loss with temperature is presented in Figure 3-10.

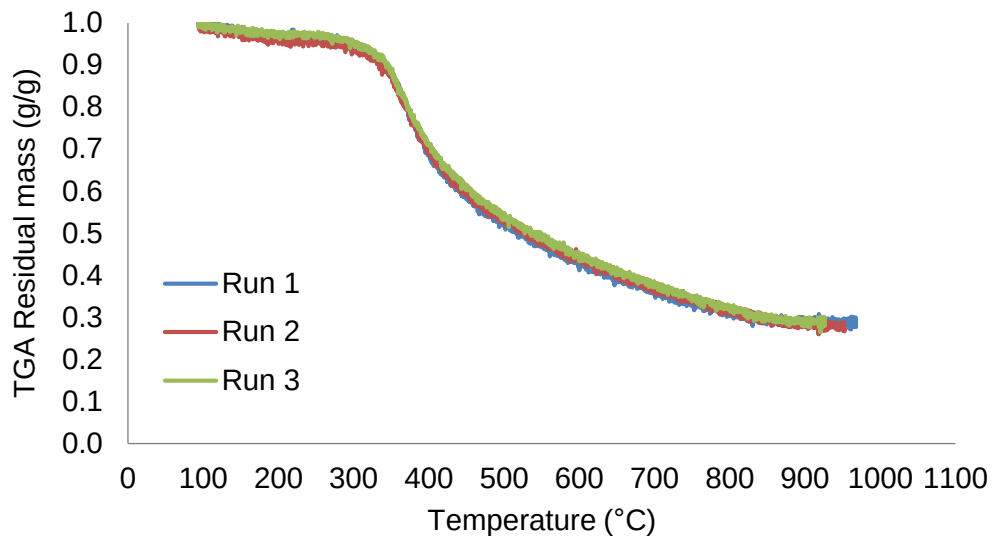


Figure 3-10: Temperature determination

Figure 3-10 is a representation of the repeatability of the thermogravimetric analyser, as the mass loss curves fall within the same bounds. The runs were done under a flow rate of 0.4 sL/min, a heating rate of 7°C/min and a final temperature set to 960°C. Also from this figure, total carbon burnout seems to occur between 850°C and 960°C. The mean was taken, and for this reason all other experiments were conducted up to 900°C. The heating rate was presumed to be too fast, since the curve does not clearly show the removal of moisture with binder or volatile components. The heating rate was subsequently lowered to 5°C/min to show the binder decomposition and evaporation effect on the curves.

Upon determination of the final temperature of 900°C, which corresponds to the final temperature used in Venter and Naudé (2015), a flow rate determination was required. Figure 3-11 is a depiction of the flow determination.

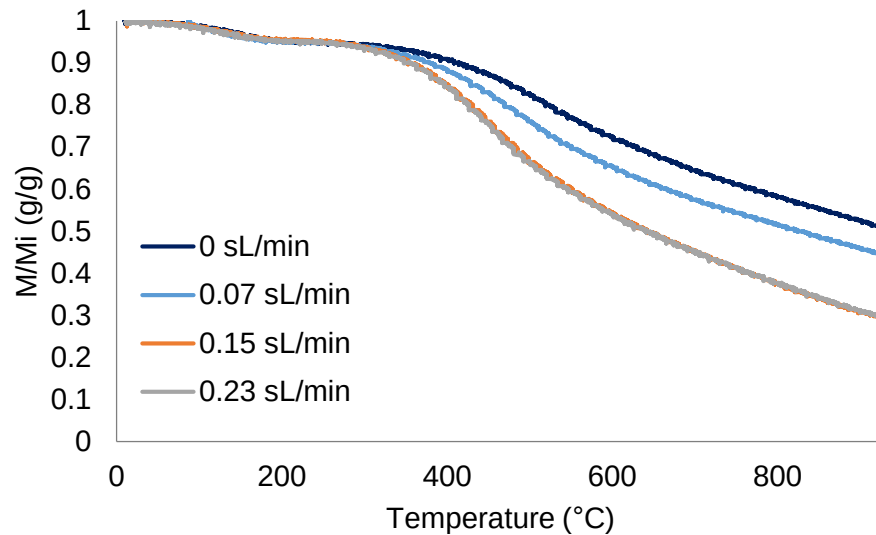


Figure 3-11: Flow rate determination up to 900°C and ambient pressure with a 5°C/min heating rate

From Figure 3-11, it is observed that the effect of gas flow has a decreasing effect on the combustion of the binderless briquettes, starting from a gas flow rate of 0.15 sL/min. Further calculation was done to determine whether this flow rate would be sufficient to combust the carbon in the coal completely. For the calculation of the actual flow rate the calibration curve shown in Annexure E was used. The air flow rate was calculated to be 0.15 sL/min, using interpolation. From the ideal gas law, the molar flow rate of air was determined to be 6.3 mole/min at 20°C and atmospheric pressure. From the molar relationship of oxygen in air, assuming constituents of N_2 and O_2 only, the molar flow rate of oxygen in the air was determined to be 1.3 mole/min.

From the ultimate analysis of Coal 1, it was found that the carbon content on a dry, ash-free basis, was 82 weight percent. It was assumed that this value was applicable to the whole of a 4.9 g briquette made from Coal 1. The amount of carbon in the briquette was determined to be 0.34 mole. The briquette does not react in one minute, but at 148 – 170 minutes depending on the heating rate, due to heat transfer limitations. The theoretical amount of oxygen required for the slowest and highest burnout rate are equal and was determined to be 0.002 mole/min. Therefore, the supply of oxygen at 1.3 mole/minute is much greater than the required supply. From this calculation and the negligent effect of flow rate on burn-out at 5°C/min, a dry air flow rate of 0.15 sL/min was deemed sufficient.

From Figure 3-11 it was observed that the combustion rate was very low. It was accepted that the limitation could not be oxygen supply from the determination of flow rate. The limitation was

therefore accepted to be due to the heating rate. The heating rate was therefore varied and the effects observed are depicted in Figure 3-12.

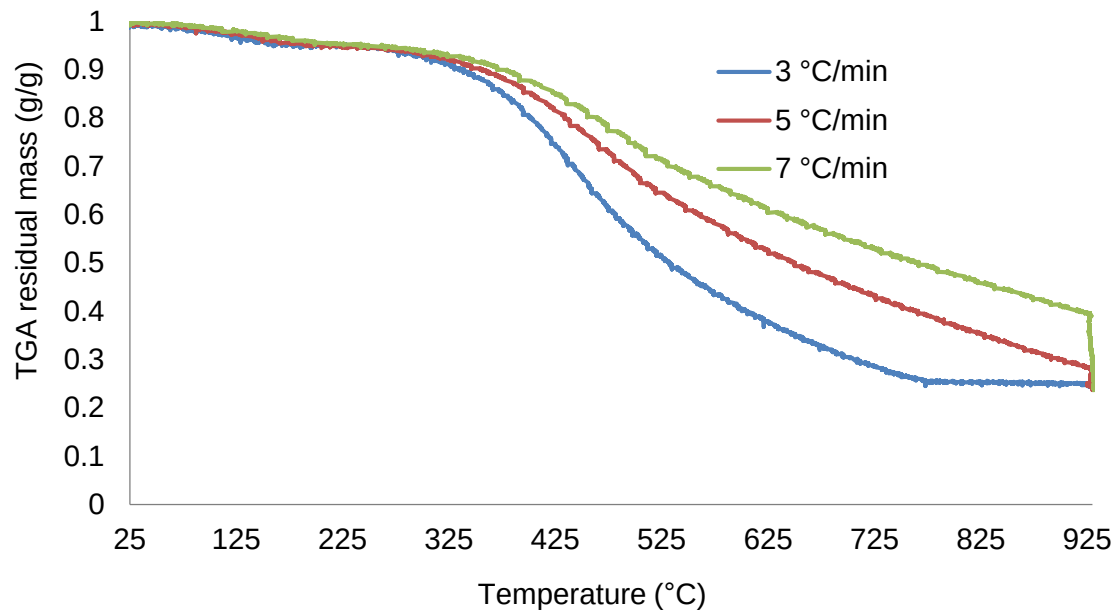


Figure 3-12: Heating rate determination

From Figure 3-12 it was observed that carbon burnout is dependent on heating rate. This could be due to the increased effectiveness of conduction in the briquette at lower heating rates. Leading to the conclusion that larger particles may require lower heating rates. For this reason, 3 °C/min was used as the final heating rate.

The briquettes were therefore tested in terms of mechanical strength using the tests described by Richards (1990) and Modiri (2016) as well as Venter and Naude (2015). Reactivity testing was done using thermogravimetric analysis at 3°C/min and 5°C/min up to 900°C, using dry air at 0.15 sL/min. The results of the mechanical and combustion tests are provided in Chapter 4 and Chapter 5 respectively.

CHAPTER 4 MECHANICAL RESULTS

4.1 Binderless briquette strength

The comparison of the compressive strength to the reactive macerals (percent) of the coals used in the briquetting of the binderless briquettes from Mangena et al (2007) shows that the two coals behave similarly to other bituminous coals from the same region. This is depicted in Figure 4-1.

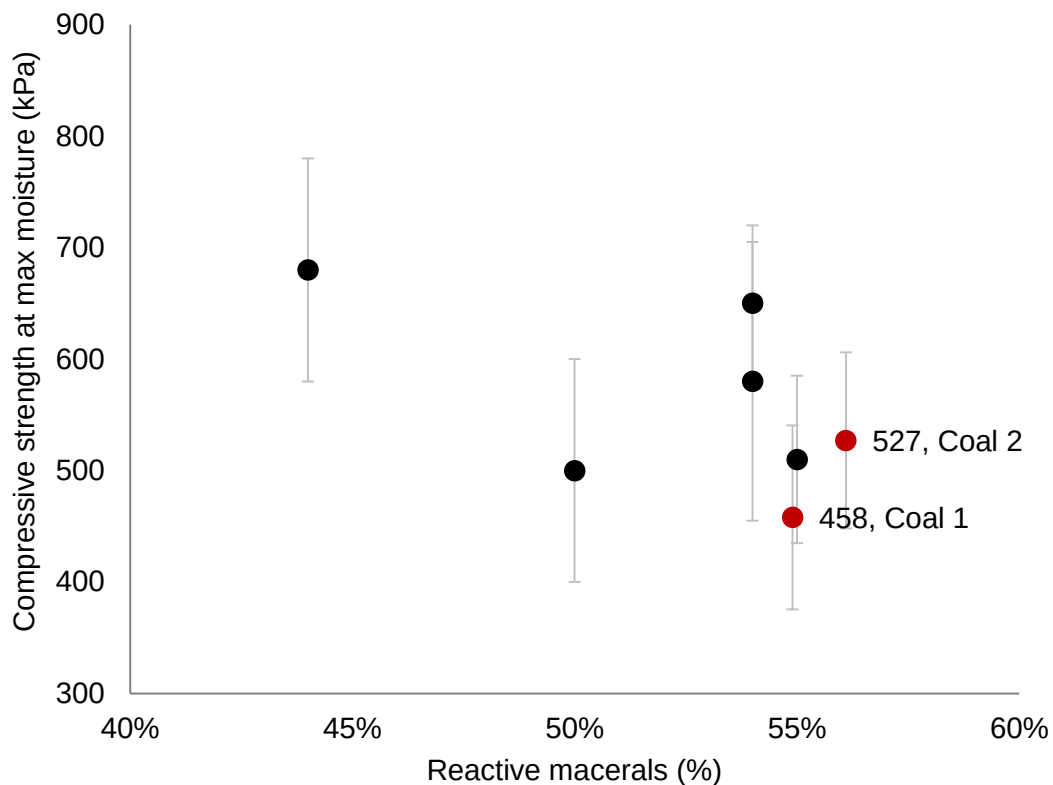


Figure 4-1: Compressive strength comparison with respect to percent reactive macerals

From the figure it is also observed that Coal 2 has a higher binderless compressive strength than Coal 1. The reactive macerals content in Coal 2 is 3 percent higher than in Coal 1 and is largely attributed to a 2.6 percent higher vitrinite content as is seen in Table 3-6 in Section 3.3. It is considered that Coal 1 has been oxidised to a greater extent due to its higher total moisture. The increased vitrinite content has an increasing effect on the plasticity of the coal-briquette (Mangena and du Cann, 2007, Modiri, 2016). While vitrinite is beneficial, the clay mineral kaolinite is known to be the main component to attribute to the coal-briquette plasticity (Mangena and du Cann, 2007). From Table 3-5, in Section 3.3, Coal 2 contains 6 percent higher kaolinite content than

Coal 1 (17.0 percent and 10.9 percent respectively). The increased kaolinite and to a lesser extent vitrinite content in Coal 2 resulted in it having a 69 kPa compressive strength increase.

Tomography analyses using the region of interest as shown in Figure 4-2 were conducted on the binderless briquettes of Coal 1. The volume of the voids between the particles is shown on the left of the figure, ranging from largest at the top to smallest at the bottom.

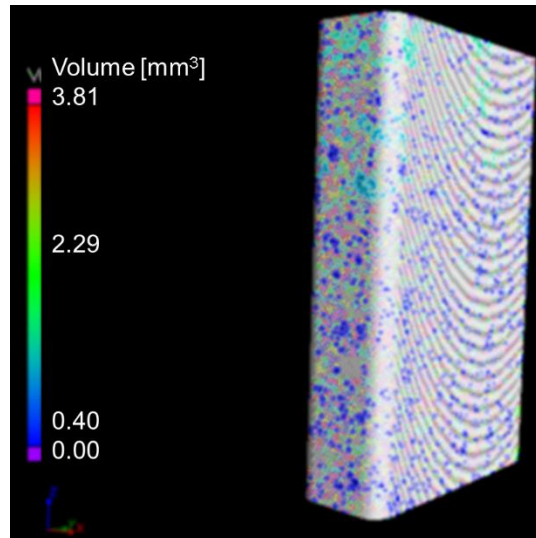


Figure 4-2: Region of interest for a single binderless briquette

The binderless briquettes, in the region of interest (ROI) chosen, were filled with voids of a maximum volume of roughly 4 mm³, of which the majority of the voids were between 0.4 – 1.1 mm³, because of the prevalence of the blue colour scale within the ROI.

This method produced relatively repeatable results, considering the heterogeneity between individual briquettes from the same batch. The repeatability of the results is depicted in Figure 4-3 below.

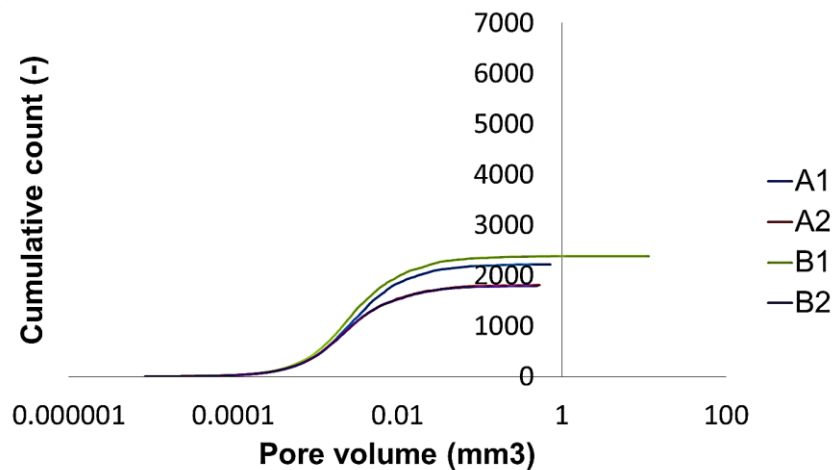


Figure 4-3: Repeatability of the tomography method

From the figure it can be seen that the briquettes have more or less the same amount of pores. However, choosing similar sized regions of interest could have led to the inclusion of cracks that were present in the briquettes due to the method of roll-compaction. This can be offered as an explanation as to why briquette B1 had larger sized voids, and B2 had fewer voids compared to the others. The prevalence and span of the crack is shown in Figure 4-4.

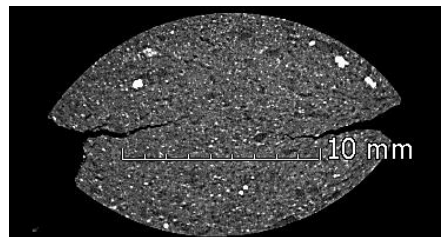


Figure 4-4: Resulting crack from the roll compaction method for producing a binderless briquette – top view

Figure 4-4 shows the top view of the three dimensional briquette. From the figure it is observed that the crack does not infiltrate deeper than the first 4 mm on either side of the briquette.

The crack was prevalent from top to bottom to a limited extent and the side view of this briquette. The scale on the left of Figure 4-5 now only shows the minimal and maximal pore volumes for the side of the briquette and not for the whole 3D region of interest as depicted in Figure 4-2.

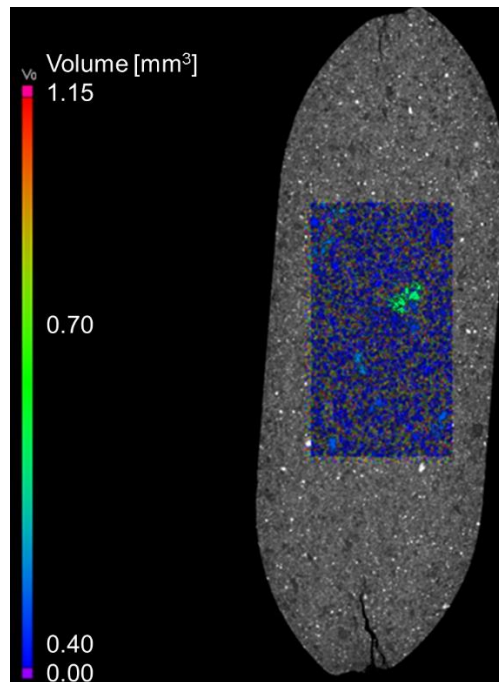


Figure 4-5: Resulting crack from the roll compaction method for producing a binderless briquette – side-view

From the figure it is seen that the greatest pore volume on this side of the briquette is around 1.15 mm^3 , and from the colouring of the image it is seen that most of the voids on this side, are in the range of $0 - 0.23 \text{ mm}^3$. It also has a visible weak spot on the side with voids in the range of around $0.46 - 0.69 \text{ mm}^3$.

4.2 Binder composition and development

Different binders were produced from the proposed components in Michailovski and Cilengi (2016). A poly-acrylic polymer was added to a polyacrylamide, and these polymers were cross-linked with a formaldehyde component. The ranges for the Component A were between 25 – 40 percent, while Component B was added between 10 – 25 percent. Finally, the cross-linking additive was added in ranges of between 0.03 and 2 percent, this was done after each component was individually hydrated with water, so that the hydrated mixture totalled to 100 percent. The component names and ranges are depicted in Figure 4-6.

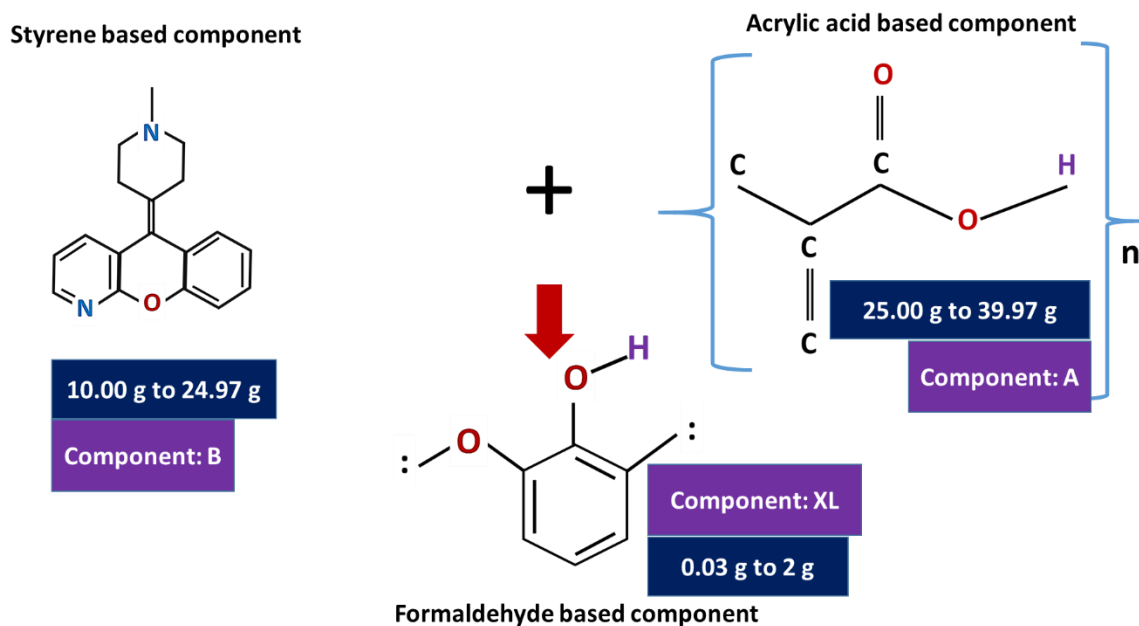


Figure 4-6: Binder development summary

These ranges were incorporated into a statistical design software package in which a D-optimal design was developed. The design was done to assist in the development of the experimental plan in which there were three independent variables (components A, B, and XL), and one dependent variable (compressive strength). The condensed design (where the duplicate runs are indicated as multiple run numbers) is presented in Table 4-1 in order of increasing component a content. The full set of results are available in Annexure H.

Table 4-1: Condensed D-optimal design with increasing component A and day 0 and day 21 compressive strength, with a standard deviation uncertainty

Run numbers	A	B	XL	H ₂ O	A/(A+B+XL)	Day 0	±	Day 21	±
8;10;16	25	10	0.03	65	71%	0.37	0.1	0.67	0.1
30;31	25	10	1.02	64	69%	0.40	0.0	0.90	0.2
1	25	10	2.00	63	68%	0.40	0.0	0.90	0.2
36	25	17	2.00	56	57%	0.40	0.0	1.00	0.2
13	25	17	1.02	57	58%	0.40	0.0	0.80	0.1
20;21	25	18	0.03	57	59%	0.40	0.1	0.70	0.1
5;6;27	25	23	2.00	50	50%	0.45	0.1	0.95	0.3
18	25	24	1.02	50	50%	0.43	0.1	0.86	0.1
12;38	25	25	0.03	50	50%	0.40	0.0	0.70	0.1
3	27	16	0.52	56	62%	0.40	0.0	0.70	0.1

11	27	12	1.51	58	66%	0.50	0.0	0.80	0.0
34	27	19	1.51	52	57%	0.40	0.0	0.70	0.0
9;29	30	15	1.02	54	65%	0.50	0.0	0.80	0.1
37	31	12	0.52	56	71%	0.40	0.0	0.90	0.2
19	32	17	2.00	50	63%	0.40	0.0	0.80	0.0
24	32	10	2.00	57	72%	0.40	0.0	0.70	0.0
14	32	10	1.02	57	74%	0.50	0.1	0.90	0.1
22	32	17	1.02	50	64%	0.40	0.0	0.70	0.0
17;33	33	10	0.03	58	76%	0.50	0.1	0.75	0.1
4;15	33	18	0.03	50	65%	0.45	0.0	0.75	0.1
8	34	12	1.51	52	71%	0.40	0.1	0.70	0.1
28.;32	38	10	2.00	50	76%	0.45	0.0	0.75	0.1
2	39	10	1.02	50	78%	0.50	0.0	0.80	0.1
7;23;25;26	40	10	0.03	50	80%	0.43	0.1	0.95	0.2

From the table it can be seen that the maximum green strength value for the briquettes resulting from the investigated formulations is 0.5 MPa, and the maximum attainable dry strength (day 21) value for the formulations is 1 MPa and the maximum attainable compressive strength for a cured briquette (day 21) is 1.00 ± 0.2 MPa. The binderless briquettes for Coal 1 remained at a compressive strength of 0.45 ± 1 MPa for the duration of the 21 curing days.

From this table it was evident that the briquette formulations all yielded results within the same range which was especially true for experiments with similar amounts of component A and cross-linker (XL). The stronger briquettes either contained less water, or more component A. From the table optimum selection was based on the strongest briquettes over a various amount of days as shown in Table 4-2.

Table 4-2: Optimum selection

Formulation number	% Improved						
	A (%)	XL (%)	Day 1	Day 2	Day 7	Day 14	Day 21
1	25.00	2.0	20	90	70	100	90
2	31.00	0.52	20	120	80	100	80
3	40.00	0.03	40	70	75	95	90

From Table 4-1 three main formulations were observed to be the strongest. The formulation that was selected (Optimum number 3) and consisted of 40% component A 10 percent component B and 0.03 percent cross-linker (XL). This was the formulation for runs 7; 23; 25; and 26. It was selected based on two reasons, firstly it increased in strength twice as much as the other formulations on day 1. This is beneficial, since a briquette that can be used sooner, is better than briquettes that have to cure longer. Secondly, because it produces briquettes that increase in strength from day 1 until they reach maximum compressive strength on day 14. In addition, the formulation is comparably strong to the other three formulations on a day 21 basis.

After an optimal binder formulation was chosen, two other formulations were chosen for screening purposes, one with a minimal strength and the other with a maximal strength value on day 21. The only difference between the two screening formulations was the amount of cross-linker. The main formulations for further studying the performance of the patented compounds were therefore chosen according to the relative amount of component A in the column $A/(A + B + XL)$.

Table 4-3: Formulations selected for further study

Run numbers	A	B	XL	H2O	$A/(A+B+XL)$	Day 0	±	Day 21	±
30;31	25	10	1.02	64	0.69	0.40	0.0	0.90	0.2
8;10;16	25	10	0.03	65	0.71	0.37	0.1	0.67	0.1
7;23;25;26	40	10	0.03	50	0.80	0.43	0.1	0.95	0.2

In Table 4-3, it was observed that two formulations, which are the formulations for runs 30, 31 ($0.69 A/(A+B+XL)$) and 8, 10, 16 ($0.71 A/(A+B+XL)$) are very similar with the exception of cross-linker amount (XL). Despite the similarity they produce significantly different compressive strengths over 0 and 21 days. This was initially thought to be solely due to the significant increase of the cross-linking additive. However, when the cross-linker amount was the only varying parameter, the significance of its contribution to compressive strength was questioned. Furthermore, runs 8, 10, and 16 were also weaker on day 0, which could indicate a relation to the briquette formation, rather than the binder added. This result was validated through the tomography results which indicated that of the binders studied (and in comparison to the binderless runs) briquettes made from the 25 percent A, 10 percent B and 0.03 percent XL formulation contained considerably more voids as shown in Figure 4-8. The cross-linker was set as the only varying parameter in the 2/3 A to B ratio in Coal 2. These results are shown in Figure 4-7.

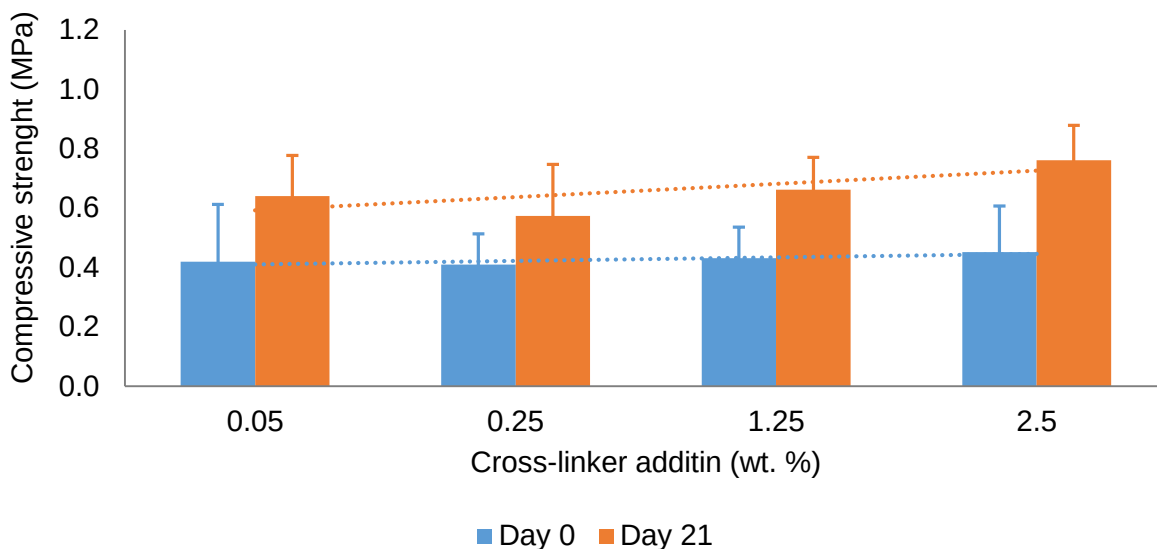


Figure 4-7: Cross-linker addition variation of the standard formulation in Coal 2

The results indicate an increase in compressive strength from day 0 to day 21. It also reflects close to constant day 0 results for all cross-linker variations, and shows an insignificant increase in compressive strength on day 21 between the various cross-linker additions.

This brings about the conclusion that the variation in cross-linker content alone could not be responsible for yielding briquettes with compressive strength differences up to 30 percent. Other factors include the non-uniform distribution of clays (specifically kaolin at 17 percent in this coal) and pyrites between the two batches of coals as a contributing factor.

The formulations in Table 4-3 were compared to each other on a mechanical strength basis in terms of briquette compressive strength, abrasion resistance, and water resistance. The formulation performance was then compared to that of a binderless briquette as well as PVA bound briquettes.

Tomography analyses were also conducted on the poly-acrylic bound briquettes to evaluate the formulation's effect on the briquettes on a qualitative basis. After the tomography results for the binderless runs were deemed comparable, the effect of binder concentration was considered. The formulation considered was made up of 25 percent Component A, 10 percent Component B, and 0.3 percent cross-linker by weight. The results are depicted in Figure 4-8.

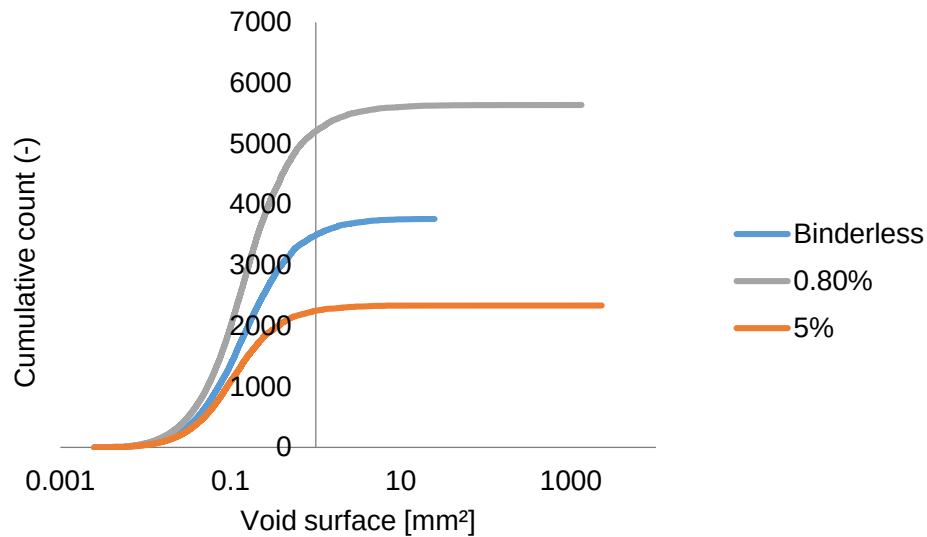


Figure 4-8: Void surface distribution of briquettes with increasing concentration of 25 percent and 0.3 percent cross-linker

From Figure 4-8 it is observed that the 5 percent binder to coal addition produces the lowest amount of voids, but that both binder bound briquettes produce voids in the same order of magnitude. The binderless briquette contains a moderate amount of voids, with a smaller volume than the binder bound briquettes. The size of the voids could be attributed to the moisture evaporated from the briquettes after the 14-day curing period all of the briquettes were subjected to. The binder is made up of components that dehydrate easily at ambient conditions, so that likely, while forming, these voids were filled with moisture and binder until it evaporated to form them. The larger voids could also be as result of the collapsing of smaller voids due to a lower density material being fed into the rollers. The 5 percent binder to coal addition with its low amount of voids could be explained by binder-void clogging. Since the binder becomes sticky while drying it is possible that it pulls more coal particles into void spaces, as it shrinks from the dehydration during curing. This would account for the low amount, but greater size of the voids. Figure 4-9 is a depiction of the top-view of the briquettes with increasing concentration.

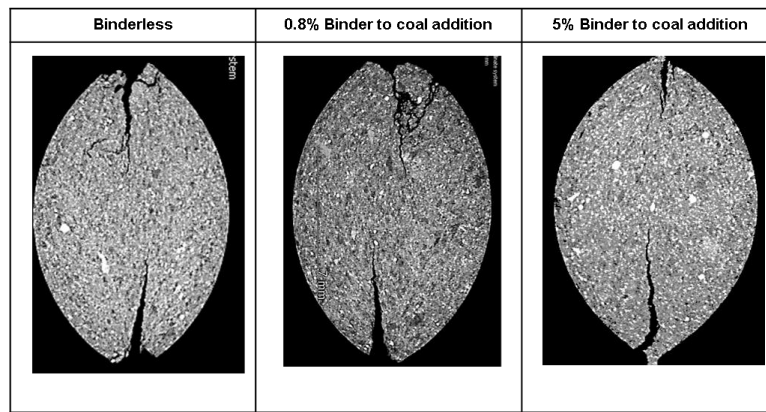


Figure 4-9: Depiction of briquettes with increasing concentration of 25 percent and 0.3 percent cross-linker

The binderless and 5 percent binder to coal addition (by weight) seem very similar, except that the 5 percent binder to coal addition briquette has an elongated and slightly narrower crack than the other two briquettes. It also seems more densely distributed. The 0.8 percent binder addition, while not only having a crack as deep as that of the binderless briquette, is potentially more porous and subsequently more brittle due to the large amount of dislodged material in the region of the upper crack. Three further formulations were prepared for tomography analysis in a 0.8 weight percent binder concentration amount. These were Component A only, and a randomly chosen 25 percent A, 10 percent B, and 0.03 percent cross-linker, as well as 27.3 percent A 16 percent B, and 0.52 percent XL, to attempt to determine the effect of 0.03 – 0.52 percent amounts of cross-linker on the void prevalence of the briquette. The results are shown in Figure 4-10.

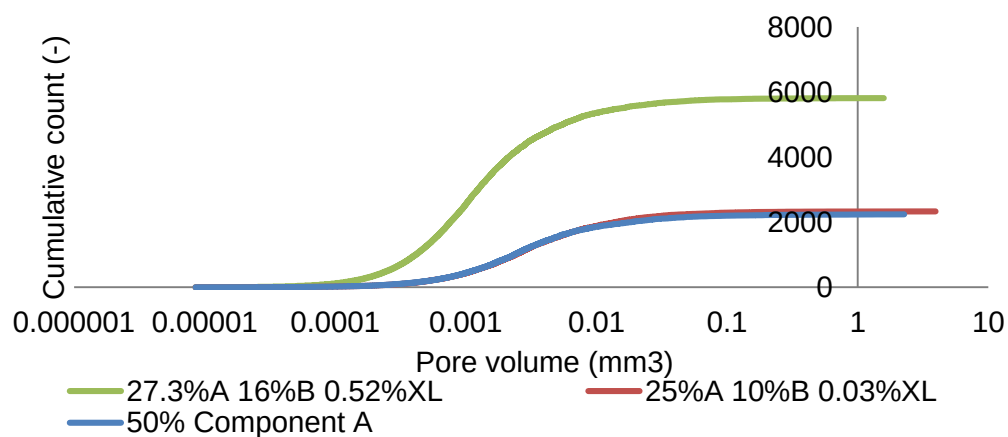


Figure 4-10: Pore surface distribution of briquettes with varying formulation

A formulation with 50 percent component A would have consisted of 50 percent water by weight, while a 25 percent A, 10 percent, 0.03 percent XL)-formulation consists of 65 percent water and

a formulation containing 27.3 percent A, 16 percent, 0.52 percent)-formulation contains 56 percent water. The 50 percent component A containing formulation has the lowest amount of water added, and it is subsequently seen to be a more free-flowing component, which when diluted with water, will disperse easily. This then explains why the more hydrated component, which is more dispersible, is comparable to the free-flowing binder that is Component A alone. This improved dispersion could improve mixing, which in turn reduces the amount of dehydrate-able material that accumulates in various air pockets of the coal to form voids once the briquette is cured. Instead of coal particles enveloped by free-flowing binder, filling the air pockets themselves, and sticking to the surrounding particles through the adhesion effects of the binder.

4.3 Compressive strength

Compressive strength testes were used to evaluate the time it took the briquettes from the poly-acrylic (PA) based formulations to reach maximal strength. The results for the three formulations are presented in Figure 4-11.

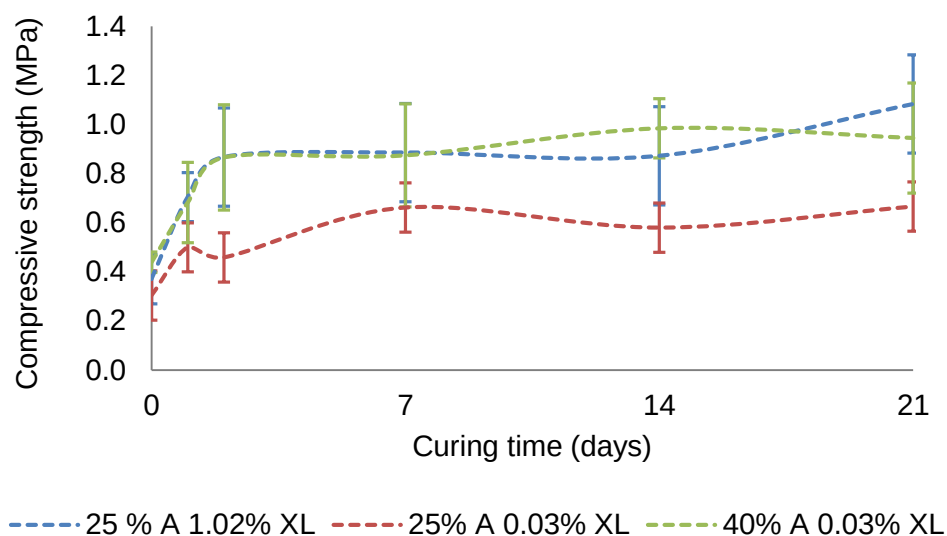


Figure 4-11: Curing profile of the poly-acrylic based formulations at 0.8 weight percent binder to coal additions

From Figure 4-11 it is seen that briquettes from formulations with larger amounts of Component A have greater compressive strengths over 21 days compared to a minimal amount of Component A. Comparing the two briquettes from these formulations with varying amounts of cross-linker only, it is seen that the addition of a greater amount of cross-linker could increase a formulation with minimal amounts of Component A to compressive strengths of formulations with maximal amounts of Component A. The formulations were added in 0.8 weight percent binder addition.

The three formulations were compared to the industry standard binder, PVA, as well as the binderless briquettes, where the binderless briquette compressive strength was used as a lower limit. The results are shown in Figure 4-12.

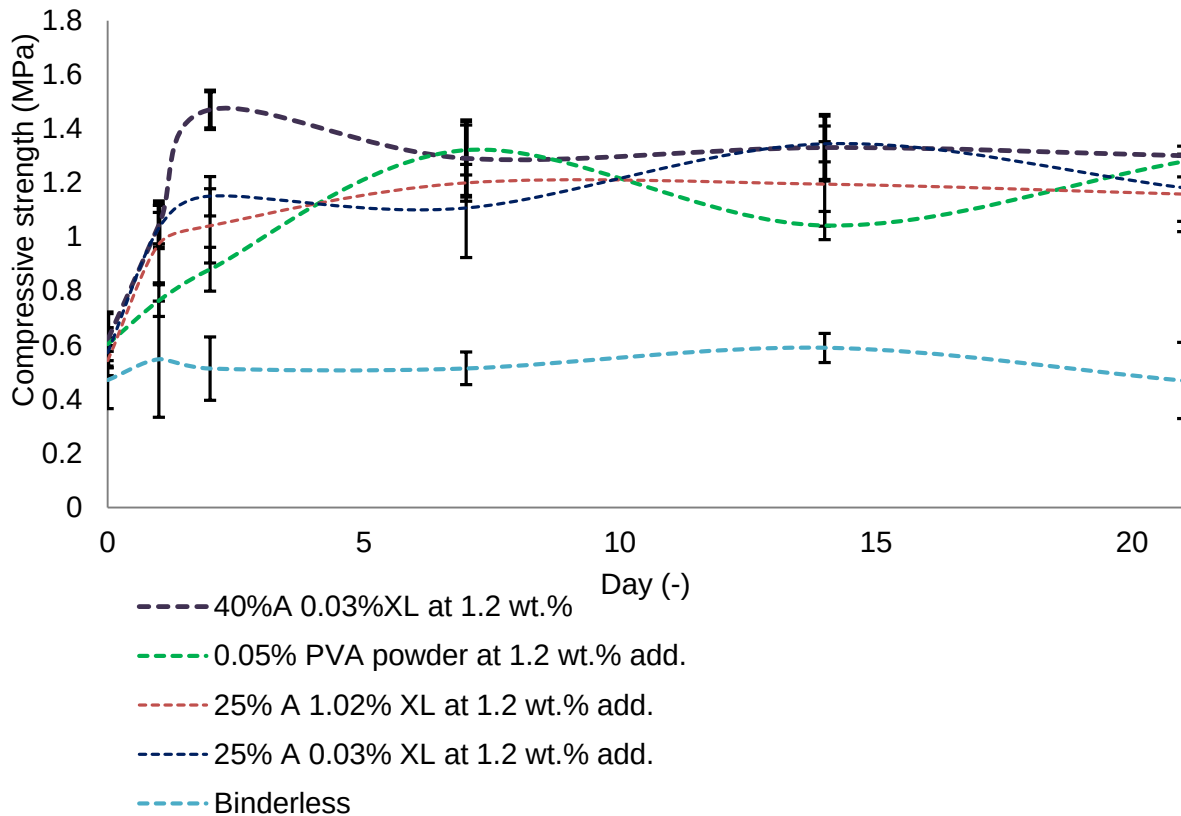


Figure 4-12: Curing profile comparison (lower limit)

From Figure 4-12 it is observed that the binderless briquette compressive strength is consistently lower than the other formulations, including PVA. PVA, unlike the poly-acrylic based formulations obtained its maximum strength on day 7. However, the poly-acrylic (PA) based formulations become stronger much sooner, and reach strengths comparable to their maximum on day 2. On day 2 PVA is still relatively weak compared to the others. According to Richards (1990) a compressive strength of 0.38 MPa allows for transport of the briquettes. In this case all briquettes, including the binderless briquettes qualify against this guideline.

Further comparison to PVA showed that the PA binders produce briquettes which were comparable to PVA in terms of compressive strength. This could mean that these PA formulations could also be used for industrial applications, based on their compressive strengths alone. The

briquettes were compared to lump coal pieces in terms of compressive strength. This comparison is shown in Figure 4-13.

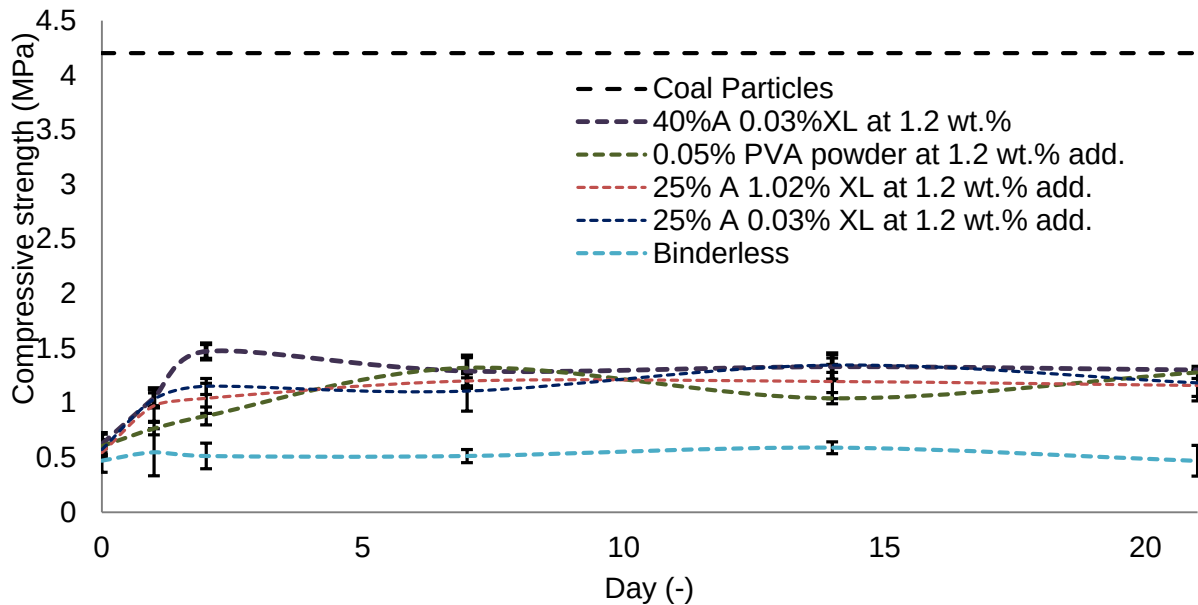


Figure 4-13: Curing profile (upper limit)

From Figure 4-13 the briquettes are observed to be much weaker than particles from the parent coal. It can therefore be expected that briquettes will not be as strong as naturally formed coal particles.

Coal briquettes made from organic polymer binders need to be cured for a minimum of 14 days to reach maximal compressive strength values. Furthermore, PA briquettes increase in strength much sooner (within 2 days) than for PVA. Due to their comparability to PVA over 21 days on a compressive strength basis, these formulations could be viable for use in industrial applications. Finally, for all formulations the briquettes are much weaker than coal particles larger than 6 mm from the parent coal.

For the briquettes to be affordable, the concentration of the formulation to coal needs to be low. For this study the binder addition to coal was kept between 0.4 – 1.2 weight percent, and not the industrially used 5 weight percent. The briquettes made from the three chosen PA formulations, PVA, and the binderless briquettes were compared. These results are shown in Figure 4-14.

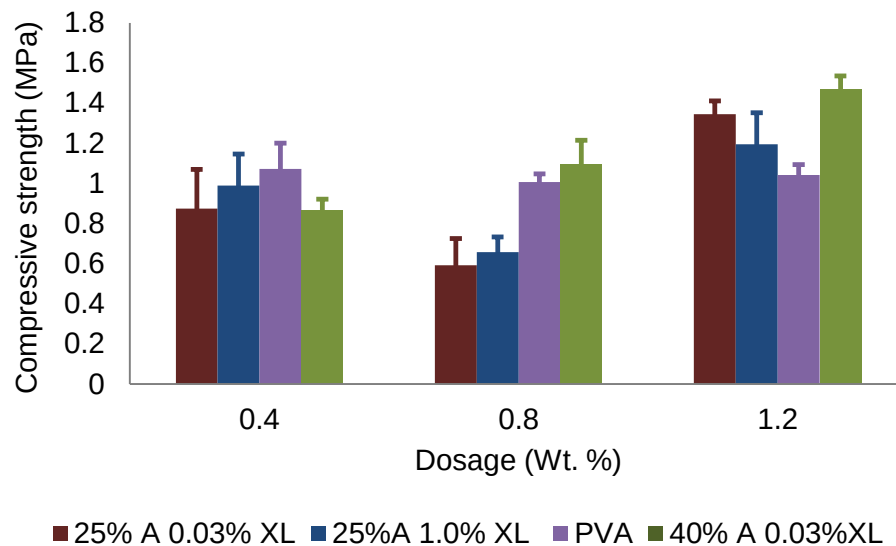


Figure 4-14: Concentration effect on day 14

From Figure 4-14 the optimal concentration can be defined as the concentration where a formulation has a greater compressive strength than that of PVA. For the optimal formulation (40 percent a 0.03 percent XL) this concentration is at 0.8 weight percent. For both alternative formulations, the optimal concentration was found to be 1.2 weight percent. Even though PVA remains the binder that can be added in the lowest concentration (0.4 weight percent); the other formulations compare marginally well with PVA at this concentration. The optimal formulation at a concentration of 1.2 weight percent produces briquettes that are much stronger than the other formulations, and PVA, on a day 14 basis. From these results for the PA briquettes, as well as for PVA, the compressive strengths are also marginally similar across all three concentrations. It can therefore be concluded that the concentration range is somewhat narrow to make definite conclusions regarding binder uptake for the first coal.

Coal 2, however, showed binder uptake in the larger binder addition range. The second coal was tested with the 2/3 A to B ratio formulation. The binder was added in concentrations between 0.27 to 3.2 weight percent. The results are shown in Figure 4-15.

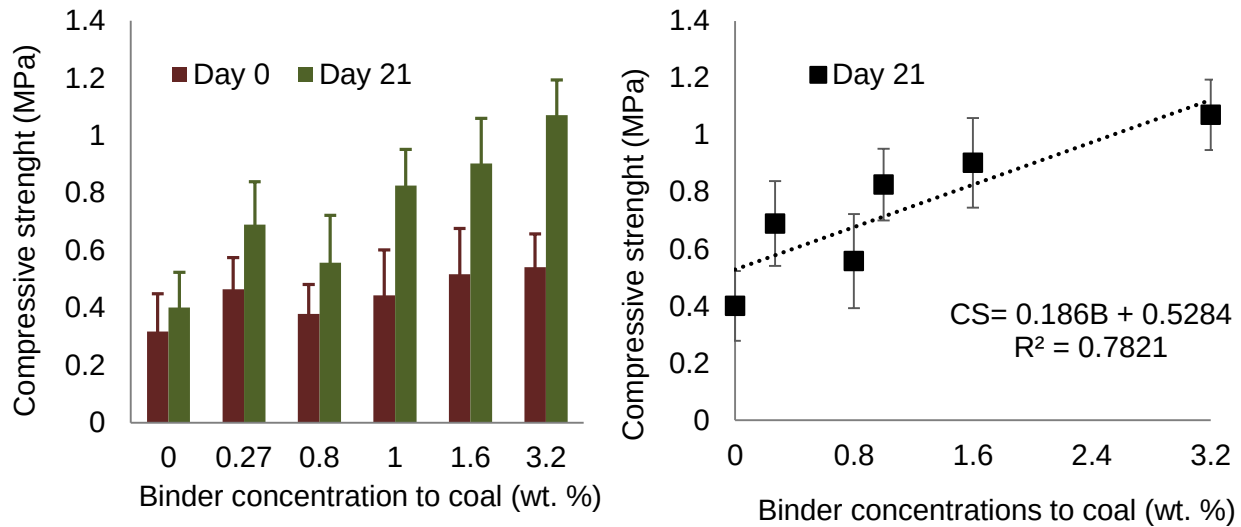


Figure 4-15: Concentration effect for Coal 2 on day 0 and 21

From Figure 4-15 it is seen that the compressive strength increases from day 0 to 21. The increase is much greater for briquettes with higher binder additions. The day 0 results are very similar to each other and the binderless briquettes (0 weight percent), especially when considering uncertainty. The results for day 21, for the binder additions of 0.27 - 1 weight percent, are very similar. This is what is also observed in Coal 1 in Figure 4-14 on day 14. These are comparable to each other, since the curing profile plateaus from day 7 as shown in Figure 4-12. The compressive strength results only show significant improvement after 3.2 weight percent binder addition. From Figure 4-15 the binder is expected to follow a linear relationship in terms of addition to compressive strength. The 0.8 weight percent binder addition is observed once more to be an outlier. This is true for both coals, anomalous behaviour for this binder was attributable to mixing-limitations.

Compressive strength can be a good indication of the quality of the briquette. This is mainly because the resistance of the briquette towards breakage is widely reported in terms of compressive strength. Abrasion resistance, in turn, is a good indication of how a briquette would perform under situations of tumbling and friction.

4.4 Abrasion resistance

In terms of abrasion resistance, the amount of fines generation is reported against the concentration of the different formulations used in briquetting the coal fines. Richards (1990) predicted that a 5 weight percent fines generation is a good target value. The fines generated on the day of optimal compressive strength is presented in Figure 4-16.

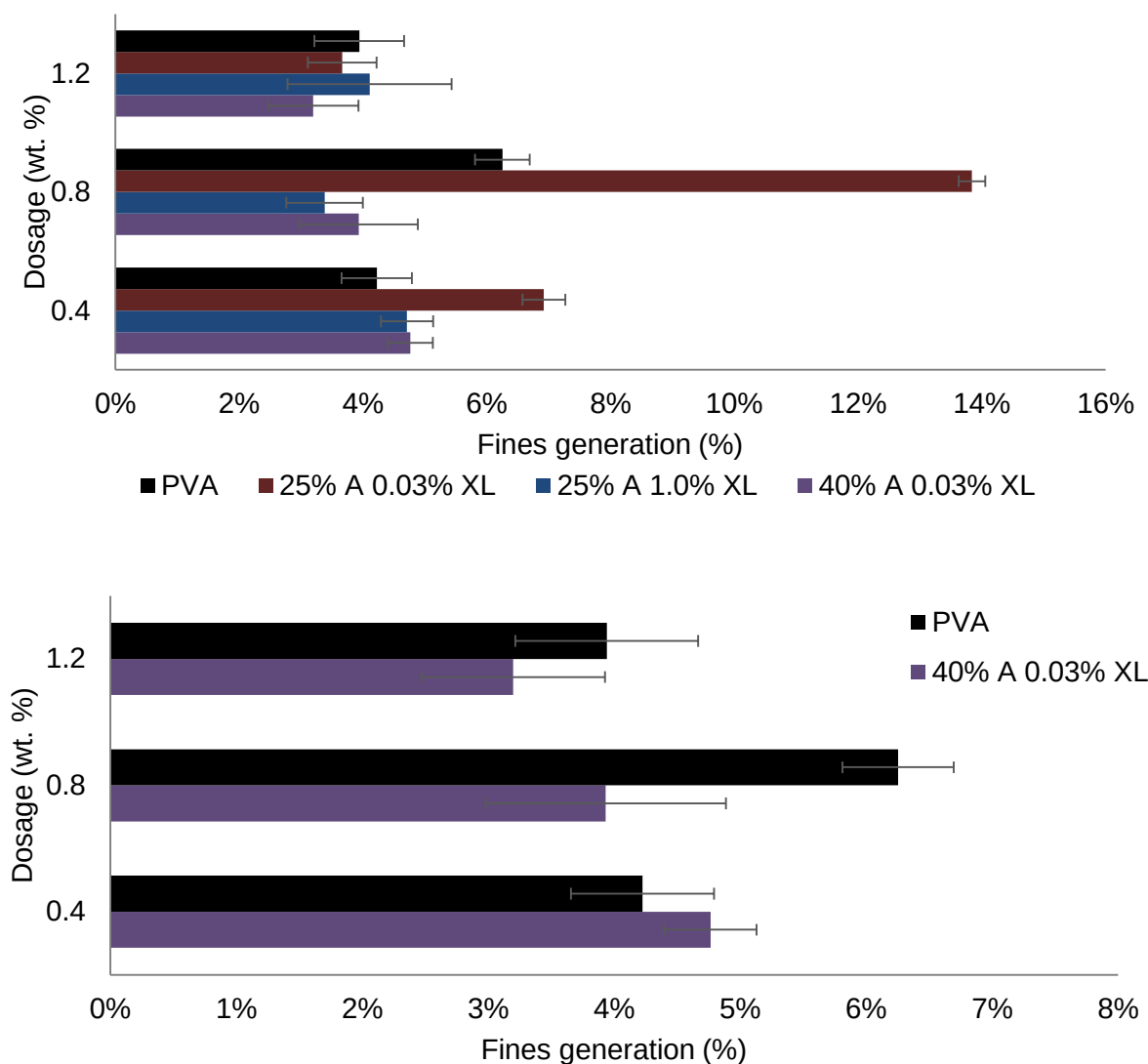


Figure 4-16: Fines generation on day 14

From Figure 4-16 it is observed that optimum and 25 percent A with 1.02 percent XL formulations perform better or comparably well to PVA along all concentrations by producing similar or less fines. At the optimal concentration (1.2 weight percent binder to coal addition) the poly-acrylic formulations produce amounts of fines that meet the 5 weight percent upper limit. PVA generally produces less fines, except at the 0.8 percent binder to coal addition, which produces anomalous results in both abrasion resistance and compressive strength. This decreased mechanical durability at the 0.8 weight percent binder addition is consistent for all except where the cross-linker amounts are increased. The cross-linker could therefore have a possible enhancing effect in terms of binder performance.

4.5 Water resistance

The low dosage briquettes could not be subjected to wet compressive strength tests as none of the formulations could withstand 30 minutes of water submersion. For each formulation the briquettes disintegrated completely within 1 minute of submersion. This result was obtained for all formulations including PVA. The process of disintegration is shown in Table 4-4 and Table 4-5.

Table 4-4: Briquette disintegration process during water resistance test

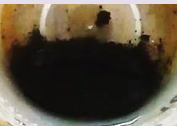
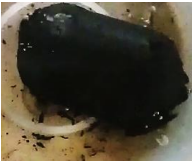
Time (s)	Binder formulation				
	Binderless	25%A 0.03%XL 0.4 % add.	25%A 1.02% XL 0.4 % add.	25%A 0.03 % XL 1.2 % add.	25%A 1.02%XL 1.2 % add.
0					
2					
5					
10					
20					
60					

Table 4-5: Briquette disintegration process during water resistance test continued

Time (s)	Binder formulation		
	PVA	40%A 0.03%XL 1.2 weight % add.	40%A 0.03%XL 5.0 weight % add.
0			
2			
5			
10			
20			
60			

From Table 4-5 it is seen that the PVA bound briquette outlasts the optimum formulation bound briquette by 15 seconds. This is very insignificant in the industrial lifetime of the briquette, but

does show that the film forming capabilities of the PVA binder is higher than that of the poly-acrylic binder. It was predicted that if the amount of binder is increased to a 5 weight percent addition; the briquettes will be somewhat water resistant. This was found to be the case, even though the binder was not developed to be added in these high concentrations. The optimal formulation in a 5 weight percent addition resulted in a briquette that not only withstood the water after 1 minute, but had a wet compressive strength of 318 ± 5 kPa. This strength was lower than the 350 kPa transportation standard which means that the wet briquettes would not be able to withstand transportation (Richards, 1990). After longer than a 2-minute period, the briquettes started to disintegrate to their detriment. It was therefore concluded that the formulation does not yet produce water resistant briquettes at low additions, and it is recommended that the formulation be further optimised for water resistance at low additions. Mangena and Du Cann (2007) found that the water resistance of the briquettes was largely dependent on the mineral matter and inherent properties of the coal. The water resistance of these briquettes could be hindered by the high prevalence of silicates (42 percent) and aluminium containing minerals (29 percent) in Coal 1 as seen in Table 3-4. It is therefore concluded that for this coal, with a high mineral matter content, the low additions of binder (either PA or PVA) will not sufficiently waterproof the briquettes and further waterproofing is required. Coal 2 was also not found to yield waterproof briquettes, this coal sample had a high amount of silicates (56 percent) and aluminium containing minerals (27 percent) as for Coal 1.

4.6 Formulation modelling

The second coal was largely used for method screening and modelling of the formulation. The formulation was modelled using a central composite design with the aim of finding a behavioural trend as well as definitive optimal point in a more condensed form than the initial design. The central composite design was obtained from in-house statistics consultation services and was developed to range slightly outside of the minimal and maximal ranges of the concentrations for components A and B. The central composite design had two blocks, to enable manageable workloads on a daily basis. The blocks were divided into ten runs, and the design is shown in Table 4-6.

Table 4-6: Central composite design generated by SCS using STATISTICA software

Run number	Block	A	B
2	1	-1.0	1.0
5	1	0.0	0.0
4	1	1.0	1.0
1	1	-1.0	-1.0
3	1	1.0	-1.0
7	2	1.4	0.0
10	2	0.0	0.0
6	2	-1.4	0.0
8	2	0.0	-1.4
9	2	0.0	1.4

With the variation in components A and B and the perceived interdependency of the components, an attempt was made to keep the cross-linker and water addition constant. It was found that the water addition could be held at 49 ± 1 weight percent, by consistently diluting each component to 50 weight percent, and the cross-linker amount could be kept 1 ± 0.4 weight percent. Here the amounts of A and B was varied as per the maximum and minimum amounts obtained from the initial design shown in Table 4-1. The interdependence between the four components led to the cross-linker, and other components being added in weight percent additions as is shown in Table 4-7.

Table 4-7: Central composite design adapted to keep water and cross-linker amount constant

Formulation no.	Block	A (%)	B (%)	XL (%)	W (%)	T (%)
2	1	24.8	24.7	1.01	49.5	100
5	1	33.4	16.0	1.13	49.4	100
4	1	30.5	19.1	0.78	49.6	100
1	1	35.2	14.1	1.44	49.3	100
3	1	39.6	9.9	1.01	49.5	100
7	2	39.5	10.1	0.71	49.6	100
10	2	33.4	16.0	1.13	49.4	100
6	2	27.1	22.1	1.56	49.2	100
8	2	39.9	9.4	1.35	49.3	100
9	2	22.8	26.8	0.77	49.6	100

The general behaviour of the formulation was characterised by evaluating the compressive strength of a coal briquette at 1.2 weight % binder addition. In the evaluation the averaged ratio of Component A to Component B was measured against its resulting compressive strength. The trend is displayed in Figure 4-17.

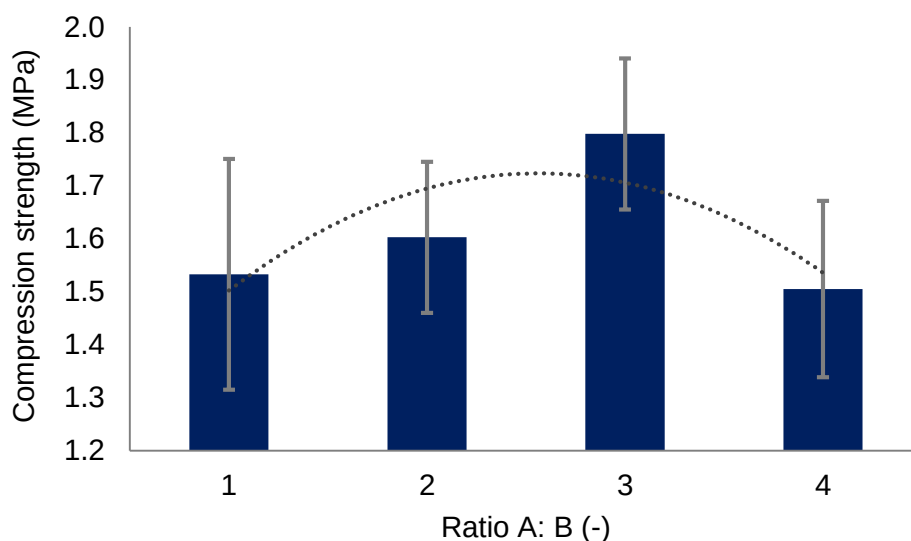


Figure 4-17: General trend of the compressive strength of briquettes compared to average ratios of components A and B

From the trend it is observed that, on average, the amount of Component A in the binder mixture should be 3 times greater than the amount of component B. This is for the formulation where the components are 50 percent diluted, and the cross-linker is kept to 1 weight percent for as far as

possible. The results were studied more closely with the added effect of abrasion resistance. These results are shown in Figure 4-18.

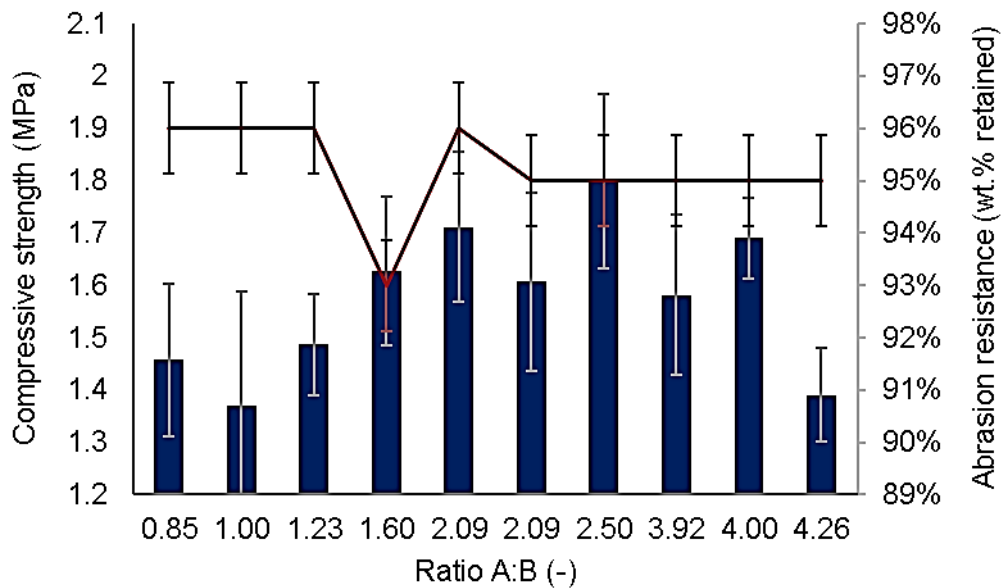
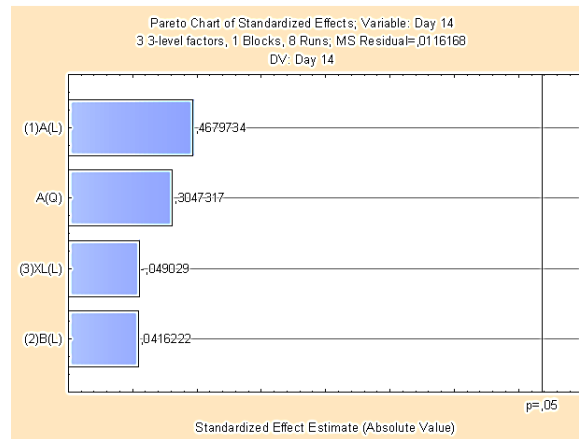


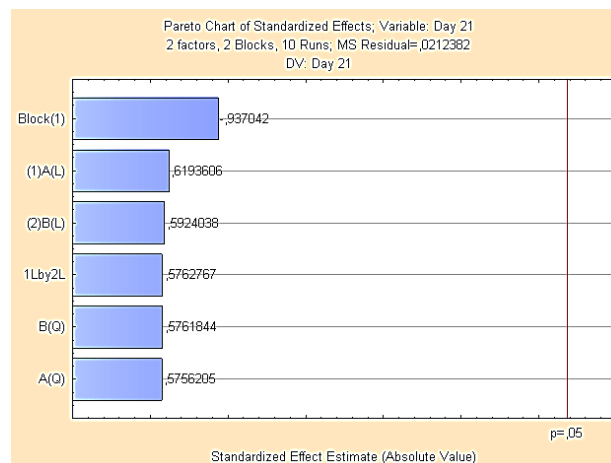
Figure 4-18: Compressive strength (left axis) and abrasion resistance (right axis) of Poly-acrylic binder based briquettes compared to average ratios of components A and B

From the it is observed that the 1.60 ratio is the least abrasion resistant, and does not meet the 95 weight percent abrasion resistance benchmark as set out by Richards (1990). Furthermore, the ratios more affected by compression, are more abrasion resistant, this statement holds true for the lower ratios, and not for the higher ratios. It is further seen that the formulation has the weakest compression response between A: B ratios of 0.85 – 2.09 as well as between 4.0 – 4.26. The formulation response improves significantly at a ratio of 2.5 at which it is optimal and performs comparatively well at a 3.92 ratio. It would seem that the B component needs to be added sparingly, although too little of this component is not necessarily beneficial, and could lead to seemingly weak, but abrasion resistant briquettes. From the chemical nature of component B and its general use as a flocculent, it is assumed that when too much is added it combines more with itself rather than cross-link to Component A. When too little is added it may negatively influence the dispersion capabilities of the binder (due to smaller binding molecules or balling of binder components). This leads to the conclusion that component B improves or weakens coagulation or in this case agglomeration of the particles, depending on its addition. As component A seems to be the major strength contributing. The p-values for the ANOVA summary of effects for the variables (components A and B after 21 days of curing) in the CCD with 50 percent hydration (Table 4-7) were not smaller than 0.05, and could therefore not be used to model the formulation.

The same result was found for the full factorial design, for which only 8 unique runs were found for a tolerance value of 0.00016, and the blocking variable had to be ignored to generate an analysis for the full factorial design. The Pareto analyses that were conducted for the full factorial and hydrated central composite design are shown in Figure 4-19.



(a)



(b)

Figure 4-19: Pareto analyses for the (a) full factorial design as shown in Table 4-1 and (b) the hydrated central composite design as shown in Table 4-7

From Figure 4-19 it is observed that none of the variables have significant p-values (all are greater than $p = 0.05$, shown to the right of each figure). This created difficulty in the determination of a predictive model based on component A and B, since models can only be obtained if the p-values fall within the acceptable range. It was observed that for both the full factorial design and central composite design high amounts of water were added (50 – 60 percent) and this could have

prevented an accurate model from being formulated, since the effects of each component were too dilute to be observed.

The central composite design, as shown in Table 4-6, was used to model an adaptation to the formulations presented in Table 4-7. In the adaptation, the components A and B were not hydrated before the mixture was formulated. Instead, water was approached as the balance of the formulation components A, B, and XL. This resulted in the dehydration of some of the formulations as shown in Table 4-8. These formulations are formulation numbers. 4, 7, and 9, with 34, 28, and 34 weight percent water respectively.

Table 4-8: Central composite design adapted to keep cross-linker amount constant with a water balance for the purpose of dehydration

Formulation number.	Block	A (%)	B (%)	XL (%)	W (%)	T (%)
2	1	25	25	1	49	100
5	1	30	14	1	54	100
4	1	40	25	1	34	100
1	1	25	10	1	64	100
3	1	40	10	1	49	100
7	2	57	14	1	28	100
10	2	30	14	1	54	100
6	2	18	14	1	67	100
8	2	30	7	1	62	100
9	2	30	35	1	34	100

The formulations were also added to Coal 2 as with the results for Table 4-7. The central composite design was done over two days (block one and block 2). The resulting compressive strengths after 21 days of curing are shown in Table 4-9.

Table 4-9: Resulting compressive strengths for the briquettes made from the formulations shown in Table 4-8

Run number	Block	A (%)	B (%)	W (%)	Day 0 (MPa)	Day 1 (MPa)	Day 2 (MPa)	Day 7 (MPa)	Day 14 (MPa)	Day 21 (MPa)
2	1	25	25	49	0.80	0.85	0.80	1.25	1.44	1.38
5	1	30	14	54	0.63	0.77	0.84	1.41	1.58	1.61
4	1	40	25	34	0.73	0.92	1.00	1.63	1.93	1.80
1	1	25	10	64	0.62	0.82	0.89	1.46	1.58	1.60
3	1	40	10	49	0.78	0.92	1.05	1.56	1.78	1.89
7	2	57	14	28	0.89	0.99	2.03	1.77	2.00	2.24
10	2	30	14	54	0.82	0.94	1.67	1.55	1.78	2.01
6	2	18	14	67	0.73	0.86	1.55	1.41	1.59	1.76
8	2	30	7	62	0.81	0.83	1.56	1.46	1.66	1.86
9	2	30	35	34	0.73	0.92	1.67	1.60	1.83	2.06

From Table 4-9 a difference was observed for 2 of the three dehydrated formulations, these formulations are formulation numbers 7, 10, and 9. For formulation number 4, the dehydration has little to no impact in comparison to the formulations that are made up of approximately 60 – 70 weight percent water. The data was processed through Statistica® a statistical design software package. The initial steps of the analysis included an ANOVA table to determine the effect of the variables on the mechanical strength of the briquettes. These variables were the components A and B, and the blocking variable, which divides the experiments in day 1 and day 2 (seen in Table 4-9 as block 1 and block 2). The p-values resulting from the ANOVA analysis are shown in Table 4-10 and the complete ANOVA analysis is shown in Annexure J, Table J-1

Table 4-10: ANOVA table for the evaluation of the p-value showing significant effects if smaller than a value of 0.05

Factor	p
Blocks	1.32E-03
(1) A (L)	1.82E-03
(2) B (L)	9.23E-01

From Table 4-10 it was observed that only the block number (day of formulation make-up) and component A significantly contribute to the mechanical strength of the briquettes made from the formulations in Table 4-8. A Pareto analysis was conducted on the linear as well as the quadratic

variables and is shown in Figure 4-20, and from the analysis it was observed that component A and the blocking variable are the only variables that significantly impact the compressive strength of briquettes cured for 21 days.

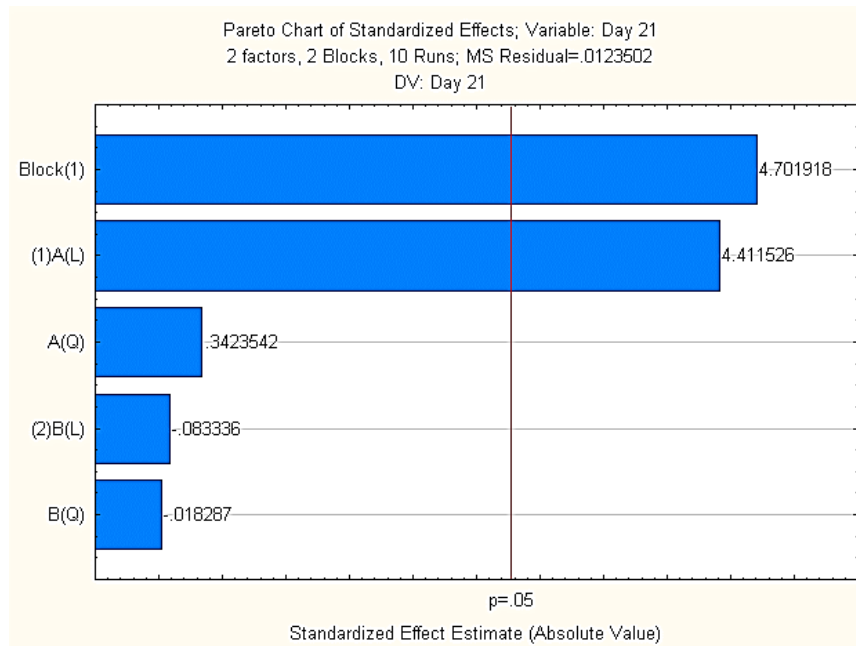


Figure 4-20: Pareto analysis on the linear and quadratic as well as blocking variables in the dehydrated central composite design

The blocking variable ideally should not have an effect on the contribution to compressive strength, but added to the increase of mechanical strengths of the model. This can be seen as a systematic human error, where the formulation in day 2 could have been made in a different way than day 1, or the moisture content could have varied due to humidity and storage conditions. It is therefore recommended that the procedure for the binder formulation be standardised. The impact of this systematic error on the model, would be related to the intercept of the linear model, where A is the only factor considered. Due to the linearity in this relationship (since the p-values of the quadratic components A and B were greater than 0.05), the optimal formulation (in terms of the ratio of A to B) could not be obtained from the central composite design. For this reason, the observed ratio of 3 parts component A to 1-part component B will be taken as an optimal formulation for Coal 2 (as is shown in Figure 4-17). This result also falls in the range of the optimal that was chosen for Coal 1 (75 -80 percent A). A desirability analysis was done on the addition of A to B and is shown in Figure 4-21.

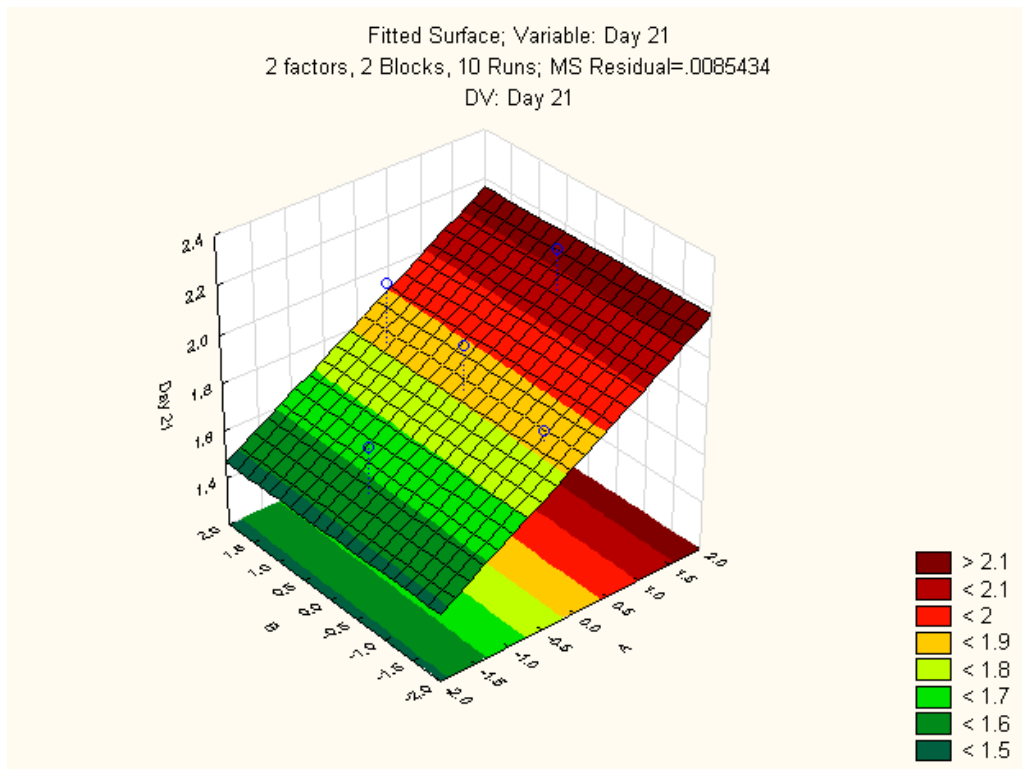


Figure 4-21: Desirability chart showing linearity in the effects contribution of both components A and B

From Figure 4-21 it is observed that component B has a limiting effect on the mechanical strength of briquettes cured for 21 days. It is also seen that component A has a linear effect on the compressive strength of briquettes cured for 21 days. A summary of effects analysis was conducted and the results are shown in Table 4-11.

Table 4-11: Summary of effects for component A as well as for the mean

Factor	Coefficient	Standard error	- 95 %	+ 95 %
Mean/ Interact.	1.807	0.09	1.531	2.083
A linear	0.173	0.04	0.042	0.289
Block	0.165	0.04	0.035	0.311

The effects can be modelled by Equation 4.1.

$$y = \beta_0 + A\beta_1 + B\beta_2 \quad \text{Equation 4.1}$$

In the equation y_{11} represents the mechanical strength of the briquettes after 21 days of curing. The term β_{10} represents the mean coefficient or intercept of the linear model.

The term $A\beta_{11}$ represents the amount of component A within the range 25 – 40 weight percent, and its contributing coefficient. The term $B\beta_{12}$ is the variable ascribed to the blocking variable and its contribution, the blocking variable in this case will only influence the slope so that the linear model is described by the equation:

$$CS(\text{day } 21) = 1.807 + 0.173(A) + 0.165(\text{Block}) \quad \text{Equation 4.2}$$

This equation can be determined for this model, in the provided range as follows:

$$CS(\text{day } 21)_{\text{part 1}} = 1.972 + 0.173(A) \quad \text{Equation 4.3a}$$

$$CS(\text{day } 21)_{\text{part 2}} = 2.137 + 0.173(A) \quad \text{Equation 4.3b}$$

Where part 1 and part 2 are the linear equations for the first and second day of testing (block) to account for the systematic error. The models are shown in Figure 4-22.

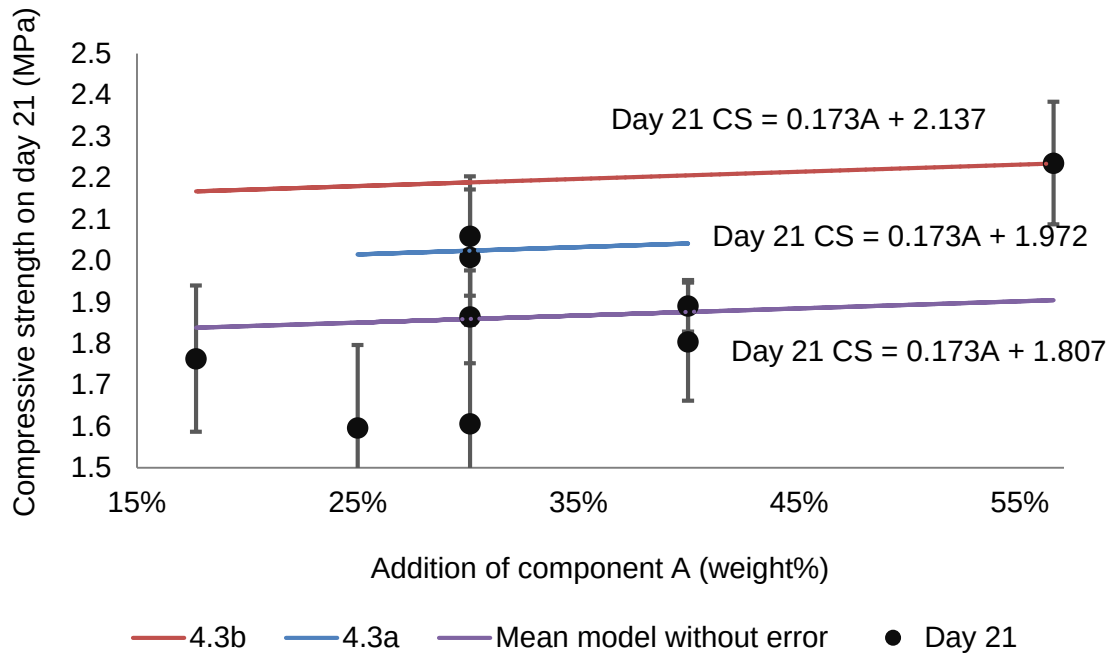


Figure 4-22: Model and data for the compressive strength of the briquettes after 21 days of curing in relation to the contribution of component A

From Figure 4-22 it is seen that the model for block 1 (Equation 4.3a) and the model for block 2 (Equation 4.3b) do not fit the data as well as when the blocking variable is ignored. From this observation the proposed model therefore ignores the contribution of the blocking variable, as its addition seems to describe the outliers well, and not the bulk data. The final model is shown in Equation 4.4:

$$\text{Day 21 CS} = 0.173A + 1.807 \quad \text{Equation 4.4}$$

To evaluate whether the model can be extrapolated briquettes were manufactured from component A only. The prediction and actual value are shown in Table 4-12.

Table 4-12: Extrapolated estimation

Value source	Compressive strength [MPa]
Experimental determination after 21 days of curing	1.17 ± 0.2
Model prediction with standard deviation on the contribution of A	2.0 ± 0.4

From Table 4-12 it is observed that the predicted value is 42 percent different to the experimental value. This is an indication that the effect observed in Figure 4-17 is valid, and that the model is only valid for addition of component A in the range 18 – 57 weight percent.

4.7 Summary

For the mechanical strength analyses 38 formulations were tested in terms of compressive strength. Of these 38 formulations 3 were selected based on the increase in mechanical strength of the resulting briquettes. From the three formulations the optimum was found to contain 40 weight percent of Component A with 10 weight percent of Component B, and a relatively low amount of cross-linker at 0.03 weight percent. The optimum formulation was evaluated in terms of concentration and binder uptake along with two other formulations. These two formulations differ to the optimum in that both are more dilute. On a 1.2 weight percent basis it was observed that a diluted formulation with a greater amount of cross-linker becomes comparable to the optimal formulation over 21 days (Figure 4-15). When compared to binderless briquettes as a lower limit, all formulations were stronger than the binderless briquettes in terms of compressive strength (Figure 4-12). The chosen formulations compared well to PVA on a 21-day basis. In terms of concentration, a lower dose of PVA (0.4 weight percent) gives results comparable to a higher dose of poly-acrylic binder (1.2 weight percent). The PVA bound briquettes reached their maximum strength in 7 days of curing, whereas the poly-acrylic (PA) binder based briquettes reached its maximum after 14 days of curing. On the second day of curing, the poly-acrylic based briquettes had reached a higher compressive strength than the PVA bound briquettes. The poly-acrylic briquettes therefore have a higher rate of increase in compressive strength than PVA as the optimal PA formulation has a significant increase after 2 days of curing.

Upon finding an optimal curing time of 14 days, further mechanical tests were conducted. These included abrasion and water resistance at the optimal curing time.

It was found, similar as with compressive strength, that a concentration of 0.8 weight percent PA binder is less abrasion resistant. The 1.2 weight percent concentration was found to be optimal for abrasion resistance. It produces fines with an acceptable range (below 5 weight percent) consistently for all three formulations as well as PVA (Figure 4-16).

The final mechanical test to assess briquette quality was water resistance, for which none of the formulations, or concentrations, were able to withstand more than 20 s of water submersion. PVA was also found to disintegrate below 1 minute. As Mangena & du Cann (2007) found, the water resistance of a briquette is largely dependent on the properties of the coal itself. It is therefore concluded that, in terms of water miscible binders, the water resistance of the briquette will depend heavily on the properties of the coal, and not so much on the chemistry of the binder, as its addition.

CHAPTER 5 REACTIVITY RESULTS

5.1 Relative comparison

The reactivity results of this study relied on combustion performance. For this two main indicators were used were the first indicator was comparability between the binder-added and binderless briquettes, on a quantitative basis, along with the ignition point determination using the tangent method, on a quantitative basis, which was the second indicator. The ignition point is an approximated value based on the rapid decrease in mass after volatile evolution. The qualitative comparison for the coal briquettes was done using dry-air (< 2.0 ppm water) under a maximum temperature of 900 °C with a heating rate of 5°C/min. For the initial comparison, the effects of burn-out were considered less important, since the briquettes were simply evaluated relative to each other under the same conditions. This comparison is shown in Figure 5-1.

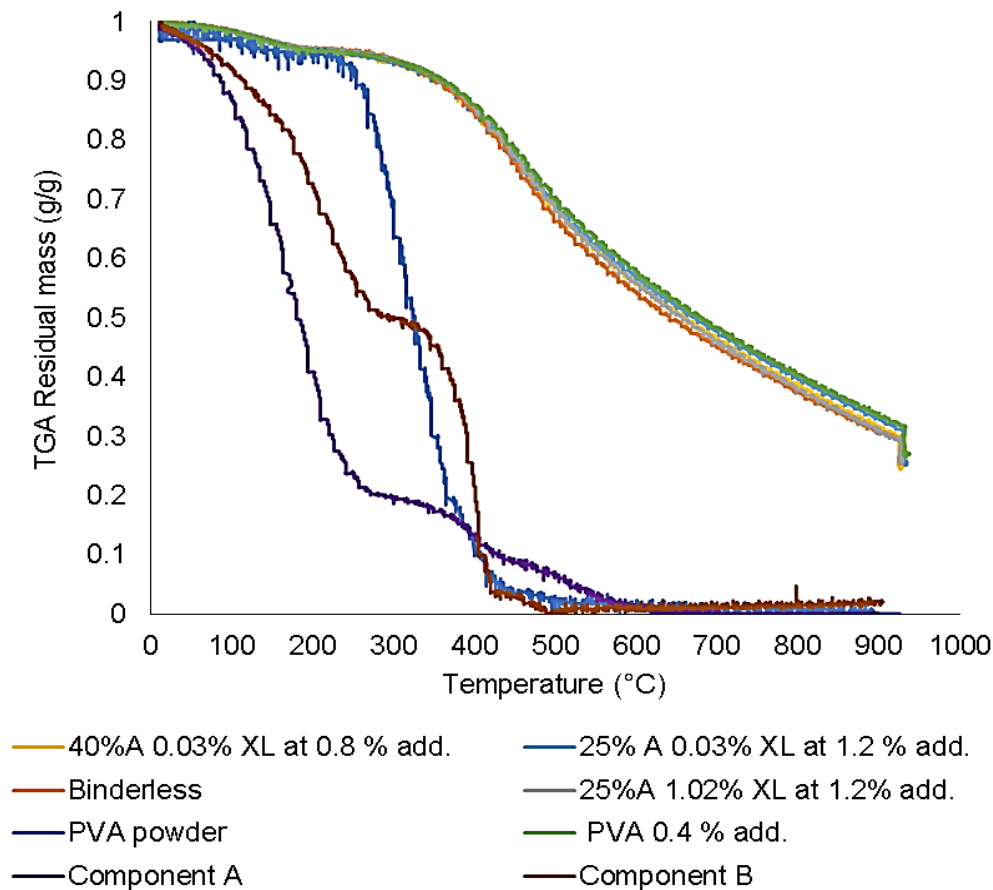


Figure 5-1: Initial comparison of the briquettes to each other and the binder components under the same conditions

From Figure 5-1 it was concluded that the addition of binder in the weight percentages added, had no significant effect on the combustion performance of the briquettes. The briquettes (including the binderless briquettes) underwent moisture loss from 100 – 160 °C, during and after which volatile evolution began and a rapid decrease (associated with the process of combustion) followed between 300 – 400 °C. This is also where the various ignition points are expected to lie. From Figure 5-1 it is also evident that, under these conditions that none of the briquettes reached the expected carbon burn-out, which was to start between 600 – 800 °C. This was seemingly due to ash particles blocking the large voids in the briquettes as observed with chars (Hu et al., 2018). It was also observed that the PVA component mostly releases moisture and volatiles after which the binder powder is completely combusted in the TGA. The two main components for the poly-acrylic binder lose moisture at different rates. Both components have a sharp decrease in moisture, since they were fed in paste form, unlike the powder phase of the PVA. Component B loses moisture and volatiles more slowly than component A, since it is a long-chain polymer whereas Component A is a cyclic styrene that dehydrates easily. No ash was observed for any of the binder or binder components. Due to the dwelling nature and slow decomposition of some of the binder elements in this study, it is recommended that an extensive and detailed environmental impact assessment on the combustion of briquettes made from these binders be undertaken. This may seem unnecessary considering the low amount of binder added to the coal, but when considering the possible amount of briquettes that could be burnt either after pulverisation in pulverised fuel combustors or as steam generators in industrial boilers.

5.2 Combustion profiles

The combustion profile includes the heating value, residual mass curves, and evolution curves of the optimal formulation and PVA bound briquettes, as well as of the binderless briquettes. The heating values serve as an initial estimate of whether the energetic difference between the types of briquettes being studied are significant. The heating values were tested with an IKA bomb calorimeter and the results are shown in Table 5-1.

Table 5-1: Heating values for the optimal formulation, PVA bound, and binderless briquettes

Binder	Concentration	CV (MJ/kg)	±
PVA	0.4	21.36	0.6
Optimal	1.2	21.52	0.3
Binderless	0	21.81	0.1

PVA was studied at a 0.4 weight percent concentration due to it being comparably strong to the optimal formulation at 1.2 weight percent. The optimal formulation was studied at 1.2 weight percent binder addition because this was the optimal concentration within the range studied. The binderless briquette was set as the control value as a benchmark for the binder bound briquettes.

The ignition of coal briquettes was determined experimentally through non-isothermal runs during which the coal briquette was placed in sufficient airflow and the heating rate that supports burnout. In this case the heating rate was found to promote burnout at 3 °C/min, and the air flow was 0.15 sL/min. The ignition point was also determined at 5 °C/min. The final temperature was taken as 900°C and the briquette was combusted in its whole form. The ignition point temperature can then be determined in many ways, these include the tangent and slope method or using the differential thermal gradient.

In coal combustion there are generally three phases, the first is moisture removal which normally occurs below 200°C and the ignition is normally between 300 – 400°C for particles and chars (Hu et al., 2018). The second phase is the volatile generation step, where volatiles are removed, this step occurs until ignition. After ignition the maximum rate of burn-out is achieved, known as the maximum rate. The third and final stage is complete burnout being achieved, and the final residual mass should depict the ash yield as obtained in the proximate analysis of the coal (22.8 weight percent). The results for the 5 °C/min were used for comparative purposes to also gauge the effects of the heating rate on ignition point.

The figure indicates the different peaks for each zone of the combustion process, as well as an isothermal zone which occurred while burning the briquettes at 5 °C/min at a fixed final temperature. Despite this isothermal zone the data remains useful to determine whether there is a significant difference between the ignition behaviour of this, the optimal binder formulation, the PVA bound, as well as the binderless briquettes. The combustion performance for the optimum formulation based briquette is illustrated in Figure 5-2.

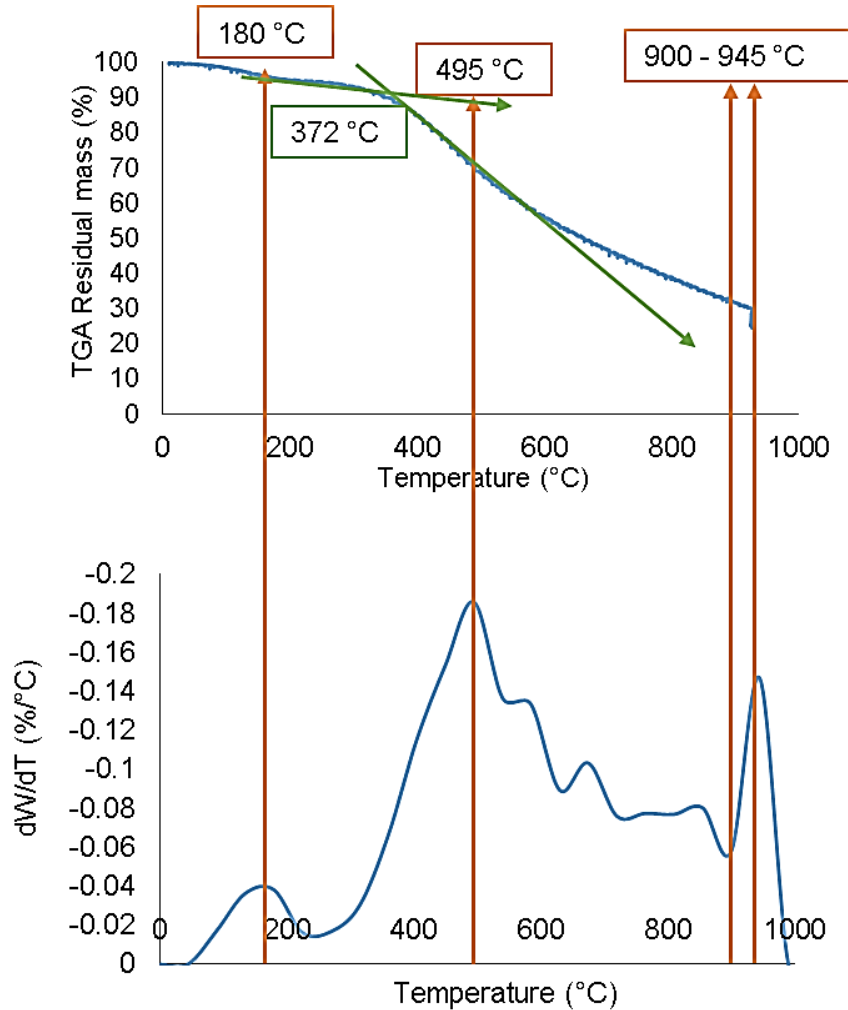


Figure 5-2: Combustion profile of an optimum formulation based briquette at 5 °C/min and 0.15 sL/min

The drying zone for the optimum formulation at 5 °C/min and 0.15 sL/min occurred between 15 – 200°C, and reached its peak at 180°C. The pyrolysis phase started at 200°C and ignition occurred at a temperature of $372 \pm 5^\circ\text{C}$, which was determined using the tangent slope method. The maximum combustion rate was achieved at 495°C.

The isothermal zone between 900°C – 945°C was responsible for an ash yield of 25%, which was within 3% of the proximate analysis value and can be considered as acceptable. The PVA based briquette showed similar combustion trends and is shown in Figure 5-3.

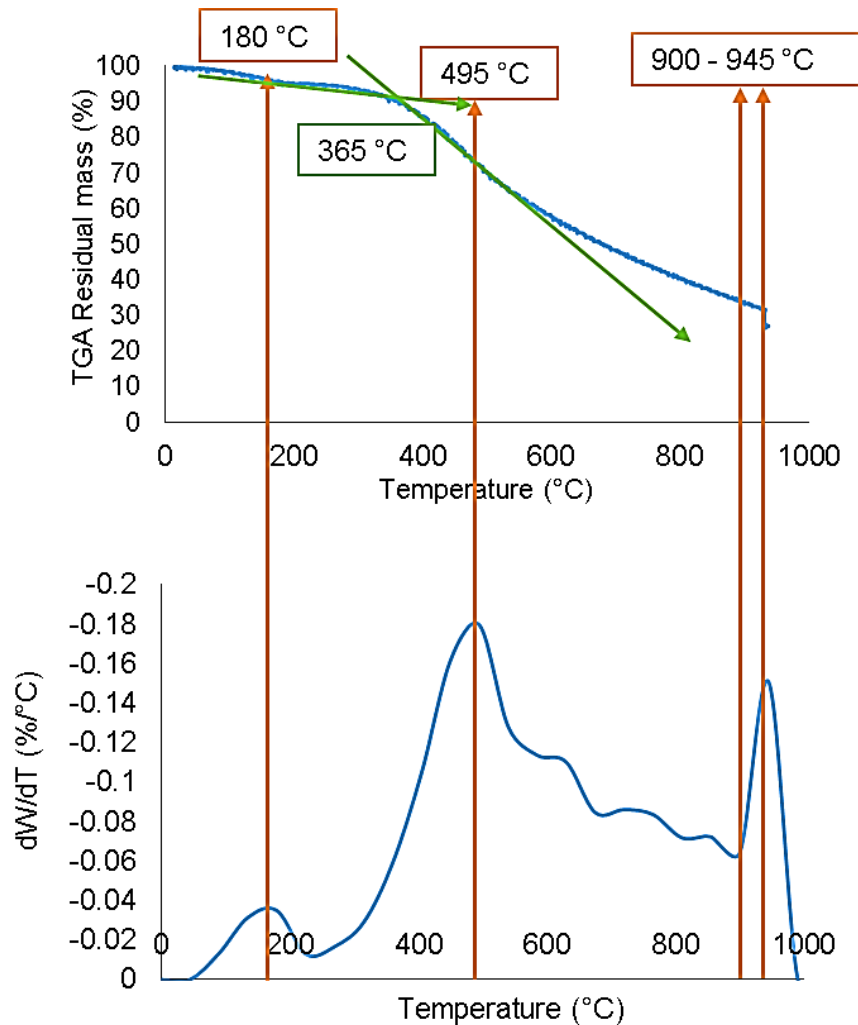


Figure 5-3: Combustion profile of a PVA bound briquette at 5 °C/min and 0.15 sL/min

As for the optimum formulation based briquette, the drying zone of the PVA based briquette reached its peak at 180°C and the devolatilisation phase started at 200°C to the ignition point of $365 \pm 10^\circ\text{C}$. The maximum combustion rate was achieved at 495°C and the isothermal burn-out region gave an ash yield of 27%, which being within 5% of the proximate analysis value is also an acceptable result.

The binderless briquette was evaluated as a final comparison to the optimal formulation, and PVA based briquettes, with the TGA residual mass curves as well as the evolution curves being depicted in Figure 5-4.

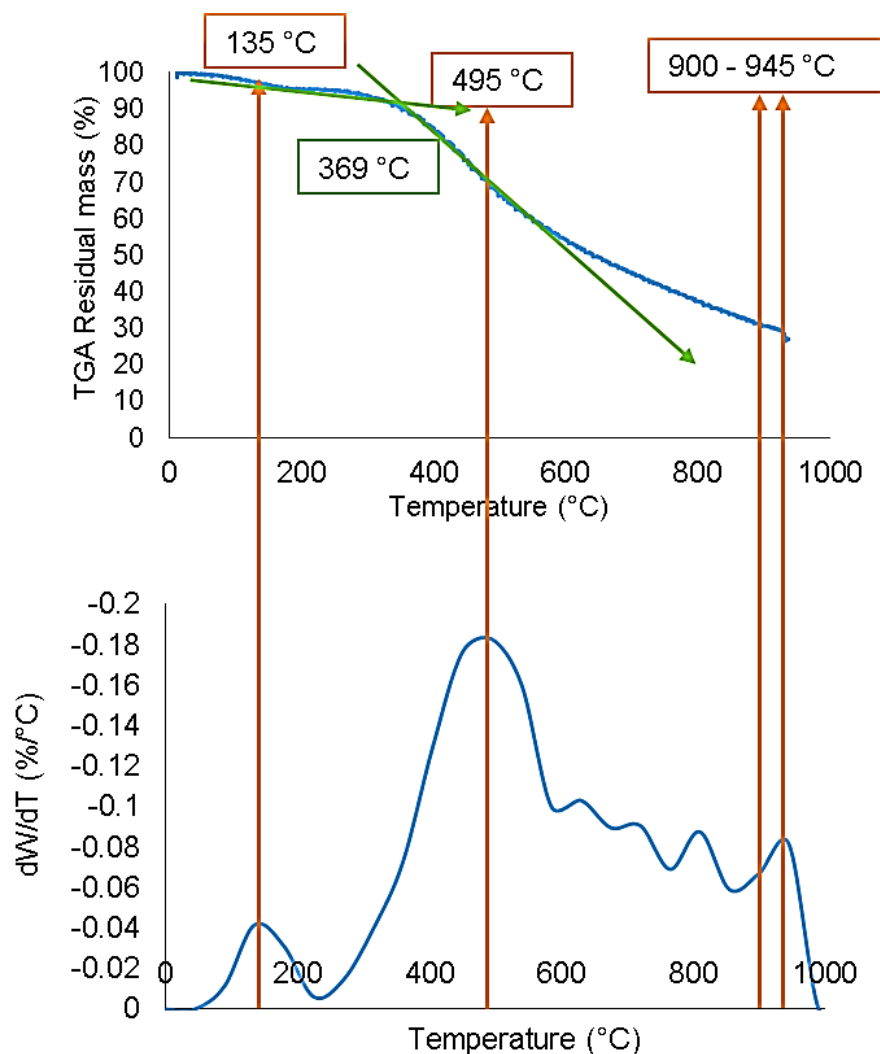


Figure 5-4: Combustion profile of a binderless briquette at 5 °C/min and 0.15 sL/min

The drying zone in the binderless briquette was again between 15 and 200°C. However, unlike with the optimal formulation and PVA based briquettes, the peak in this zone was reached at a much lower temperature of 135°C. The binderless briquettes weigh less than the binder based briquettes, which had an initial mass of 4.40 ± 0.1 g and 4.68 ± 0.1 g respectively. It can therefore be concluded that the binderless briquette does not retain moisture as much as the binder based briquettes. This is due to the film forming potential of each of the two binders, which inhibits moisture evaporation. Furthermore, the drying zone within the binder based briquettes could also contain overlapping instances of the start of binder decomposition. This would lead to a higher temperature required to achieve maximum drying rate, with more interstitial and chemically bonded water molecules being released as the binder decomposes. This would make the binder based briquettes more difficult to dry in solid form.

The ignition point of the binderless briquette was found to be 369°C and the maximum rate of burning was found to be 495°C and the final ash yield was again found to be acceptable at 27%.

It is also important to note that the binderless briquette did not rely much on the isothermal region for complete burn-out, which was the case for the binder based briquettes. This could be due to the looseness of the particles that will allow the combustion gas to flow more freely through the briquette. Conversely, the film in the binder based briquettes, as well as the added solid structure of bound particles, would inhibit penetration of the combustion gas.

The briquettes were compared in terms of their evolution curves and this comparison is shown in Figure 5-5 below.

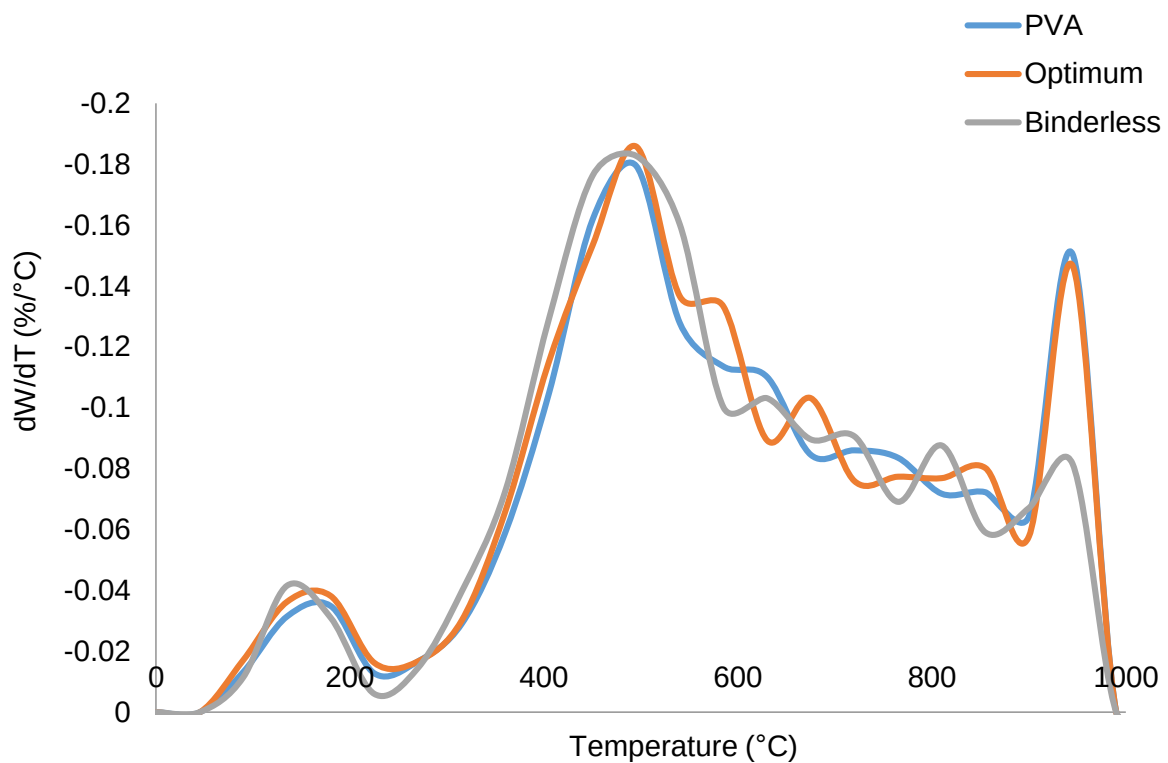


Figure 5-5: Comparison of the evolution curves of the binder bound and binderless briquettes at 5 °C/min and 0.15 sL/min

The comparison of the evolution curves for the binder based and binderless briquettes showed that there was no significant difference between the addition of a binder or keeping the briquettes binderless. This supports the initial comparison result and the conclusion can be drawn that neither of the binders hinders or improves the briquette combustion performance.

The combustion profiles of the fully burnt out binderless, optimal formulation, and PVA based briquettes were compared to each other at a 3 °C/min heating rate as a more definitive way of determining the ignition point. The slope method was used to evaluate the reaction temperatures and the results are shown in Figure 5-6.

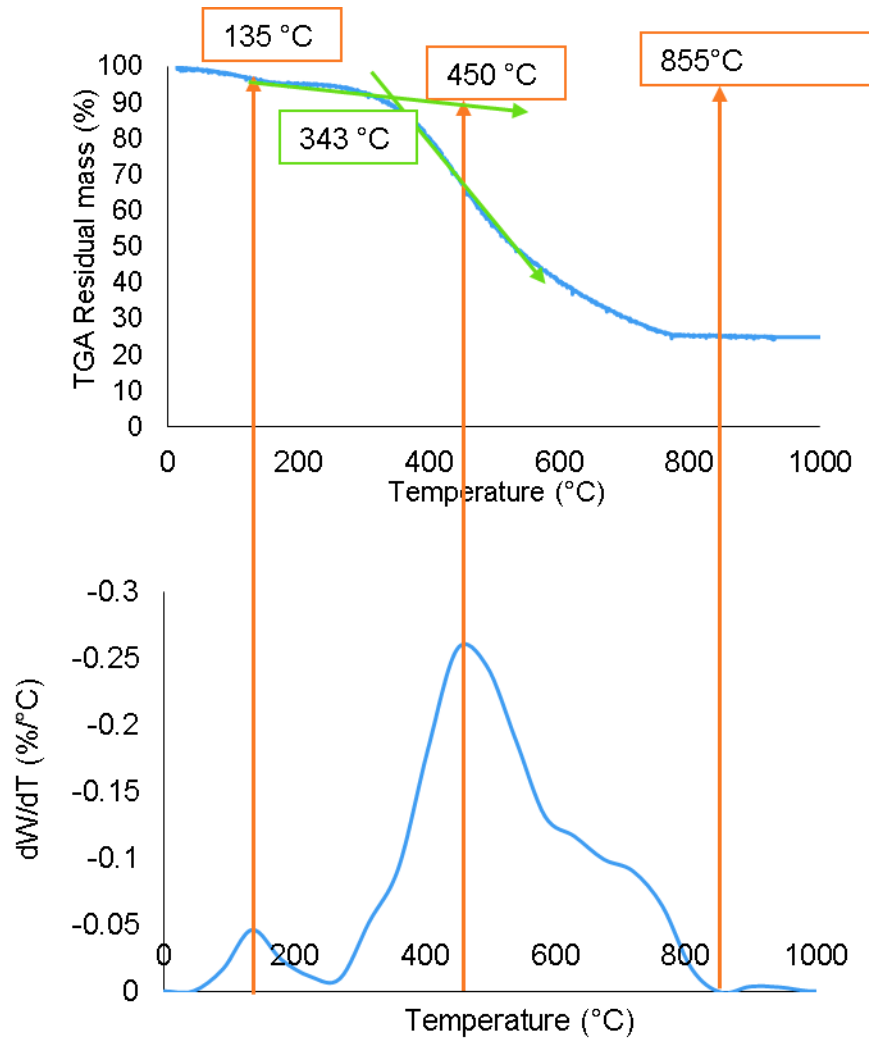


Figure 5-6: Residual mass and evolution curve of 40 percent A 0.03 percent binder formulation at 1.2 weight percent addition, with a heating rate of 3 °C/min, and 0.15 sL/min air flow-rate

Figure 5-6 is also a depiction of the mass-time differential to evaluate the point where mass loss occurs to the greatest extent. This temperature is considered the maximum burning rate. For the briquette produced by the optimum formulation the maximum burning point is approximately 450 °C. Most of the moisture and some volatiles are driven off between 15 and 215 °C as expected. The final volatile liberation stage occurs between 215 – 450 °C. The ignition point of the briquette is at 450 °C, after this point the final stage, carbon burnout, is reached up to approximately 815 °C.

The PVA based briquettes had similar trends and the residual mass, as well as evolution curve are depicted in Figure 5-7.

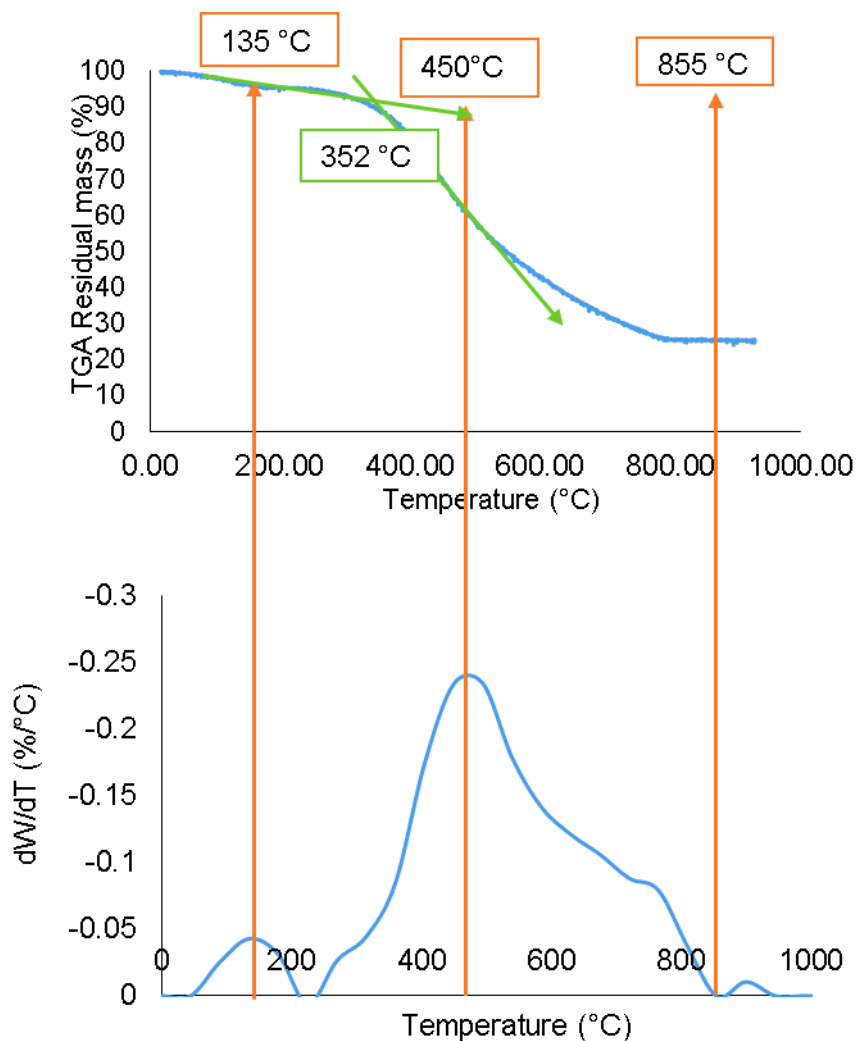


Figure 5-7: Residual mass and evolution curve of PVA at 0.4 weight percent addition, with a heating rate of 3 °C/min, and 0.15 sL/min air flow-rate

Figure 5-7 mirrors the results for the optimum formulation bound briquette. The drying zone in the PVA based briquette was also found to be between 0 – 200°C, and the temperature at the maximal heating rate was found to be 450°C. The final temperature at which burnout was achieved for briquettes based on both binders was approximately $815 \pm 20^\circ\text{C}$. The ignition points of both formulations were also identical at approximately $335 \pm 50^\circ\text{C}$. The binderless briquette behaved somewhat differently and is shown in Figure 5-8.

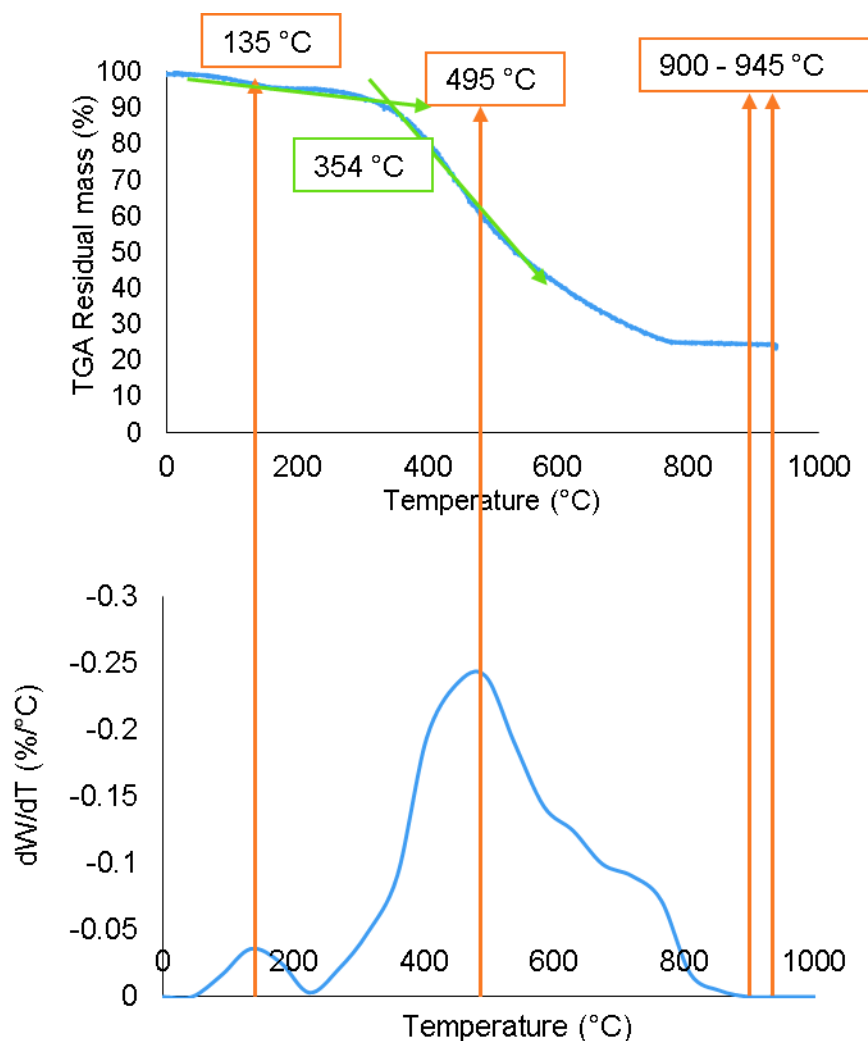


Figure 5-8: Residual mass and evolution curve of the binderless briquette, with a heating rate of 3 °C/min, and 0.15 sL/min air flow-rate

The binderless briquette also dried at 135°C, most of the volatiles were driven off from 135 – 354 °C where the briquette ignited. The maximal burning rate of the binderless briquette seemed to have been achieved 45°C later than the binder based briquettes. The binderless briquette, like the binder based briquettes, burns out in the same range starting from 855°C.

The evolution curve for the binderless, optimal formulation and PVA bound briquettes were compared. This comparison is shown Figure 5-9.

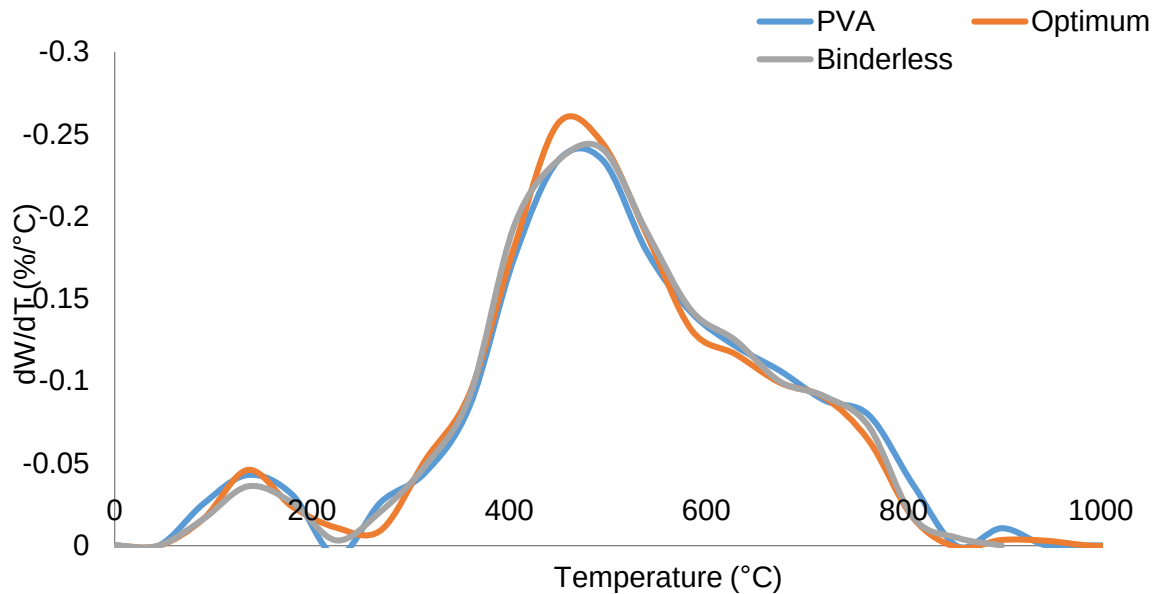


Figure 5-9: Comparison of an optimal formulation and PVA bound briquettes, with a heating rate of 3 °C/min, and 0.15 sL/min air flow-rate

From this comparison it is observed that the PVA and optimal formulation based briquettes behave similarly in terms of combustion. However, an isotherm exists for the PVA based briquette in terms of maximal burning rate, where this rate is constant between 450 – 495°C. The poly-acrylic binder's optimal burning rate occurs at 450°C. Therefore the binderless briquettes' optimal burning rate was in range with that of the PVA briquette, but later than the optimal formulation based briquette. The poly-acrylic binder could be beneficial in reaching the maximal burning rate sooner than the binderless briquettes. This could be due to the lingering volatiles that remain when the briquette starts to ignite at approximately 350°C compared to the complete burn-out of the PVA based briquette at 280 – 500°C that produce no residual components as is shown in Figure 5-1. The evolution comparison results are summarised in Table 5-2.

Table 5-2: Combustion profile summary for optimal formulation and PVA bound briquettes at different heating rates

Heating rate	5 °C/min						3 °C/min					
Temperature & Meaning	Binderless		Poly-acrylic		PVA		Binderless		Poly-acrylic		PVA	
	°C	±	°C	±	°C	±	°C	±	°C	±	°C	±
T _D : Drying zone maximum	135	0	180	2	180	3	135	0	135	0	135	0
T _{ig} : Ignition point	369	15	365	5	372	1	354	1	352	3	343	1
T _M : Maximum burning rate temperature	495	0	495	0	495	0	495	0	450	0	450	0
T _f : Final burnout temperature	>900		>900		>900		855	20	855	0	855	0

There is no significant difference between the two binders with regard to evolution temperatures. From the table it is observed that the evolution temperatures are higher for the 5 °C/min heating rate than for the 3 °C/min heating rate. It is then expected that the reaction of combustion would occur much faster for the lower heating rate as this was also evident from the literature. This is due to the particles being exposed to a fixed temperature for a longer period of time, allowing the heat through radiation, convection, and finally conduction to penetrate more effectively throughout the briquette. Whereas with the higher heating rate, the outside of the briquette is heated more rapidly and penetration of heat through the briquette is hindered by the reaction on the surface. The reaction continues inward, but never fully reaches the core.

5.3 Repeatability

The repeatability was tested by first testing a binderless run for 3 runs to see whether the combustion behaviour is consistent. These results are shown in Figure 5-10.

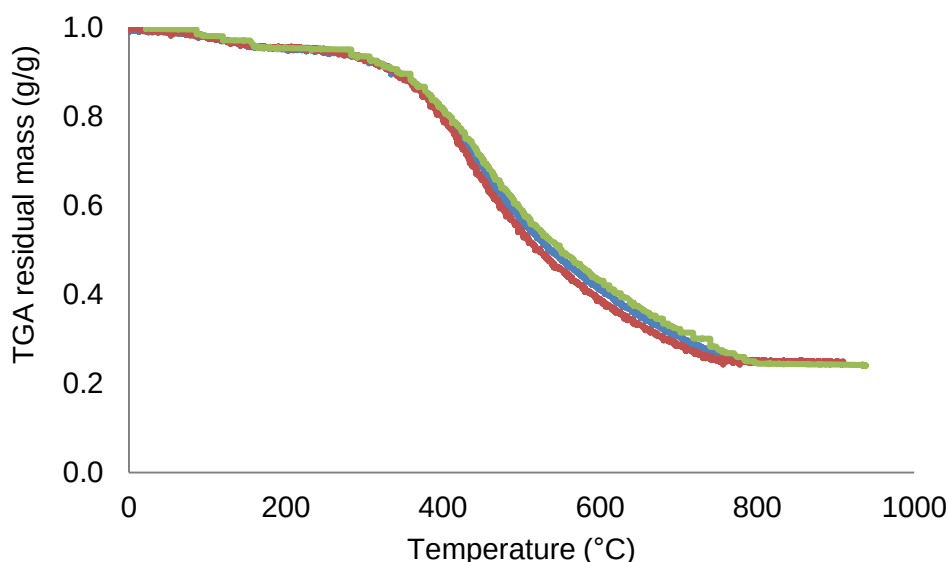


Figure 5-10: Repeatability test for the binderless runs

The results indicate that the different runs behave much the same, and gave an ash yield of between 23 – 26 %. This is consistent with the proximate analysis for this coal, which returned an ash yield of 22.8 %. The repeatability was also evaluated for the optimum formulation and PVA based briquettes. The results are shown in Figure 5-11.

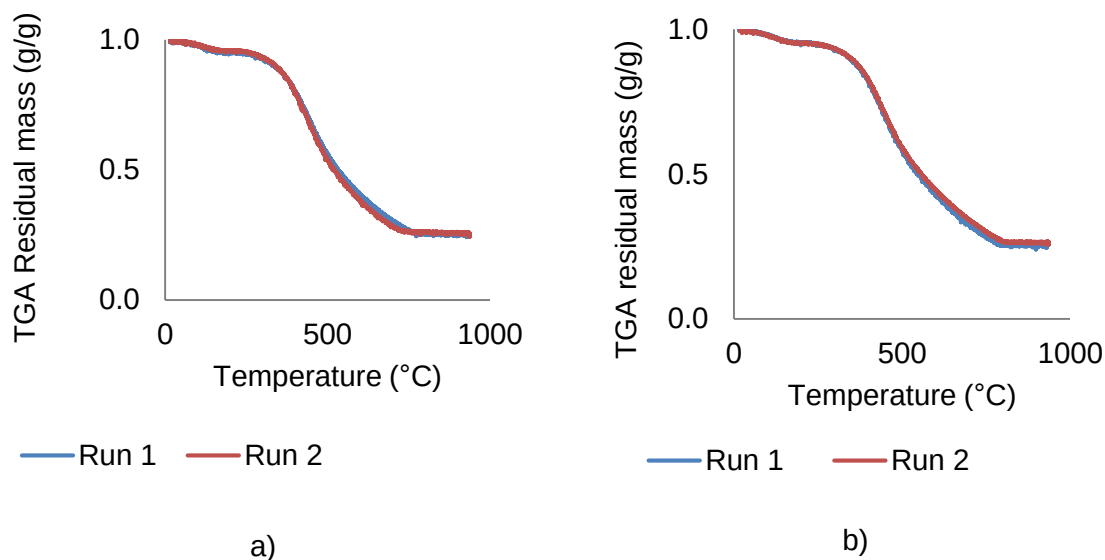


Figure 5-11: Repeatability test for the optimal formulation a), and PVA bound b) briquettes

The results indicated once more, that the combustion profiles were repeatable and that the conclusions that were drawn for these briquettes were precise.

5.4 Summary

The results show that the binder has minimal effect on the burning profile of the fine coal briquette. The initial comparison and burn-out profiles correspond in this regard. The binders are therefore expected to neither hinder nor improve the function of the briquettes as feedstock for combustion processes such as pulverised fuel combustors or industrial boilers. From the relative comparison, however, it is highly recommended that the briquettes be studied in terms of emission, due to some of the components decomposing in portions (Figure 5-1). This is especially important, since the briquettes are to be used for large scale applications

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The conclusions presented in this chapter could be better supported with greater investigations into binder and briquette-formation mechanisms. It is one of the greatest recommendations of this study that the mechanism of mixing and bonding within this briquetting-method be further studied. Then and only after this, can valid conclusions be drawn based on the shearing and mixing of the polymer binders to the coal.

6.1.1 Formulation make-up and optimum formulation

It was firstly observed that the poly-acrylic binder does not require advanced mixing techniques, and that the reagents are expected to behave similarly regardless of the mixing method employed. The poly-acrylic binder is therefore superior to PVA in that the PVA requires solubilisation under heat and could create problematic situations like fouling in its formulation stage, prior to briquetting.

The range for the addition of the components towards the poly-acrylic binder make-up is too narrow. This is especially true for component A which range from 60 – 80 Weight percent. This was observed after the results were seemingly similar especially when considering their uncertainty.

The cross-linker content alone does not significantly alter the compressive strength of the briquettes and further studies are suggested to determine the interaction between the binder and clays as well as pyritic minerals. It is offered as a conclusion that the binder – although it may become slightly stronger with the addition of more cross-linker – it may be more affected by mineral type imperfections. Mixing properties could also determine the porous nature of the briquette which could weaken it.

6.1.2 Binding properties

The binding mechanisms, from Section 2.4, that can be applied to briquetting in this study are the adhesion, dense water, and mechanical-chemical mechanisms. The adhesion mechanism is reliant on inherent capillary moisture within the coal. Coal 1 is expected to especially show this type of binding, since it has higher inherent moisture at 6.4 weight percent which is 2.2 weight percent greater than that of Coal 2. The binderless briquettes yielded compressive strength results that corresponds to this type of adhesion, since the binderless compressive strength for Coal 2, with less capillary moisture, was lower (458 kPa) than for Coal 1 (527 kPa).

The dense water mechanism further explains binding phenomena in the binderless and binder based briquettes, since the water used to reach a 10 percent moisture content is local and most of this water is high in slightly hydrated calcium, sodium, and other hard-water producing ions. These ions disorder the water molecules around the coal particles creating a cation layer to draw coal particles closer to each other so that they are bound. Finally, the mechanical-chemical mechanism, is used to describe the final binding step and is a composite of all other forces that could be endured by the briquette, including the 30 kN force exerted to form the briquette, as well as the capillary forces created while compressing and forming new capillary entrances. Then, finally it also includes the ionic, covalent, and attraction and repulsion forces, due to high prevalence of slightly negatively charged metals in the coal, and the addition of slightly positively charged binder components to the coal. The mechanisms however do not describe the further bonding experienced by the briquette while it is being cured in ambient conditions. This type of bonding is considered to be film-formative bonding, where a film starts to harden from the polymer addition, strengthening the bridge between the coal particles. The final strength of the briquette, after 21 days, has undergone adhesion, dense water, chemical and mechanical binding within the briquetting process and film formative binding in the curing process. The properties and condition of the coal could have an impact on the wettability and binding characteristics as discussed in Section 2.5. The higher moisture (Table 3-1), lower oxygen (Table 3-3) along with the higher siderite (Table 3-5) observed from Coal 1 could indicate that it is much more oxidised than Coal 2. This could have an impact on the wettability of the coal, along with the combustion properties of the briquettes formed from the coal.

6.1.3 Combustion profiles

The addition of the binder had low to minimal effect on the burning-profile of the briquette and the results indicate that the binders are suitable for use in combustion processes, provided that the emissions control analysis indicates that the decomposition of the components within them are safe for large scale application. It was observed that the briquettes would ignite at 335°C and reach a maximum burn-out rate at 450°C, after which the final burn-out is achieved at 850°C. The briquettes yielded the same amount of ash as obtained in the proximate analysis, within an acceptable 4 percent error margin. Comparatively, for combustion there is no difference in adding either PVA or the poly-acrylic binder. There is also no difference between adding a binder to the coal, so that the final conclusion with regards to the addition of these binders to coal fine briquettes, is that it solely depends on the mechanical strength needs of the intended application, along with its ability to capture organic and inorganic emissions.

6.2 Industrial application

The briquettes can be effectively used for combustion processes, since the poly-acrylic binder does not affect the combustion profile of the briquette significantly. The briquettes can therefore be used in either a chain grate stoker boiler designed for small to medium lump particles. The dimensions of the briquettes were 35 x 22 x 12 mm, granted they are smaller than those used by Zhang (2001), but they are still above the required 8 mm standard minimum size. The crack in the briquette is not detrimental to its use, although it is recommended that the alleviation of the formation of the crack be studied. The briquettes hold their shape after combustion, which could be due to the room within the particles to expand without forming cracks. The briquettes break at most into two to four parts upon being dropped, and these particles are typically larger than 6 mm. The briquettes produce around 10 weight percent fines after being tumbled in a cascading bed. The amount of fines produced after being tumbled in a more rigorous motion, is approximately 48 weight percent. These fines are smaller than the limit of 6 mm. Despite the fines generation potential, the briquettes do surpass the compression limit (375 kPa) set out by Richards (1990) for the transportation of agglomerates. More precise industry standards need to be created for fines-briquettes, since they are not comparable in strength to lump coal, and should be regarded as a separate product, however this does not mean that the briquettes are inferior in terms of combustion, since the briquettes still combust within 3 – 5 weight percent of the ash yield from the proximate analysis of the coal. The ease with which these briquettes are transported and subsequently crushed, makes them ideal for application in pulverised fuel combustion processes.

A major limitation in transportation and storage could occur, however, due to the briquettes not being water resistant. The briquettes need to be transported and stored under dry, and covered conditions, so that they are not exposed to rain. Testing of the briquettes while being cured in an outside environment, where there is sunlight, is recommended, and the addition of sunlight is expected to enhance the strength of the briquettes as was found for PVA (Venter and Naude, 2015). Further addition of more hydrophobic components could enhance the ability of the briquette to withstand wet conditions. This addition of waterproofing components into the optimum formulation should be further studied, as waxing and coating processes, may be expensive. Water resistance could also be an inherent quality which would be different for each coal. The properties within coal for which water resistance is improved, should be more explicitly defined so that the right coal is selected for a specific binder type. This would be done where waterproofing is overly expensive. The storage limitation could be somewhat deterred by the short curing time that the briquettes require, and results indicate that the briquettes could be used within two days after curing.

The greatest drawback for the optimum formulation based briquettes may be the decomposition of poly-acrylic, and organic components within the binder. Further study is recommended to evaluate emissions from burning these briquettes, as well as on the remediation of the effects. The sulfur yield, for instance, could be retained by adding CaCO_3 , and the effect of this should be tested (Bunt et al., 2018).

6.3 Statistical validation

Component A has the greatest effect on the mechanical strength of the briquettes. From this, the choice for the optimum formulation, which had the highest amount of component A, was validated. A model was obtained using Coal 2, by evaluating a central composite design. From the design analysis it was again observed that component A had the highest contribution to the mechanical strength of the briquettes made from poly-acrylic binder, after 21 days of curing. The full factorial design and central composite design with high hydration properties could not be analysed. This was determined from the ANOVA tables for the two block design, for which the p-values were larger than 0.05. From the Coal 2 central composite design that could be analysed, it was observed that component A ($p = 0.001823$) and the blocking variable ($p = 0.001315$) were significant in modelling the formulation and predicting compressive strength for a poly-acrylic binder bound briquette. Due to the impact of the blocking variable, that is not ideal in modelling, it was concluded that a systematic human error was present as a strength bias in the data. The resulting model therefore consisted of two parts and these parts were shown in Equation 4.3a and Equation 4.3b. The compressive strengths of the poly-acrylic bound briquettes were fitted to these two models, as well as to the model where the blocking variable is ignored. The data fit the model that ignored the blocking variable the best. This predictive model was shown in Equation 4.4, and was not found to be viable for extrapolation beyond the range of component A addition between 18 – 57 percent. This was due to the compressive strength of briquettes made from 100 percent component A not reflecting the predicted value, where the difference between these two values were 41 percent of the experimental value. The model was predicted with a 95 percent confidence interval. The combustion of the briquettes were performed with good repeatability and the effects observed in the thermogravimetric analysis was validated through the use of higher heating values, where no significant difference was observed between the heating values or the thermograms of the binderless and binder based briquettes.

6.4 Contribution to the coal science and technology field

The following contributions have been identified:

- Poly-acrylic binders allow for low dosage use, addressing the high addition of binders during coal briquetting, which can alleviate high briquetting costs.
- Poly-acrylic based binders can be considered as a substitute for polyvinyl alcohol, since it is comparable in briquette strength and cost.
- The combustion properties of the briquettes are not hindered by the addition of the poly-acrylic binder, within the limits of the formulations tested.
- Briquetting with poly-acrylic binders, using coal as-received, utilises a waste material (coal fines) to enable the possible expansion of South-Africa's coal reserves.

BIBLIOGRAPHY

- ALI, I. 2013. Some studies on coal briquetting. *Carbon*, 60, 88.4.
- BOGER, D. V. 2009. Rheology and the resource industries. *Chemical Engineering Science*, 64, 4525 - 4536.
- BUNT, J. R., MARX, S., WAANDERS, F. & LEOKAOKE, N. 2018. Green coal development for application in fixed-bed catalytic gasification. *Journal of the Southern African Institute of Mining and Metallurgy*, 118, 419-429.
- CATF 2001. Cradle to Grave: The Environmental Impacts from Coal. Boston: Clean Air Task Force.
- DENIZ, V. 2016. A new binder in production of water-resistant briquettes from bituminous coals: Co-polymer binder. *Energy sources, Part A: Recovery, utilization, and environmental effects*, 38, 1068 - 1074.
- ENGLAND, T. 2012. *Avoidance of Excessive Fines Production*, The South African Coal Processing Society.
- ENGLAND, T. 2013. The Economic Agglomeration of Fine Coal for Industrial and Commercial use. Coaltech 2020.
- ENPROTEC. 2018. *Briquetting Technology* [Online]. Available: <https://enprotec.co.za/technologies/briquetting-technology/> [Accessed].
- ESI-AFRICA. 2014. *The economic possibilities of South African coal fines* [Online]. ESI Africa. Available: www.esi-africa.com/the-economic-possibilities-of-south-african-coal-fines/ [Accessed 17 November 2018].
- EXXARO. 2018. *Mafube Life Extension* [Online]. Available: <https://www.exxaro.com/operations/mafube-life-extension> [Accessed 02/11/2018 2018].
- GARLING, R. Tailings - A Wasted Resource. 2015 Brisbane. TRADD PTY LTD.
- HADZI, D. 2013. *Hydrogen Bonding*, Elsevier.
- HARDMAN, D. R. & LIND, G. 2003. Generation of Fine Coal in Section. Coaltech 2020.
- HU, Y., WANG, Z., CHENG, X. & MA, C. 2018. Non-isothermal TGA study on the combustion reaction kinetics and mechanism of low-rank coal char. *RSC Advances*, 8, 22909-22916.
- INVESTSA, D. O. T. A. I. S. A. -. 2018. The Case for Investing in South Africa *In: INVESTSA* (ed.).
- JAFFE, D. A., HOF, G., MALASHANKA, SOFYA, PUTZ, J., THAYER, J., FRY, JULIANE L, AYRES, B. & PIERCE, J. R. 2014. Diesel particulate matter emission factors and air quality implications from in- service rail in Washington State, USA. *Atmospheric Pollution Research*, 344 - 351.

- JAYARAMAN, K., KOK, M. V. & GOKALP, I. 2017. Pyrolysis, combustion and gasification studies of different sized coal particles using TGA-MS. *Applied Thermal Engineering*, 1446 - 1455.
- JEFFREY, L. S. 2005. Characterization of the coal resources of South Africa. *Journal of the South African Institute for Mining and Metallurgy*, 105, 95 - 102.
- JINSHENG, G. 2009. *Coal, Oil Shale, Natural Bitumen, Heavy Oil and Peat-Volume I*, EOLSS Publications.
- KALENDER, W. A. 2006. X-ray computed tomography. *Physics in Medicine & Biology*, 51, R29.
- KARMAKAR, N. Mineral Processing Technology Mpt-2005. International Seminar for Material Processing Technology, 2005. McGraw Hill, 275 - 276.
- KATALAMBULA, H., HAYASHI, J.-I., CHIBA, T., KITANO, K. & IKEDA, K. 1997. Dependence of single coal particle ignition mechanism on the surrounding volatile matter cloud. *Energy & fuels*, 11, 1033-1039.
- KLIMA, M. S., ARNOLD, B. J. & BETHELL, P. J. 2012. *Challenges in Fine Coal Processing, Dewatering, and Disposal*, Society for Mining, Metallurgy, and Exploration, Inc.
- LAHAYE, L. & PRADO, G. 2012. *Fundamentals of the Physical-Chemistry of Pulverized Coal Combustion*, Springer Netherlands.
- LE ROUX, M., CAMPBELL, Q., VAN RENSBURG, M., PETERS, E. & STIGLINGH, C. 2015. Air drying of fine coal in a fluidized bed. *Journal of the Southern African Institute of Mining and Metallurgy*, 115, 335-338.
- MAITRA, J. & SHUKLA, V. K. 2014. Cross-linking in Hydrogels - A Review. *American Journal of Polymer Science*, 4, 25 - 31.
- MANGENA, S. J., DE KORTE, G. J., MCCRINDLE, R. I. & MORGAN, D. L. 2004. The amenability of some Witbank bituminous ultra fine coals to binderless briquetting. *Fuel processing technology*, 1647 - 1662.
- MANGENA, S. J. & DU CANN, V. M. 2007. Binderless briquetting of some selected South African prime coking, blend coking and weathered bituminous coals and the effect coal properties on binderless briquetting. *International Journal of Coal Geology*, 303 - 312.
- MASSARO, M. M., SON, S. F. & GROVEN, L. J. 2014. Mechanical, pyrolysis, and combustion characterization of briquetted coal fines with municipal solid waste (MSW) plastic binders. *Fuel*, 115, 62 - 69.
- MASUDA, H., HIGASHITANI, K. & YOSHIDA, H. 2007. *Powder Technology: Fundamentals of Particles, Powder beds, and Particle generation*, Taylor & Francis.
- MICHAILOVSKI, A. & CILENGI, W. 2016. *Coal binder composition*.
- MODIRI, N. T. 2016. An evaluation of coal briquettes using fixed-bed gasification. Magister thesis. Potchefstroom: North West University School for Chemical and Mineral Engineering.

- MODISE, D. & MAHOTAS, V. 2011. *South African Energy Sector* [Online]. Department of energy. Available: <https://www.usea.org> [Accessed May 2018].
- MOLYNEUX, P. 2018. *Water-Soluble Synthetic Polymers: Volume II: Properties and Behavior*, CRC press.
- MUZENDA, E. Potential uses of South African coal fines: a review. 2014. International Conference on Mechanical, Electronics and Mechatronics Engineering.
- MZAMO, P. 2017. CoalTech completes industry's first economically viable industrial plant. Available: <http://www.miningne.ws/2017/02/06/coaltech-completes-industrys-first-economically-viable-industrial-plant/> [Accessed February 6].
- NKOLELE, A. 2004. Investigations into the reduction of moisture in fine coal by plant tests with surfactants. *The Journal of The South African Institute of Mining and Metallurgy*, 104, 172 - 176.
- OKOLO, G. N., NEOMAGUS, H. W., EVERSON, R. C., ROBERTS, M. J., BUNT, J. R., SAKUROVS, R. & MATHEWS, J. P. 2015. Chemical– structural properties of South African bituminous coals: Insights from wide angle XRD– carbon fraction analysis, ATR– FTIR, solid state ¹³C NMR, and HRTEM techniques. *Fuel*, 158, 779-792.
- POPOV, V. K., POSOSKHOV, Y. M., RACHEV, I. L. & ZAOSTROVSKII, A. N. 2011. Relationship between mineral matter and ash contents of coals from the Bogatyr strip mine of the Ekibastuz deposit. *Solid Fuel Chemistry*, 45, 128 - 134.
- PRODIFLEXCOAL(PTY)LTD 2009. Coal Briquetting. In: LTD, P. C. P. (ed.). Prodiflex Coal (Pty) Ltd.
- REDDICK, J., VON BLOTTNITZ, H. & KOTHUIS, B. 2007. A cleaner production assessment of the ultra-fine coal waste generated in South Africa. *International Journal of Coal Preparation and Utilization*, 4, pp.224-236.
- RICHARDS, S. R. 1990. Physical Testing of Fuel Briquettes. *Fuel Processing Technology*, 89-100.
- SABS 2004. *South African National Standard SANS 10320:2004*, Pretoria, Standards South Africa.
- SCAFER, H. G., CIESLIK, W., OPDENWINKEL, H., VOGTS, A., POPPEL, G. & SCHURMANN, H. 1989. Fuel briquettes. Google Patents.
- SCHÜCKING, H. 2013. Banking on Coal. Available: https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=3&ved=0ahUKEwjEr8Wx46jSAhWLOsAKHekcCLQQFggpMAI&url=https%3A%2F%2Fwww.urgewald.org%2Fsites%2Fdefault%2Ffiles%2Fbanking_on_coal_4_67_6.pdf&usq=AFQjCNHew3zyZovEq5zhUTB6QcAHQ2YvtA&sig2=l8gW0U3ecC5q [Accessed November 04].
- SEKI, H., ITO, O. & IINO, M. 1990. Effect of mild oxidation of bituminous coals on caking properties. *Fuel*, 69, 317-321.

- SELVIG, A. & GIBSON, F. H. Analysis of ash in United States coals. 1956. United States Department of the Interior.
- SINGH, N. 2017. Weathering the 'perfect storm' facing the mining sector. *Journal of the Southern African Institute of Mining and Metallurgy*, 117, 223-229.
- SPEIGHT, J. G. 2005. *Handbook of coal analysis*, John Wiley & Sons.
- SPEIGHT, J. G. 2013. *The chemistry and technology of coal*, CRC Press Taylor and Francis.
- SPENCER, D. 2016. Energy in 2015: A year of Plenty. <http://www.bp.com> [Online]. Available: <http://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2016/bp-statistical-review-of-world-energy-2016-spencer-dale-presentation.pdf> [Accessed June 8].
- STEYN, M. & MINNET, R. C. A. 2010. Thermal coal products in South Africa. *The Journal of the Southern African Institute of Mining and Metallurgy*, 110, 593 - 599.
- TAITS, E. 1976. Plastic properties of coals and their briquetting.
- TAYLOR, J. & MIDDLETON, B. 2004. Comparison of litter decomposition in a natural versus coal-slurry pond reclaimed as a wetland. *Land Degradation & Development*, 15, 439-446.
- VENTER, P. & NAUDE, N. 2015. Evaluation of some optimum binder conditions for coal fines briquetting. *Journal of the South African Institute for Mining and Metallurgy*, 115, 329 - 333.
- VOGT, D. 2016. A review of rock cutting for underground mining: past, present, and future. *Journal of the Southern African Institute of Mining and Metallurgy*, 116, 1011-1026.
- WAGNER, N. 2008. The characterization of weathered discard coals and their behaviour during combustion. *Fuel*, 87, 1687-1697.
- WELLINGTON, S. L. & VINEGAR, H. J. 1987. X-ray computerized tomography. *Journal of Petroleum Technology*, 39, 885-898.
- WOODRUFF, E. B., LAMMERS, H. B. & LAMMERS, T. F. 2017. Coal. *Steam Plant Operation*. McGraw-Hill Education.
- XU, C., HU, S., XIANG, J., YANG, H., SUN, L., SU, S., WANG, B., CHEN, Q. & HE, L. 2014. Kinetic models comparison for steam gasification of coal/biomass blend chars. *Bioresource technology*, 171, 253-259.
- YOON, R. H., PHILLIPS, D. I. & LUTTRELL, G. H. Applications of advanced fine coal cleaning and dewatering technologies. 2000 Virginia. Virginia Polytechnic Institute and State University.
- ZANJANI, N. G., MOGHADDAM, A. Z. & DOROSTI, S. 2013. Physical and Chemical Properties of Beet Pulp/Mezino Bituminous Coal Briquettes. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 35, 2173 - 2180.
- ZHANG, G., SUN, Y. & XU, Y. 2018. Review of briquette binders and briquetting mechanisms. *Renewable and Sustainable Energy Reviews*, 477 - 487.

- ZHANG, J., GE, S. & BAI, Z. 2001. Boiler briquette coal versus raw coal: part II—energy, greenhouse gas, and air quality implications. *Journal of the Air & Waste Management Association*, 51, 534-541.
- ZHONG, Q., YANG, Y., LI, Q. & XU, B., JIANG, TAO 2017. Coal tar pitch and molasses blended binder for production of formed coal briquettes from high volatile coal. *Fuel Processing Technology*, 12 - 19.

ANNEXURES

Annexure A. Batch press results with moisture content

Upon initiation of the project a series of initial tests were performed. These were done on a standard formulation as set out by the patent. The binder was mixed by adding 50 weight % component A (polyacrylic acid) to 50 weight percent de-foamed water. Parallel to this 50 weight percent of component B was added to 50 weight percent de-foamed water. These diluted components were then added in concentrations 2:1. The polyacrylic acid component was the greater of these. A formaldehyde activator was added to the mixture and the mixture was hand shaken. The coal was used on an as is basis and no additional moisture was added to this batch of coal. The binder was mixed in with the coal by dropping using a dropper and manually stirring with a spatula. The binder was added in concentrations of 0 – 1.2 weight percent. Thereafter, the coal was weighed in 1.5 g amounts to fit into a dye for a Lloyd LRX plus press. The results for the different binder additions were found to be lower than the binderless value. This could have been due to the difficulty in capillary suction due to the increase in density of the moisture in the coal. The binderless moisture of this coal batch was around 13 weight percent. The optimal moisture of this coal is presented in Figure A-1 and shows that addition of water above 15 weight percent led to disintegration in the 13 x 13 mm briquette. This was observed along with the squeezing out of water from the coal mixture at water additions above 13 weight percent. This is an indication of the coal approaching its water saturation point.

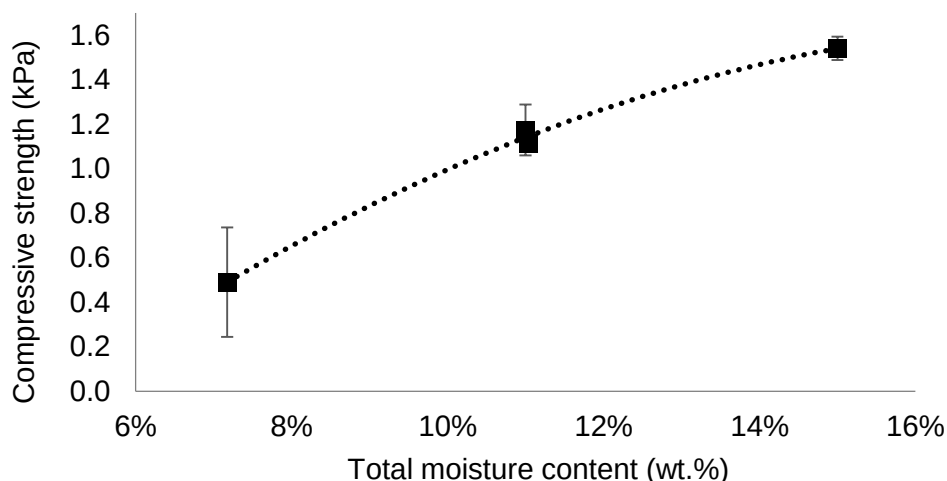


Figure A-1: The moisture addition curve to the binderless coal from air dried to 15 weight percent

As the figure indicates, higher moisture contents should be resultant in higher compressive strength up to a point. From the error bars, it is also noted that the variability decreases with an increase in moisture. The polymeric binder, however, has a density close to that of milk, which could hinder the capillary working in the coal, which works to strengthen the briquette, by creating columns of incompressibility. Table A-1 is a representation of the results obtained from a 13 weight percent moisture batch of coal, to which binder was added in concentrations from 0 – 1.2 weight percent.

Table A-1: Day 0 batch briquetting results for different binder additions for the conclusion on moisture content effects on the briquette strength

Binder addition (weight percent)	Day 0	RSD (%)
0	2.4	4%
0.5	2.2	8%
0.8	1.4	6%
1.2	2.3	15%

From the table it was observed that the variability increases with increase in binder addition. This could be as a result of both mixing limitations caused by an increase in the density and viscosity of the added binder. Figure A-2 is a depiction of the values from Table A-1.

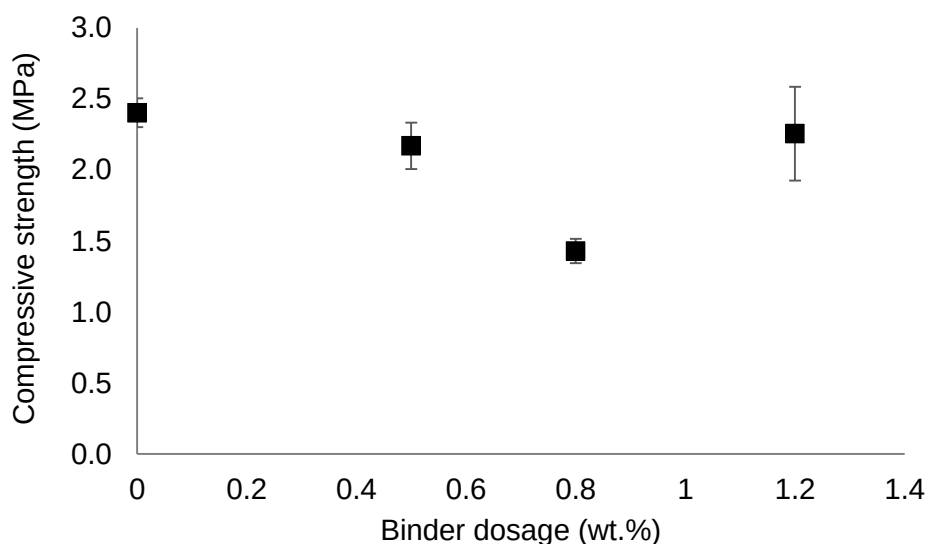


Figure A-2: Resulting compressive strength of the different binder additions up to a 1.2 weight percent concentration

Anomalous behaviour was noted on the 0.8 weight percent binder addition and it was evaluated over 5 days to see whether water evaporation could reverse the decreasing effect. The low variability was a cause to trust that the day 0 results were accurate. The ambient curing profile of the 0.8 weight percent binder addition is shown in Figure A-3.

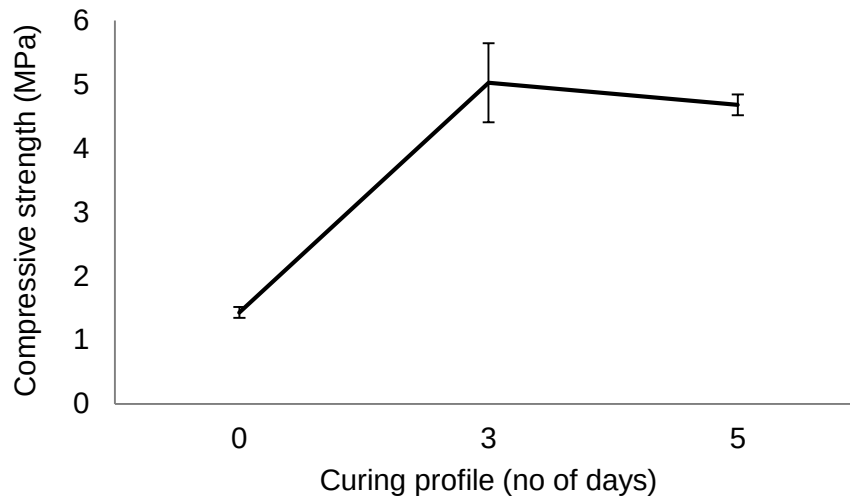


Figure A-3: The curing profile of the 0.8 weight percent binder addition for which anomalous behaviour was noted

The evaporation of water from the surface of the briquette worked to increase the compressive strength. The compressive strength was now higher than its binderless counterpart. The same behaviour was observed from the dry coal (moisture content of around 7 weight percent) as is depicted in Figure A-4.

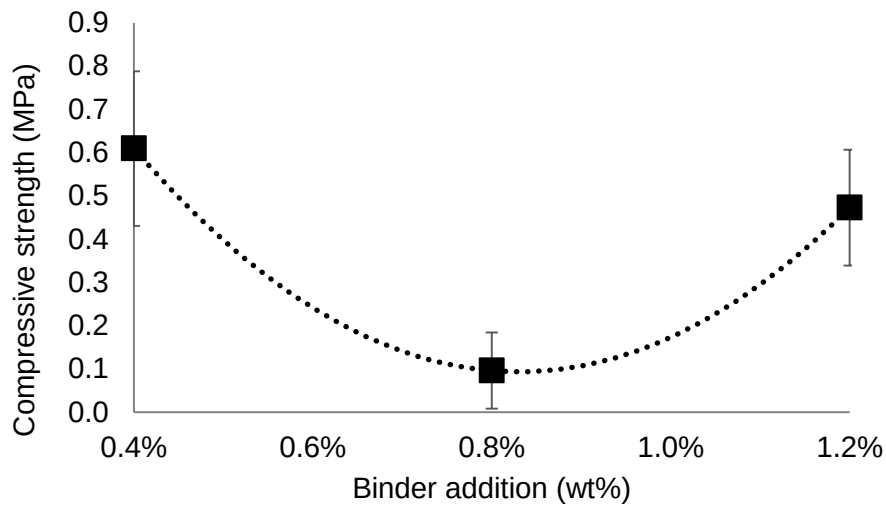


Figure A-4: The concentration profile of a 7 weight percent moisture content coal

The duplicated behaviour of the 08 weight percent binder addition in the air dried coal, is an indication that the 0.8 weight percent binder addition is consistently lower in compressive strength in the binderless mixture.

In conclusion, an increase in surface moisture increases the uniaxial compressive strength. Generally uniaxial compressive strength is increased with increase in binder. Anomalous behaviour is observed in both the dry and moisture added coal.

Annexure B. Variability in mechanical results

The briquettes with a 1.2 weight percent binder addition of standard solution (2:1) was tested and the average of the data was taken. The results would consistently have a high error, since the data would be scattered in such a way that in a single batch of briquettes, there would be some significantly strong and other significantly weak briquettes. This variability in results is depicted in Figure B-5.

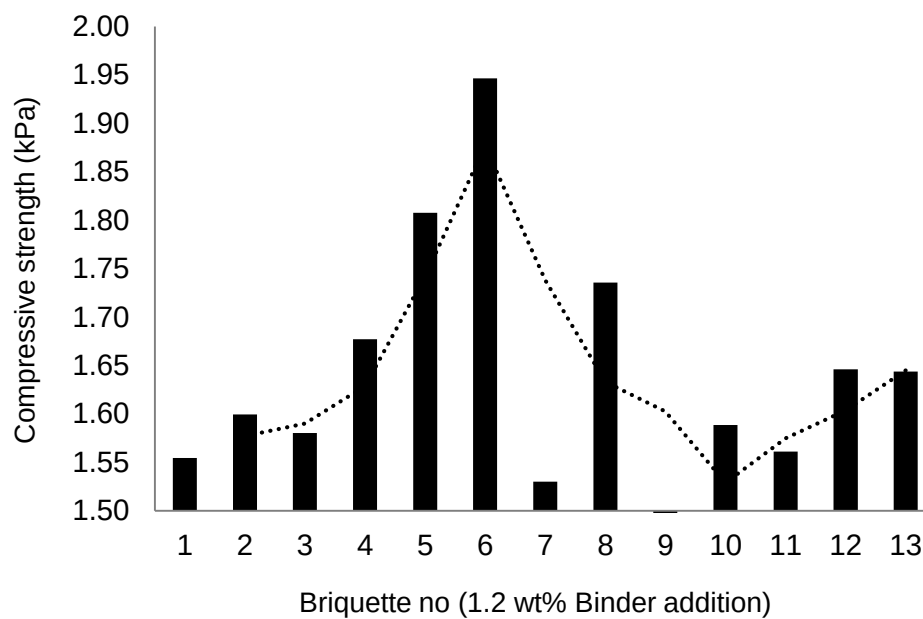


Figure B-5: The data distribution in a batch of briquettes

This is largely due to the variability in the properties of the briquette. This can be attributed to the mixing properties of a low amount of binder into the coal. It can also be attributed greatly to the inhomogeneity of the coal, since the distribution of minerals could then cause a higher affinity towards the binder by certain regions where there are a higher distribution of certain charges and minerals.

Annexure C. Batch press results concentration variation

The batch pressed briquettes were also tested for 3 different variations in components A and B and constant amounts of cross-linker. The concentrations were mixed manually and were homogeneous in appearance. The binder was immediately added to the coal and the coal was briquetted in a 13 by 13 mm mould. No binder or water was depressed from the coal which is an indication that saturation had not yet occurred. The results are shown in Figure C-6.

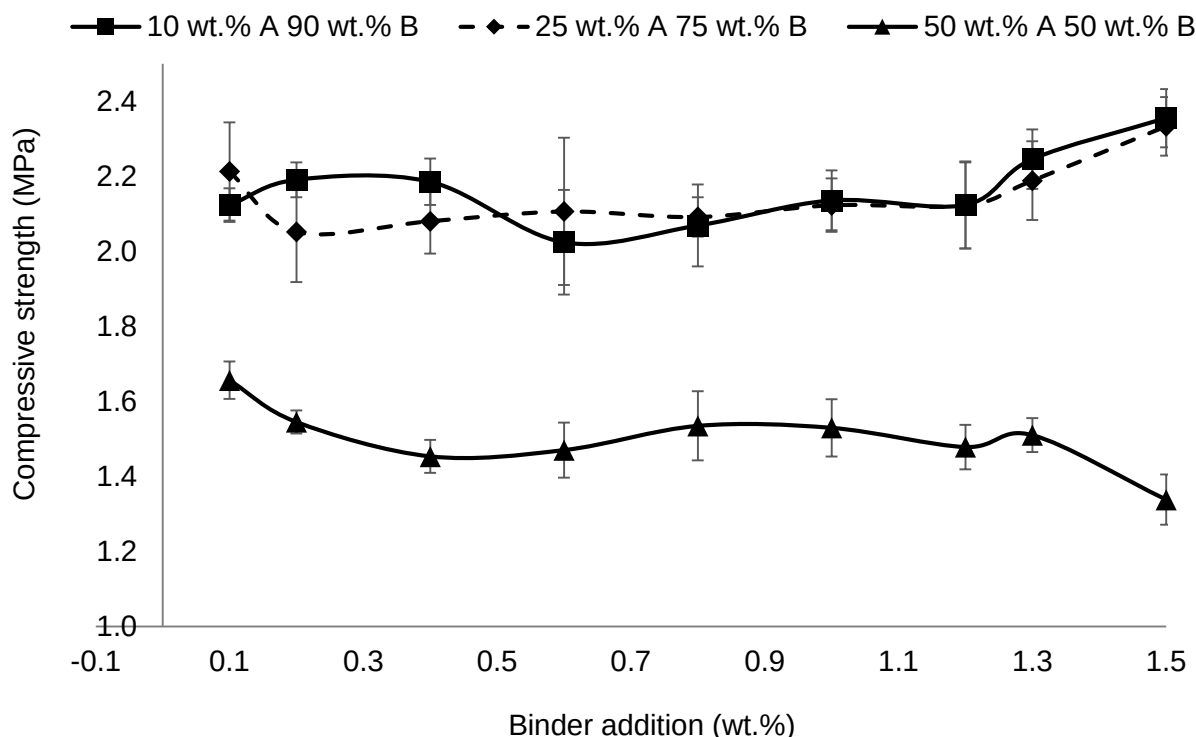


Figure C-6: The uniaxial compressive strength in three variations of binder to scope the effect of the two components with constant amount of cross-linker

The results indicate a correlation between lower amounts of Component A (film forming additive) and higher compressive strengths. Equal measure of the two components yielded relatively low results compared to the two alternate compositions. It can therefore be concluded that at higher concentrations of component A, the briquettes are weaker, so that the component has a maximal amount in which it can be added until the compressive strength is reduced. From the data it can also be seen that the two alternate mixtures show a significant increase in binder uptake from 1.3 weight percent and higher, whereas the opposite is true for the equimolar mixture.

Annexure D. Komarek B050 settings

The Komarek B050 briquetting machine was used in this study for the continuous briquetting of the fine coal. It includes a screw feeder, roller wheels, a pneumatic pump, and a Kenwood mixer. The Kenwood mixer was operated at a mixing speed of 1 which corresponds to 5 rpm. The feed screw was set to 80.4 ± 0.2 rpm and was found to make briquettes that glimmered at this speed (which is a sign of good compression (Mangena et al., 2004)). The briquetting force corresponding to this glimmering briquette was found to be 30 kN (3.0 kgf). After the screw feeder speed and briquetting pressure was fixed, the roller speed was adjusted, to adjust the residence time during which a portion of material was subjected to a force A . This should be equal upwards and downwards for both rollers due to the contact force between the material and the rollers from both sides (Figure D-7).

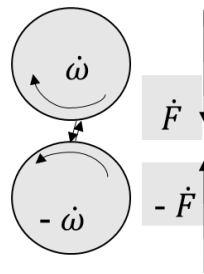


Figure D-7: Rollers on the roller press

The roll speed was set to around 3.2 rpm because of the consistent quality of the briquette. This was determined as is shown in Figure D-8.

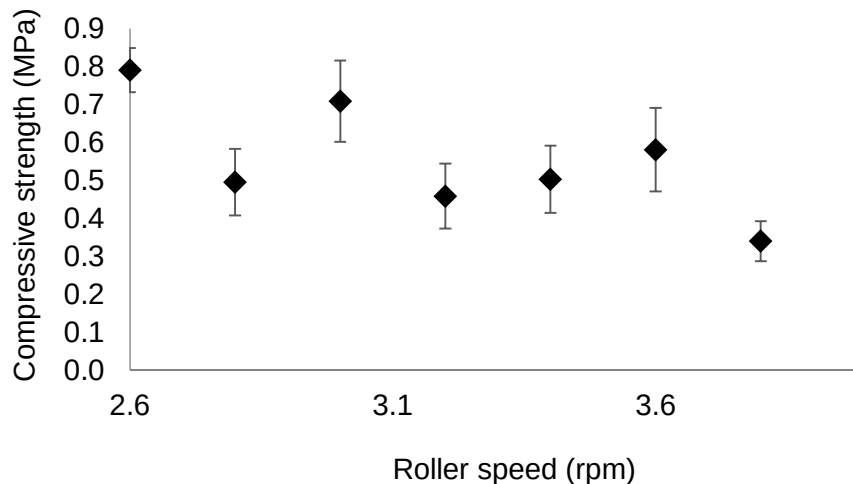


Figure D-8: Roll speed setting vs. compressive strength

Annexure E. Reactivity calibrations

Reactivity calibrations include gas flow calibration and temperature profiling. As well as choosing appropriate settings for TGA analysis. To choose appropriate settings for the TGA analysis dry runs were conducted to evaluate where the different substances would ignite. The flow variation was done to determine possible flow rates that could be used for mass flow effect determination. It was primarily done to determine the error on the Brooks mass-flow controller that had been older and less accurate. The setting in sL/min was plotted against the actual flow rate in Figure E-9.

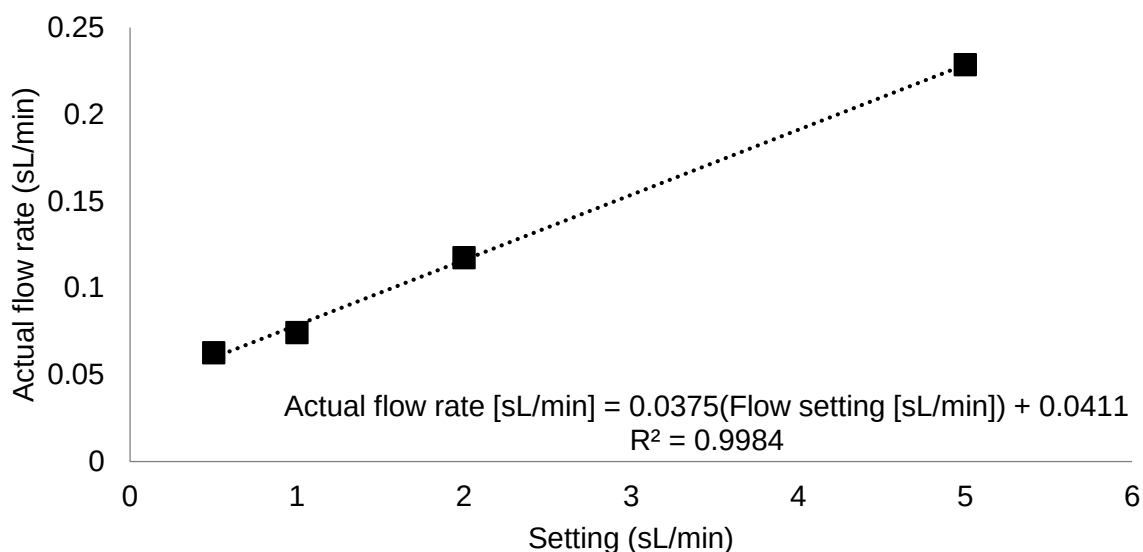


Figure E-9: Flow rate determination

From Figure E-9 it is clear that at a particular setting (x) only 3.7 – 3.8 percent of the mass flow of dry-air was sent through to the TGA. This is the slope of the linearly upward trending line resulting from the correlated plot. The correlation factor of which was found to be 99.8 percent, and relates to the accuracy of these readings.

Annexure F. Variation in Binder Mixing

During the formulation phase of the poly-acrylic binder used in this study, two methods of mixing could have been used. The first was one by which the binder components were added together in their hydrated forms and vigorously shaken by hand. This was done in an air-tight container for ten minutes. The second method involved mixing the binder components in their hydrated forms in an overhead stirrer for different time durations. The results are shown Figure F-10.

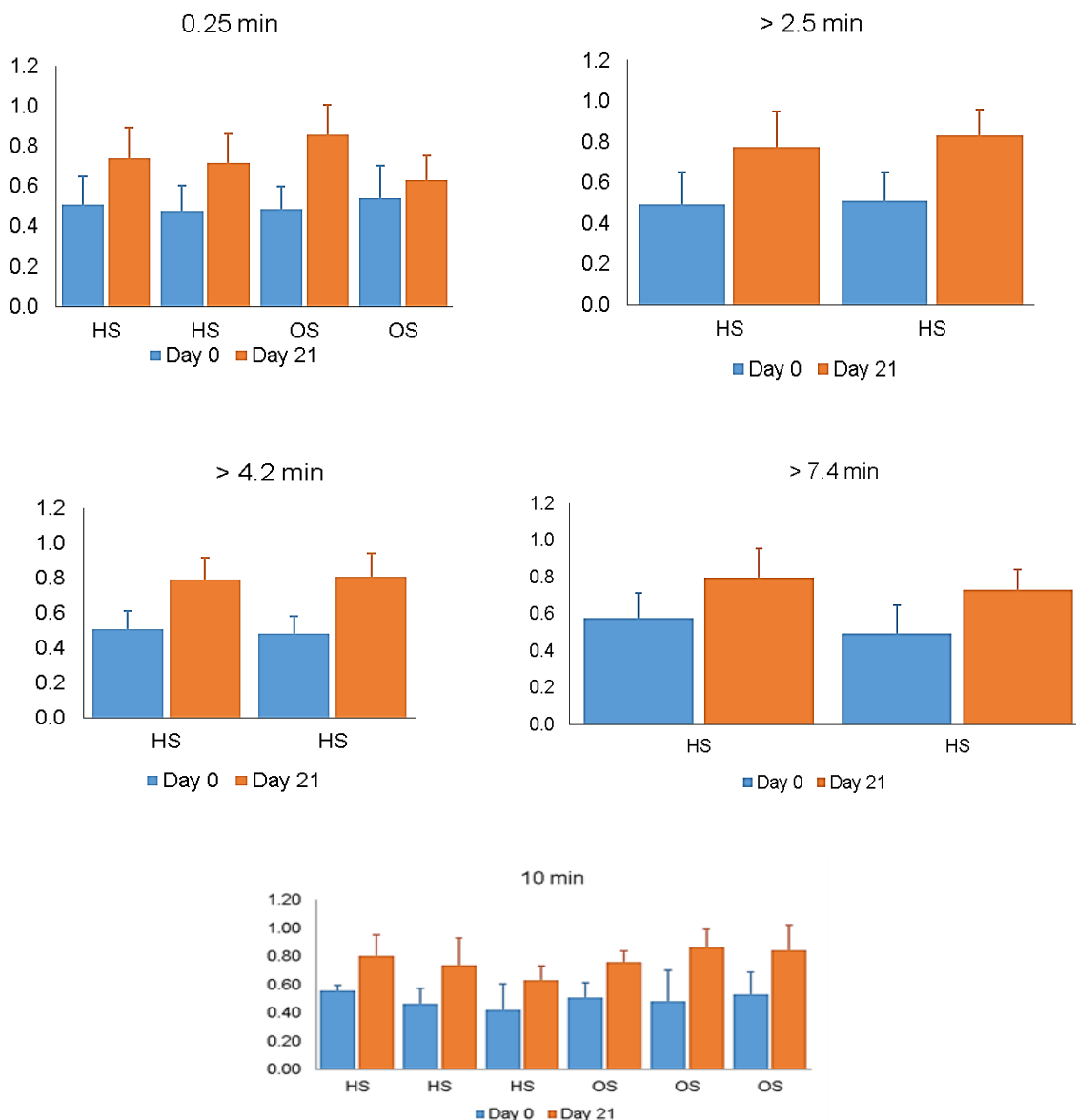


Figure F-10: Cross-linker to components mixing method variation

Figure F-10 shows that the results for both methods are strikingly similar.

It was therefore concluded that the mixing method is not a significantly contributing factor to the compressive strength of the briquettes. It was also observed that the longer mixing of the cross-linker in the binder formulation occurs, the stronger the briquettes, this is especially true for 7.4 and 10 minutes.

The time taken to mix the binder in the coal was also tested, and from the results presented in Figure F-11 it was observed that longer mixing times in the briquetting press led to lower compressive strengths for Coal 2. This could be due to the shearing of the binder within the coal. However, because the margin for error is great in the test method, as well as the formulation make-up, with the added heterogeneity of the coal, it is difficult to isolate a specific reason for this drop. It can also be further debated whether the drop exists, or if there was not a systematic increase in the amount of the very prevalent mineral pyrite, which could hinder the mixing of the binder in the coal. Certainly it would be more reasonable to conclude, that because we lack knowledge of the mechanisms for binding, we cannot with certainty conclude on the shearing of polymers within the coal briquetting process, and more research is required to make valid assumptions.

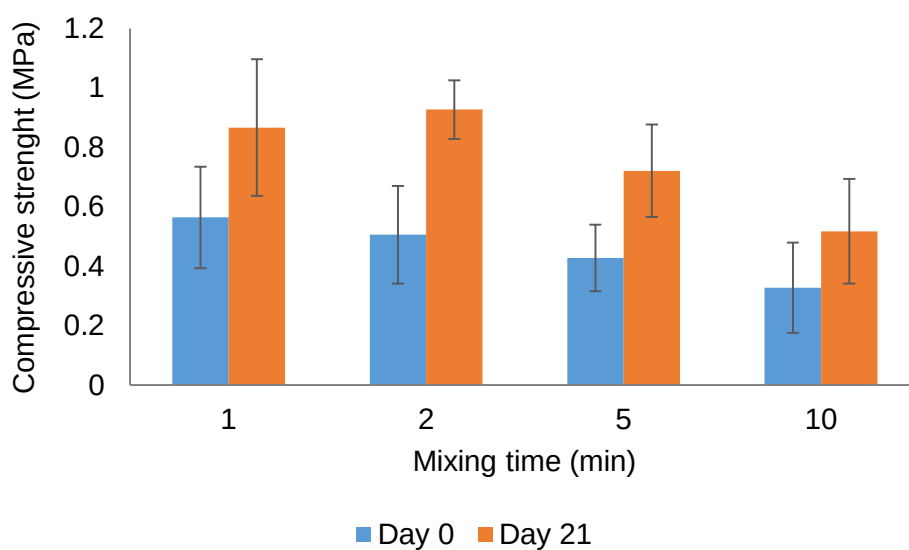


Figure F-11: Binder to coal mixing time variation

Annexure G. Tumbler tests continued

The fines generation potential was observed for various ratios of the active component A, which spanned between 50 – 80 weight percent. For most of the formulations, the briquettes produced less than 10 weight percent fines. The exception to this observation was a formulation containing 71 w. Percent Component A. The results are shown in Figure G-12.

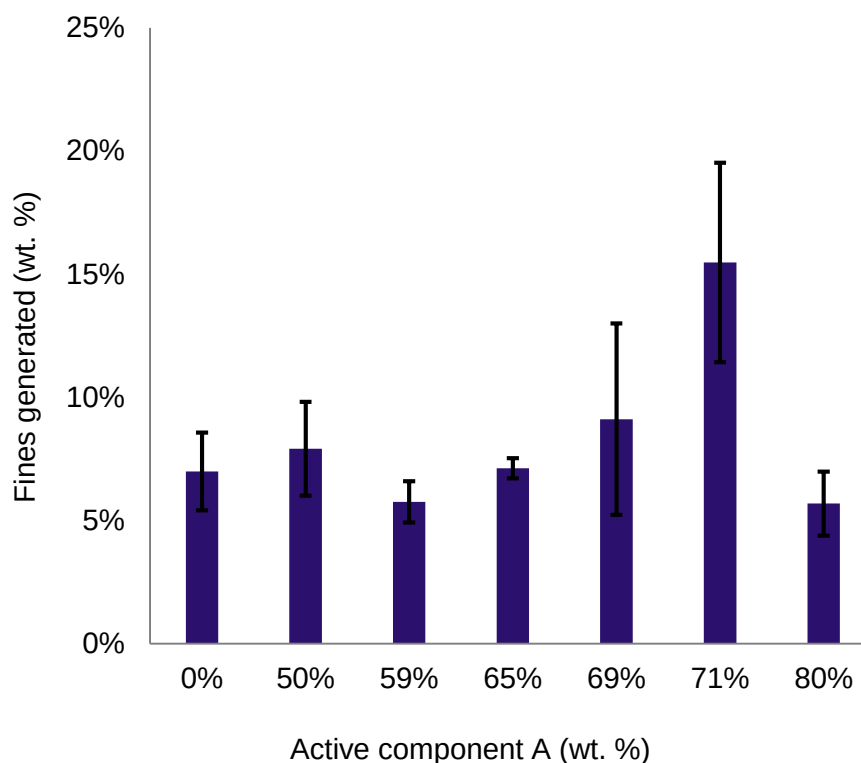


Figure G-12: Fines generated by briquettes of various formulations identified by the amount of Component A in terms of the active components, including binderless at 0 weight percent

It was predicted that once the addition of the various binders to coal was increased less fines would be generated. This was observed to a nearly insignificant extent, considering the uncertainties, except for the anomalous 71 weight percent A, which was later considered an anomalous run, which could be deemed an outlier. Systematic errors could have crept in due to human or equipment errors, creating a batch of significantly weaker briquettes. The 80 weight percent Component A formulation produces less fines than the benchmark PVA, and is therefore the favourable choice for transportation purposes. The results are shown in Figure G-13 and Figure G-14.

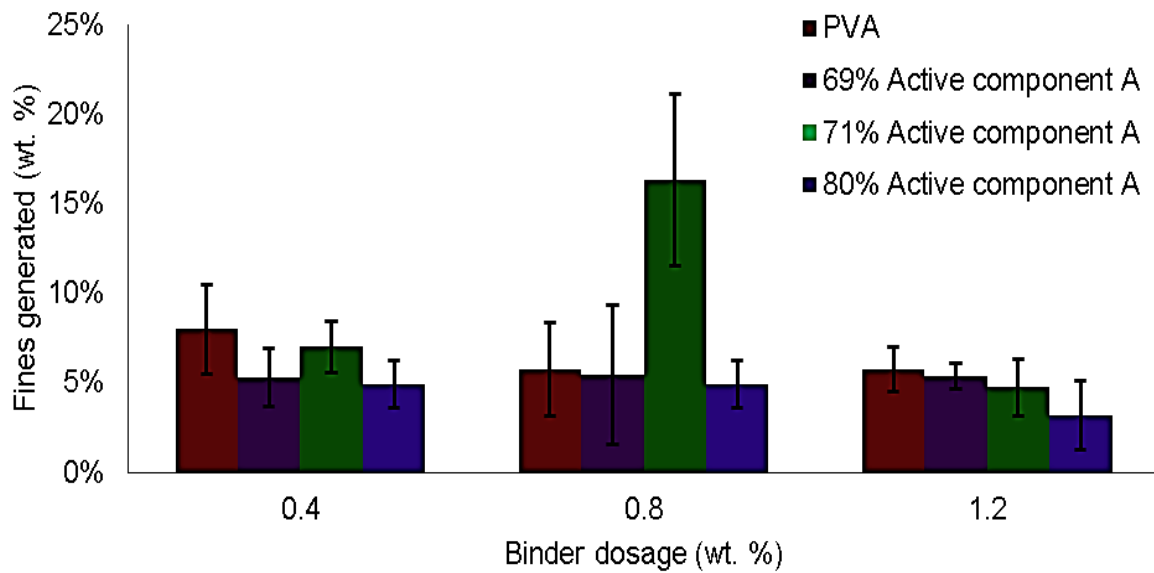


Figure G-13: Fines generated by briquettes of various concentrations and binders

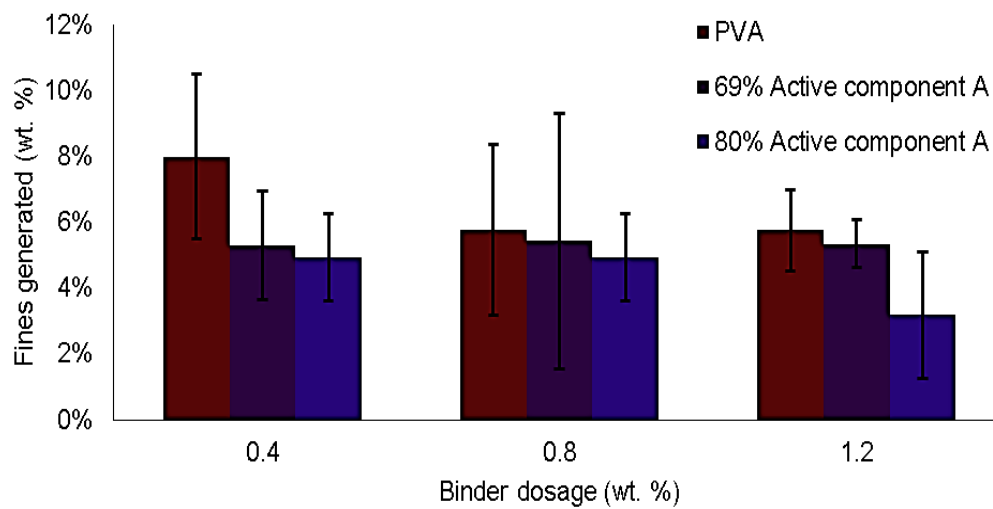


Figure G-14: Fines generated by briquettes of various concentrations and binders without the anomalous run

Annexure H. Full data for experimental design

Table H-1: Full FED data for 0.8 weight percent binder addition

Block/ day	Experiment Number	A	B	XL	H ₂ O	Binder concent ration	0	1	2	7	14	21
Block 1	1	25	10	2	63	0.8	0.4	0.6	0.8	0.7	0.9	1.0
Block 1	2	39	10	1	50	0.8	0.5	0.6	0.8	0.8	0.9	0.8
Block 1	3	27	16	1	56	0.8	0.5	0.5	0.7	0.8	0.9	0.8
Block 1	4	32	17	0	50	0.8	0.4	0.5	0.7	0.7	0.9	0.7
Block 1	5	25	23	2	50	0.8	0.4	0.5	0.7	0.7	0.8	0.8
Block 2	6	25	23	2	50	0.8	0.6	0.8	0.8	1.0	0.9	1.0
Block 2	7	40	10	0	50	0.8	0.4	0.5	0.7	0.7	0.9	0.8
Block 2	8	25	10	0	65	0.8	0.4	0.5	0.7	0.7	0.8	0.8
Block 2	9	30	15	1	55	0.8	0.4	0.6	0.7	0.7	1.0	0.8
Block 2	10	25	10	0	65	0.8	0.4	0.6	0.6	0.7	0.7	0.7
Block 2	11	27	12	2	59	0.8	0.4	0.7	0.7	0.6	0.9	0.7
Block 2	12	25	25	0	50	0.8	0.4	0.6	0.6	0.5	0.8	0.7
Block 3	13	25	17	1	57	0.8	0.4	0.6	0.6	0.6	0.8	0.8
Block 3	14	32	10	1	57	0.8	0.5	0.6	0.6	0.7	0.9	0.8
Block 3	15	32	17	0	50	0.8	0.5	0.6	0.7	0.8	0.8	0.8
Block 3	16	25	10	0	65	0.8	0.4	0.8	0.7	0.9	0.9	0.8
Block 4	17	32	10	0	57	0.8	0.5	0.6	0.7	0.7	0.9	0.7
Block 4	18	25	24	1	50	0.8	0.4	0.5	0.6	0.7	0.9	0.7
Block 4	19	32	17	2	50	0.8	0.4	0.5	0.6	0.7	1.0	0.9
Block 4	20	25	17	0	57	0.8	0.4	0.5	0.7	0.7	0.9	0.7
Block 5	21	25	17	0	57	0.8	0.6	0.9	1.3	1.1	1.2	1.2
Block 5	22	32	17	1	50	0.8	0.4	0.5	0.6	0.7	1.0	0.7
Block 5	23	40	10	0	50	0.8	0.4	0.6	0.7	0.7	0.8	0.7
Block 5	24	32	10	2	57	0.8	0.4	0.5	0.7	0.7	0.9	0.7
Block 5	25	40	10	0	50	0.8	0.5	1.0	1.2	1.3	1.2	1.2
Block 6	26	40	10	0	50	0.8	0.6	0.9	1.1	1.1	1.1	1.1
Block 6	27	25	23	2	50	0.8	0.5	0.8	1.0	1.0	1.1	0.9
Block 6	28	38	10	2	50	0.8	0.4	0.5	0.7	0.8	0.9	0.7
Block 6	29	30	15	1	55	0.8	0.5	0.7	1.1	1.0	1.0	0.9
Block 6	30	25	10	1	64	0.8	0.4	0.6	0.7	0.7	0.9	0.7
Block 7	31	25	10	1	64	0.8	0.5	0.8	1.1	1.1	1.0	1.1
Block 7	32	38	10	2	50	0.8	0.5	0.5	0.6	0.7	1.1	0.8
Block 7	33	32	10	0	57	0.8	0.4	0.6	0.5	0.8	1.0	0.8
Block 7	34	27	19	2	52	0.8	0.5	0.6	0.6	0.7	0.9	0.8
Block 8	35	34	12	2	52	0.8	0.4	0.5	0.5	0.7	0.9	0.8
Block 8	36	25	17	2	57	0.8	0.4	0.5	0.6	0.7	0.8	0.8
Block 8	37	31	12	1	56	0.8	0.4	0.5	0.6	0.7	0.8	0.7
Block 8	38	25	25	0	50	0.8	0.4	0.5	0.6	0.7	0.9	0.8

Annexure I. Other bases for the proximate analysis of the coal

The proximate analysis shown in Section 3.3.1 was a grouping of the different bases used. The following tables are a step-wise base determination that was employed to achieve the table in Section 3.3.1.

Table I-1: Air dry basis for inherent moisture determination

Variable	Standard used	Coal 1	Coal 2
Inherent moisture (%)	ISO 13909-4:2001	6.4	4.2
Ash yield (dry basis) (%)	ISO 1171:2010	22.9	28.9
Volatile Matter (dry-ash free) (%)	ISO 562:2010	23.4	21.2
Fixed carbon (dry-ash free) (%)	By difference	49.4	46.8

Table I-2: Dry basis for ash determination

Variable	Standard used	Coal 1	Coal 2
Ash yield (dry basis) (%)	ISO 1171:2010	23.9	29.8
Volatile Matter (dry-ash free) (%)	ISO 562:2010	24.5	21.9
Fixed carbon (dry-ash free) (%)	By difference	51.6	48.3

Table I-3: Dry ash free basis for fixed carbon and volatile matter determination

Variable	Standard used	Coal 1	Coal 2
Volatile Matter (dry-ash free) (%)	ISO 562:2010	32.2	31.2
Fixed carbon (dry-ash free) (%)	By difference	67.8	68.8

Annexure J. ANOVA analysis for modelled central composite design

The p-values, used to determine factor significance, were obtained from an ANOVA analysis. The analysis was generated with the use of Statistica® 2017 software. This analysis was performed on the central composite design composed of dehydrated components A and B, and is shown in Table J-1.

Table J-1: ANOVA table for the evaluation of the p-value showing significant effects if smaller than a value of 0.05

ANOVA; Variables: Day 21; $R^2 = 0.91$; Adj.:0.86 (CCD) 2 factors, 2 blocks, 10 runs, MS Residual DV: Day 21					
Factor	SS	DOF	MS	F	p
Blocks	2.73E-01	1	2.73E-01	3.20E+01	1.32E-03
(3) A (L)	2.40E-01	1	2.40E-01	2.81E+01	1.82E-03
(4) B (L)	8.60E-05	1	8.60E-05	1.00E-02	9.23E-01
Error	5.13E-02	6	8.54E-03	-	-
Total SS	5.65E-01	9	-	-	-

*SS is the sum of squares, DOF is the degrees of freedom, MS is the mean squares, F is the F-ratio, and p is the p-value.