An evaluation of coal briquettes using various binders for application in fixed-bed gasification

NT Modiri
20897952

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

Supervisor: Prof JR Bunt
Co-supervisors: Prof HWJP Neomagus
                    Prof FB Waanders

November 2016

NORTH-WEST UNIVERSITY
YUNIBESITI YA BOKONE-BOPHIRIMA
NOORDWES-UNIVERSITEIT

It all starts here ™

DECLARATION

I, Nthabiseng Tumelo Modiri, hereby declare that the dissertation entitled: "An evaluation of coal briquettes using various binders for application in fixed-bed gasification", submitted in fulfilment of the requirements for the degree M.Eng (Chemical Engineering) is my own work, except where acknowledged in the text, and has not been submitted at any other tertiary institution in whole or in part.

Signed at Potchefstroom

_____   __21 November 2016__

Nthabiseng T. Modiri   Date

PREFACE

Dissertation format

The format of this thesis is in accordance with the academic rules of the North-West University (as approved on 18 November 2014), where rule **A.4.4.2.9** states: "*Where a candidate is allowed to submit a dissertation or mini-dissertation in the form of a published research article or articles **or as an unpublished manuscript or manuscripts in article format** and more than one such article or manuscript is used, the dissertation or mini-dissertation must still be presented as a unit, supplemented with an inclusive problem statement, a focused literature analysis and integration and with a synoptic conclusion, and the guidelines of the journal concerned must also be included.*"

Due to the dissertation format selected, repetition of discussions may occur.

STATEMENT FROM CO-AUTHORS

To whom it may concern,

The listed co-authors hereby give consent that **Nthabiseng Tumelo Modiri** may submit manuscript(s) as part of her thesis entitled: ***An evaluation of coal briquettes using various binders for application in fixed-bed gasification***, for the degree *Magister in Chemical Engineering*, at the North-West University.

The following manuscript, prepared from Chapter 3 of the dissertation, was accepted in *Journal of The Southern African Institute for Mining and Metallurgy*:

Modiri, N.T.; Bunt, J. R.; Neomagus, H. W. J. P.; Waanders, F.B.; Strydom, C.A. Manufacturing and testing of briquettes from inertinite-rich low grade coal fines using various binders. *Journal of the Southern African Institute for Mining and Metallurgy* (In press).

The manuscript (based on Chapter 4 of the dissertation) to be submitted to *International Journal of Coal Preparation and Utilization, is:*

Modiri, N.T.; Bunt, J. R.; Neomagus, H. W. J. P.; Waanders, F.B. CO_2 reactivity of lignosulphonate and resin bound briquettes.

(This letter of consent complies with rules ***A4.4.2.10*** and ***A.4.4.2.11*** of the academic rules, as stipulated by the North-West University)

Signed at Potchefstroom

_____   _____21 November 2016_____

John R. Bunt   Date

_____   _____21 November 2016_____

Hein W.J.P. Neomagus   Date

_____   _____21 November 2016_____

Frans B. Waanders   Date
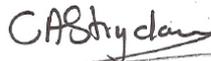
_____   _____21 November 2016_____

Christien A. Strydom   Date

LIST OF PUBLICATIONS

Journal articles

Modiri, N.T.; Bunt, J. R.; Neomagus, H. W. J. P.; Waanders, F.B.; Strydom, C.A. Manufacturing and testing of briquettes from inertinite-rich low grade coal fines using various binders. *Journal of the Southern African Institute for Mining and Metallurgy* (In press).

Conference proceedings

Modiri, N.T. (*presenter*), Bunt, J.R., Neomagus, H.W.J.P. and Waanders, F.B. 2015. Manufacturing and mechanical testing of briquettes from inertinite-rich high ash coal fines using various binders. Poster presented at the 7th Annual Granulation Conference and Workshop, Sheffield, United Kingdom. **(P*oster presentation*)**

Modiri, N.T. (*presenter*), Bunt, J.R., Neomagus, H.W.J.P. and Waanders, F.B. 2015. Manufacturing and testing of briquettes from inertinite-rich high ash coal fines using various binders. Paper presented at the Southern African Coal Processing Society International Coal Conference: August 2015, Secunda, South Africa, ISBN number 978-1-86822-665-8. **(*Oral presentation*)**

Modiri, N.T. (*presenter*), Bunt, J.R., Neomagus, H.W.J.P. and Waanders, F.B. 2015. Manufacturing and testing of briquettes for use in fixed-bed gasification. Presented at the 2015 Fossil Fuel Foundation Conference on sustainable energy, Potchefstroom, South Africa. **(*Oral presentation*)**

ACKNOWLEDGEMENTS

ABSTRACT

South Africa continues to rely considerably on coal as a source of energy and carbon derived chemicals. The rigorous coal mining processes result in the production of over 28 Mt of coal fines per annum. Depleting coal reserves coupled with the dependency of the South African economy on coal utilisation and exportation initiated explorations into fine discard coal utilisation. Binderless agglomeration of vitrinite-rich coal has previously shown great potential, producing mechanically stronger and more water resistant briquettes as compared to briquettes produced from inertinite-rich coal. Fine coal briquetting, while making use of a suitable binder, enhances agglomeration and therefore reduces briquetting (pressing) temperatures and pressures, paving the way for producing durable products to be utilised in industrial applications. In this study, inertinite-rich, low grade coal was used along with 12 binders: clays (attapulgite and bentonite), bio char, cow dung, granulated medium tar pitch, coal tar sludge, flocculant, fly ash, lignosulphonates, polyester resin and 2 South African coal tar pitches in order to produce mechanically strong and water resistant briquettes. The binders were added in various concentrations, and the compressive strength, friability and water resistance of the resultant briquettes were determined. The briquettes manufactured using lignosulphonate and resin as binders resulted in the strongest briquettes, with compressive strengths of 16 and 12 MPa respectively at a 7.5 wt% binder concentration. Cured and uncured, with and without binder addition, the briquettes all retained their shape and size during drop tests, but none proved to be water resistant. Paraffin and wax were therefore used as waterproofing agents after pressing and curing. The reactivity of the lignosulphonate and resin briquettes was compared to that of run of mine coal (lump coal) from the same colliery. Run of mine coal and briquette chars were prepared by devolatilising samples non-isothermally up to 1000°C with a hold time of 15 min. Carbon dioxide gasification was subsequently performed at 875, 900, 925, 950 and 1000°C for the lump coal, binderless, lignosulphonate and resin briquette chars. During the gasification process, the chars exhibited Arrhenius-type dependency on temperature with the initial reactivity increasing with increasing reaction temperature. The addition of the two binders brought no significant change to the reactivity of the chars, but significant reactivity differences were observed between the manufactured briquettes and the run of mine coal chars. Surface area analysis by means of CO_2 adsorption indicated an increase in micropore surface area development of the briquettes post devolatilisation, which was postulated to be the major contributor to the increased CO_2 reactivity of the briquettes when compared to the ROM coal char. Using structural models, the reactivity constants for CO_2 gasification of the run of mine coal, binderless, lignosulphonate, and resin briquette chars were determined. The

mechanical and thermal analyses of the briquettes showed promising results for industrial application, meriting a techno-economic study prior to implementation.

Keywords

Table of Contents

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1. INTRODUCTION

1.1. Overview

Chapter 1 serves as introduction to fine coal briquetting and provides the motivation of this study. In Section 1.2 a brief background is provided, highlighting the importance of coal as well as the purpose of the study. The aim and objectives of the study are given in Section 1.3, and in Section 1.4 the scope of the investigation is set out. An overview of the dissertation layout is presented in Section 1.5.

1.2. Background and motivation

Coal is an organic, combustible rock formed due to the pressures exerted on partially decayed plants (peat) over time, and is used as a primary source of energy. In 2015, coal accounted for 30% of the world's energy needs and 40% of the world's electricity needs as seen in Figure 1.1 (World Coal Association, 2016; BP Global, 2016). In that year, 8165 Mt of coal was produced globally and South Africa, amongst the top 5 coal producers, accounted for 3% thereof as also shown in Figure 1.1 (BP Global, 2016).
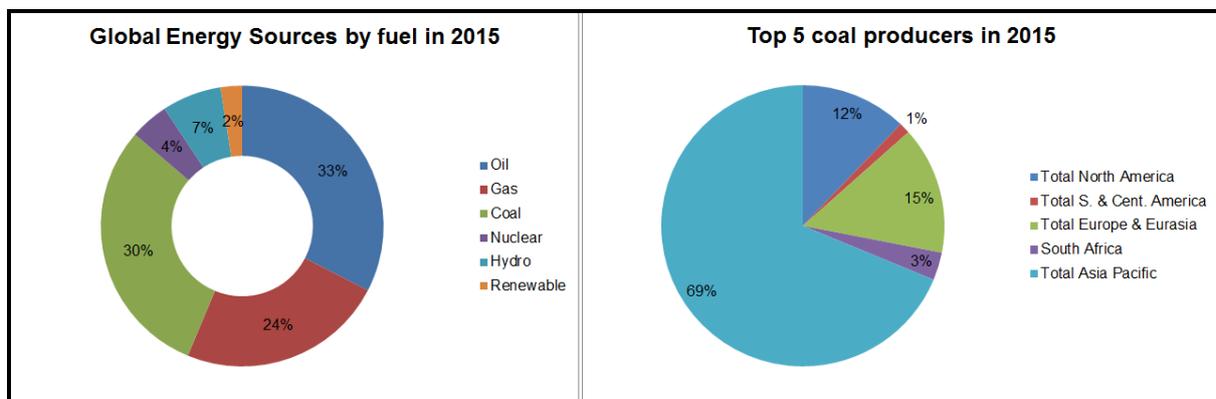
Figure 1.1 Global energy sources and the top 5 coal producers in 2015 (Adapted from BP Global, 2016)

Coal continues to play an essential role in the South African energy industry due to its relative abundance and low cost (SANEDI, 2011). The coal combustion process eventually produces, on average, 90% of South Africa's electricity (Department of Energy, 2016). During coal gasification, synthesis gas is produced for various applications, including the generation of 30% of South Africa's liquid fuels (SANEDI, 2011). South Africa is home to the fixed bed dry bottom (FBDB) gasification technology, which accounts for the conversion of over 30 Mt of coal into liquid fuels annually (van Dyk *et al.*, 2006).

As a result of post mining processing, 11% of South African run-of-mine (ROM) coal generally becomes classified as fine (-0.5 mm) and ultrafine (-0.1 mm), which until recent years, have been discarded into slime dams and underground workings (England, 2000; SANEDI, 2011). Emphasis on the utilisation of fine discard coal locally is continuously increasing as a result of depleting coal mines in conjunction with the deteriorating coal quality of various mines (Jeffrey, 2005; Eberhard, 2007). The heating values associated with South African fine discard coal were found to be up to 21 MJ/kg and can therefore be classified as a viable source of energy (Wagner, 2008). One method of utilising fine coal is through agglomeration for use in technologies that require lump coal, which include fixed-bed gasifiers. There are several techniques for agglomerating fine coal, which are agglomeration by means of (Sastry, 1991):

- Rotating beds, e.g. pelletisation
- Liquid-suspended solids, e.g. flocculation
- Pressure compaction, e.g. briquetting

In this study the focus is on agglomerating fine discard coal through briquetting for application in FBDB gasification. Similar to their ROM coal counterparts, the manufactured briquettes must be mechanically strong, water resistant, thermally stable and similar reactivity. Binderless agglomeration of vitrinite-rich coal fines has yielded mechanically strong and water resistant briquettes. This is mainly due to the vitrinite maceral that deforms and subsequently agglomerates into joined masses at the surface of the briquette with applied pressure – a phenomenon observed to a lesser extent with inertinite-rich coals (Mangena & du Cann, 2007). In order to manufacture acceptable inertinite-rich coal briquettes, binder addition is required. A binder functions as a coherent or adhesive medium between the fine coal particles. Binders can be classified as organic (e.g. coal tar pitch, lignin extracts and starch), inorganic (e.g. alkali silicates, cement and clay), or combinations of both (e.g. coal tar and lime) (Mangena, 2001). Binders that have been investigated for coal briquetting include (Mishra *et al.*, 2000; Dehont, 2006):

- Coal tar pitch
- Petroleum bitumen
- Clay
- Cow dung
- Starch (maize, corn or potato)
- Molasses (beet or sugarcane)
- Lignosulphonates (paper mill residue)

For a binder to be of good quality it must have the following characteristics (Das, 2011):

- Low ash yield
- Easy-burn character
- Non-abrasive
- Easily dispersed
- Non-toxic and environmentally friendly
- Economically feasible

During the FBDB gasification process coal particles are exposed to temperatures ranging between 200 and 1400°C, depending on the existence of hotspots within the gasifier (Glover *et al.*, 1995; Bunt & Waanders, 2008). When inertinite-rich coal is heated to such elevated temperatures at high heating rates, it may undergo thermal fragmentation depending on the initial particle size (van Dyk *et al.*, 2006; Bunt & Waanders, 2008). The creation of fine particles during fragmentation may result in pressure losses within the reactor, causing unstable operation at the top of the gasifier (Keyser *et al.*, 2006; Bunt & Waanders, 2008). Although the FBDB gasifier was designed for a top particle size of 70 mm and a bottom size of 5-8 mm (van Dyk *et al.*, 2006), a study conducted by Bunt & Waanders (2008) showed that the most thermally stable particle size in a FBDB gasifier is between 6.3 and 25 mm by tracking the physical property changes of particles in the reaction zones of the reactor.

The suitability of coal briquettes for fuel production, electricity generation as well as domestic use should continuously be investigated to ensure the lifespan expansion of this finite energy source which motivates this study.

1.3 Aim and Objectives

The aim of this study is to produce and characterise briquettes from inertinite-rich, high ash yield fine discard coal that are mechanically and thermally stable, water resistant and have sufficient reactivity for application in FBDB gasification.

The following objectives were formulated to assist in producing and testing the briquettes:

- Identify suitable binders.
- Quantify the effect of binder type and concentration on the mechanical strength of the manufactured briquettes.
- Determine the effect of binder addition on the water resistance of the briquettes.
- Assess the effect of binder addition on the thermal stability of the briquettes.
- Evaluate the effect of binder addition on the reactivity of the briquettes

- Suggest a suitable kinetic model to predict CO_2 gasification rates for the produced briquettes and ROM coal.

1.4 Scope of investigation

In order to achieve the objectives set out in Section 1.3, the project will be divided into 2 phases, i.e. (1) agglomerate preparation and (2) a reactivity study on the most promising briquette-binder combinations. During the agglomerate preparation phase, the effect of binder type and concentration on the mechanical strength and water resistance of the briquettes will be analysed. The second phase entails the evaluation of the thermal stability and reactivity of the manufactured briquettes. The following scope of investigation was developed:

- Binders are to be acquired and evaluated for their ability to briquette inertinite-rich, high ash coal. These binders are: bio char, clays (attapulgite and bentonite), cow dung, granulated medium tar pitch, coal tar sludge, flocculant, fly ash, lignosulphonates, polyester resin and 2 South African coal tar pitches
- During the agglomerate preparation phase, the effect of binder type and concentration will be analysed by means of compression, drop shatter and water resistance tests. The 2 binders resulting in the strongest and water resistant briquettes will then be identified for use in the second phase of the project.
- During thermal reactivity testing, an in-house large particle thermogravimetric analyser (TGA) will be used to analyse the thermal stability of the briquettes as well as emulate gasification conditions with CO_2 as the reaction gas. Different kinetic models will be tested in order to identify an appropriate model for the determination of CO_2 gasification rates of the manufactured coal briquettes.

1.5 Study outline

In this section, the outline of the dissertation is provided and a schematic thereof is depicted in Figure 1.2.

Chapter 1 provides the background and motivation of this study, highlighting the importance of coal as well as the dependency of South Africa on coal as a primary energy source. The use of fine discard coal through briquetting is motivated as a method of beneficiation and efficient utilisation of coal, in order to increase the lifespan of coal reserves in South Africa. The aim and objectives of the study are also set out in this chapter.
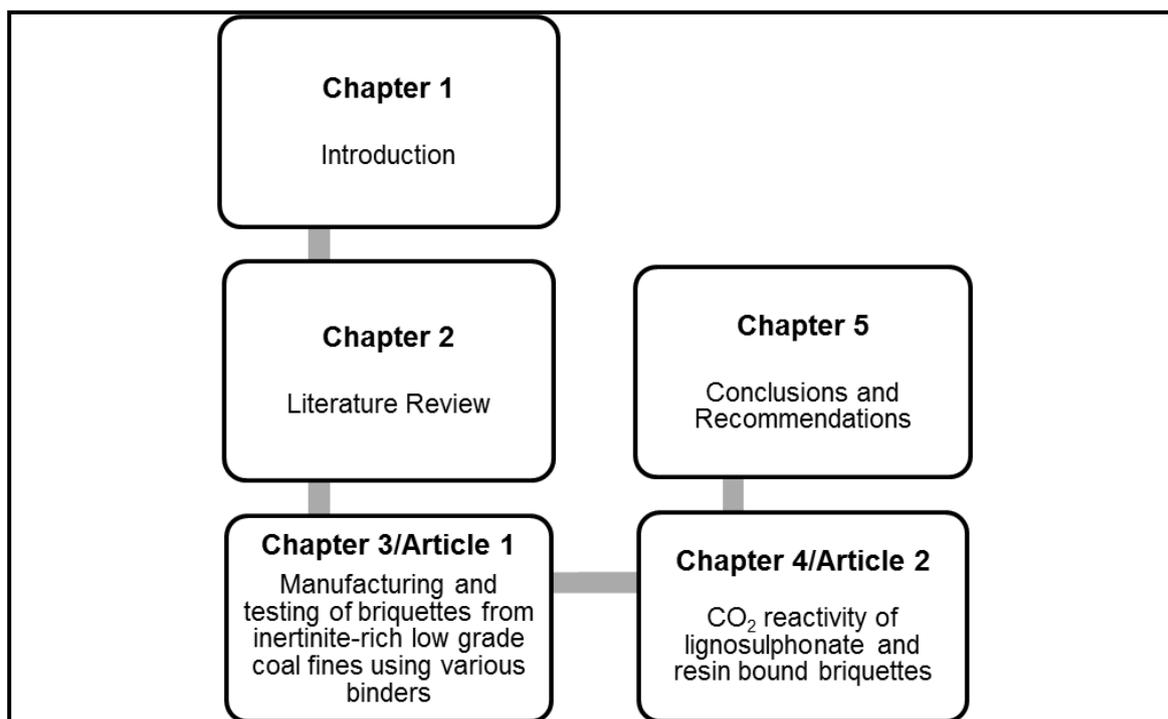
Figure 1.2 Schematic representation of the study outline

The literature review is presented in Chapter 2, providing information regarding the origin and uses of coal. An in depth discussion on fine coal briquetting is provided, presenting the important process variables to be considered during briquetting. The various uses of coal briquettes parallel to those of ROM coal are also given, with the focus on fixed-bed gasification for synthesis gas production. The kinetic models associated with coal gasification are also discussed within the chapter.

South African coal fields are mostly comprised of inertinite rich coal and the first objective of this study is aimed at exploring methods of producing mechanically strong and waterproof briquettes from a South African inertinite-rich, low grade coal. In Chapter 3 the effect of various binders and waterproofing agents on the mechanical strength of the briquettes is determined by means of compressive strength, drop shatter and water submersion tests. The binders and waterproofing agents producing the strongest water resistant briquette configurations will thereby be identified for use in the second phase of the study. This chapter will be reported in article format.

In phase 2 (Chapter 4), the thermal stability and reactivity of the coal briquettes are determined using the binders and waterproofing agents identified from the first phase. The rate determining step during gasification is the reaction between the carbon and steam or carbon dioxide, and the latter will be analysed. The temperatures investigated include 875, 900, 925, 950 and 1000°C. The effect of binder addition on reactivity is assessed while

comparing the briquettes to ROM coal from the same origin. Chapter 4 will also be reported in article format.

The conclusions drawn from the study are provided in Chapter 5, with a list of recommendations regarding future studies on the briquetting and utilisation of inertinite-rich coal fines provided.

Chapter 1 Bibliography

BP GLOBAL. 2016. Statistical Review of World Energy. http://www.bp.com Date of access: 17 September 2016.

BUNT, J.R. 1997. *Development of a fine coal beneficiation circuit for the Twistdraai colliery.* Cape Town.

BUNT, J.R. & WAANDERS, F.B. 2008. An understanding of lump coal physical property behaviour (density and particle size effects) impacting on a commercial-scale Sasol-Lurgi FBDB gasifier. *Fuel*, 87(13-14):2856-2865.

DAS, S. 2011. *Study of decomposition behaviour of binders and the effect of binder type on strength and density of alumina samples.* Doctoral dissertation, National institute of Technology Rourkela.

DE KORTE, G.J. 2010. Coal preparation research in South Africa. *The Southern African Institute of Mining and Metallurgy*, 110(7):361-364.

DEHONT, F. 2006. Coal briquetting technology. Date of access: 1 August 2013. <http://www.sahutconreur.com>

DEPARTMENT OF ENERGY. 2016. Basic Electricity. http://www.energy.gov.za/files/electricity Date of access: 17 March 2016.

EBERHARD, A. 2007. *The future of South African coal: market, investment and policy challenges. Program on Energy abd Sustainable Development.* Stanford.

ENGLAND, T. 2000. *The economic agglomeration of fine coal for industrial and commercial use.* Report for Coaltech 2020.

GLOVER, G., VAN DER WALT, T.J., GLASSER, D., PRINSLOO, N.M. & HILDEBRANDT, D. 1995. DRIFT spectroscopy and optical reflectance of heat-treated coal from a quenched gasifier. *Fuel*, 74(8):1216-1219.

JEFFREY, L.S. 2005. Characterization of the coal resources of South Africa. *The Journal of The South African Institute of Mining and Metallurgy*, 105(2):95-102.

KEYSER, M.J., CONRADIE, M., COERTZEN, M. & VAN DYK, J.C. 2006. Effect of coal particle size distribution on packed bed pressure drop and gas flow distribution. *Fuel*, 85(10-11):1439-1445.

LE ROUX, M., CAMPBELL, Q.P. & SMIT, W. 2012. Large-scale design and testing of an improved fine coal dewatering system. *The Southern African Institute of Mining and Metallurgy*, 112(7):673-676.

MANGENA, S.J. 2001. *The Amenability of some South African bituminous coals to binderless briquetting*. Magister Technologiae dissertation, Technikon Pretoria.

MANGENA, S.J. & DE KORTE, G.J. 2004. *Development of a process for producing low-smoke fuels from coal discards*. Report, Division of Mining Technology, CSIR.

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 of coal properties on binderless briquetting. *International Journal of Coal Geology*, 71(2):303-312.

MISHRA, S.L., SHARMA, S.K. & AGARWAL, R. 2000. Briquetting of lignite for domestic fuel. *Science and Industrial Research*, 59(5):413-416.

MOTAUNG, J.R., MANGENA, S.J., DE KORTE, G.J., MCCRINDLE, R.I. & VAN HEERDEN, J.H.P. 2007. Effect of coal composition and flotation reagents on the water resistance of binderless briquettes. *Coal Preparation*, 27(4):230-248.

RADLOFF, B., KIRSTEN, M. & ANDERSON, R. 2004. Wallerawang colliery rehabilitation: The coal tailings briquetting process. *Minerals Engineering*, 17(2):153-157.

SANEDI. 2011. Release of the coal roadmap. Date of access: 17 March 2016. <http://www.sanedi.org.za/coal-roadmap>

SASTRY, V.S. 1991. *Pelletization of fine coals*. (No. DOE/PC/89766-T4). California Univ., Berkeley, CA (United States). Dept. of Materials Science and Mineral Engineering.

VAN DYK, J.C., KEYSER, M.J. & COERTZEN, M. 2006. Syngas production from South African coal sources using Sasol-Lurgi gasifiers. *Coal Geology*, 65(3):243-253.

VAN DYK, J.C., KEYSER, M.J. & VAN ZYL, J.W. 2001. Suitability of feedstocks for the Sasol-Lurgi fixed bed dry bottom gasification process. (*In* Gasification Technologies Conference. San Francisco. pp. 1-11).

WAGNER, N.J. 2008. The characterization of weathered discard coals and their behaviour during combustion. *Fuel*, 87(8):1687-1697.

WOODS, M.F., HABBERJAM, G.M., ELSWORTH, K. & BENNETT, S. 1963. The effect of maceral compostion on the binderless briquetting of hot char. *American Chemical Society Division of Energy and Fuels Preparation*, 7(2):125-144.

WORLD COAL ASSOCIATION. 2016. Statistics: Coal facts 2015. Date of access: 17 March 2016. <http://www.worldcoal.org/resources>

CHAPTER 2. LITERATURE REVIEW

2.1. Introduction

In Chapter 2 a literature survey on coal and fine coal agglomeration is presented, while highlighting the importance of efficient coal utilisation. Section 2.2 gives an overview of the origin and importance of coal in South Africa, while in Section 2.3 the briquetting process as well as the important process variables involved, are discussed. Finally, Section 2.4 elaborates on the different uses of coal briquettes.

2.2. Coal formation and statistics

The process of forming coal from kerogen is known as coalification. Of the four types of kerogen, Type III (higher plants which are a source of lignin) is the most likely to result in the formation of coal. This is due to the low hydrogen/carbon (H/C) ratio of Type III kerogen that produces a carbon-rich product during catagenesis. The process of coalification is well depicted by the van Krevelen diagram as seen in Figure 2.1 (Schobert, 2013).
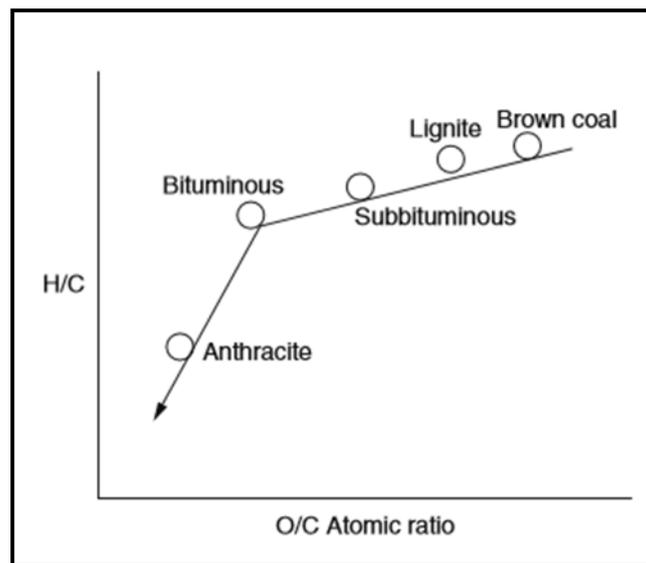
Figure 2.1 van Krevelen diagram taken from Schobert (2013)

As the catagenesis process proceeds, the H/C ratio decreases and the solid matter produced becomes increasingly dense, hard and insoluble. This is clearly indicated by the change in rank of the solid matter, with peat forming brown coal, lignite, sub-bituminous, bituminous coal, anthracite and ultimately graphite (100% carbon) represented by the origin of the van Krevelen diagram (Waters, 1969; Schobert, 2013).

South Africa is amongst the top 5 coal producers in the world having mined just more than 260 million tonnes of saleable coal in 2014 (BP Global, 2015). 70% of the South African coal

reserves are contained within the Highveld, Waterberg, and Witbank (nearing depletion) coalfields (Jeffrey, 2005) and were estimated at 30.2 billion tonnes in 2010 (World Energy Council, 2013).

Coal mined in South Africa accounts, on average, for 90% of the electricity generated (Department of Energy, 2016), over 30% of the petrol and diesel produced as well as the synthesis of over 200 major chemicals (Spath & Dayton, 2003; van Dyk *et al.*, 2006). Coal is furthermore one of the highest contributors to revenue generated by primary mineral commodities through domestic trade and export (SAMI, 2015). It is essential to continue using the remaining coal resources cautiously considering the dependency of South Africa on coal. One such method for prolonging the coal lifespan is through the briquetting of discarded coal fines for use in lump coal applications, which is discussed in depth in the sections to follow.

2.3. Fine coal agglomeration

Coal fines are produced as a result of the rigorous mining and post-mining processes (Mangena, 2001; Radloff *et al.*, 2004). Approximately 11% of mined coal (run of mine or ROM) is classified as fine and ultrafine, resulting in the generation of 28.7 million tonnes of coal fines in South Africa in 2014 (England, 2000; SANEDI, 2011; BP Global, 2016). It is often difficult to handle, transport or use these fines as-received due to their high moisture content (in the order of 20%) and high ability to be carried by wind, which thereby increases pollution concerns. The high moisture retention of coal fines results in low calorific values, high transportation costs as well as difficulty in off-loading due to the sticky nature of the fines (England, 2000; Mangena, 2001). Considering South Africa's continued dependency on coal along with the depreciation of economically extractable coal, it is safe to conclude that fine coal agglomeration for commercial use has become a necessity.

Agglomerates can be manufactured by means of briquetting, pelletizing or spherical agglomeration – flocculation. The main differences in agglomeration techniques include the equipment used, agglomerate shape, size and density (Sastry, 1991; England, 2000; Kaliyan & Morey, 2009). During spherical agglomeration oil is added to a suspended coal-water slurry which will act as a binder at adequate oil concentrations and mixing speeds (Sastry, 1991; England, 2000). Pelletizing can be achieved with the aid of extrusion, pan pelletizing or drum agglomeration with a final pellet size of at least 6 mm (Sastry, 1991; England, 2000; Kaliyan & Morey, 2009). Briquettes are produced either continuously using a roller press or individually by applying pressure on material inserted inside a die (England, 2000; Kaliyan & Morey, 2009). The majority of South African coalfields contain inertinite-rich coal (Falcon &

Ham, 1988); hence the focus is on the applicability of briquetting inertinite-rich fine discard coal.

The first briquettes produced date back to the 15th century, when the Chinese manufactured briquettes using cow dung and clay as binders. The briquettes were moulded into the desired shape and size and left to dry. This technique resulted in briquettes that were not mechanically strong and possessed low calorific values. Only in the 1850's did briquetting methodologies become more progressive, but reached an ultimate high in the 1960's when oil and gas prices increased (England, 2000). Declining coal reserves and environmental legislations have led to the re-visiting of coal briquetting as a form of fine discard coal utilisation in coal dependent countries such as South Africa (Mangena *et al.*, 2004).

Briquettes can be produced with or without the use of a binder. When manufacturing binderless briquettes, high pressures are employed either at low or high enough temperatures for the coal to go into the plastic state (England, 2000; Mangena *et al.*, 2004). Although binderless briquetting is the most economic form of briquetting, it is not always applicable. Process variables to be considered during briquetting with the aid of a binder are discussed in the sections to follow.

2.3.1. Forces associated with briquetting

Prior to agglomerating, inter-particle voids are generally in the range of 35 – 55% depending on the particle size distribution of the fines. When applying pressure to the fines, the particles are brought into closer proximity, thereby reducing the inter-particle voids to approximately 10% (Waters, 1969). The reduction of inter-particle spaces gives rise to several forces that aid the agglomeration process. Waters, (1969) and Sastry, (1991) listed the forces under consideration as capillary, magnetic and electrostatic, mechanical interlocking (attractive forces) of the particles, solid bridges, and van der Waals forces. While considering the forces associated with briquetting on a microscopic level, Chung (1991) proposed that attractive forces between particles of miscellaneous shapes are initiated by bringing particles into close proximity (as close as 9 Å). Upon reaching maximum force, chemical bonding is activated. Macroscopically, Chung (1991) suggested that binding could be possible with or without solid bridge formation. In the absence of solid bridges, attractive forces such as valence forces, hydrogen bonds, van der Waals, electrostatic and magnetic forces dominate. Solid bridges form as a result of the hardening of added binders wetting various particle surfaces.

2.3.2. Particle Size Distribution (PSD)

In order to formulate durable briquettes, good mechanical interlocking of particles is required (Dehont, 2006). Particle interlocking is enhanced when a wide particle size distribution is utilised, allowing finer particles to fill the voids created by bigger particles (Dehont, 2006; Kaliyan & Morey, 2009). Various researchers found that a particle size distribution of 0 – 3 mm produced mechanically strong briquettes, with the majority of the particles in the range of -1 mm (Payne, 2006; Kaliyan & Morey, 2009). Table 2.1 provides the average particle size distribution required to manufacture mechanically strong briquettes as suggested by Dehont (2006) and Payne (2006).

Table 2.1 Average particle size distribution for durable briquettes

Sieve size (mm)	Material retained on sieve (%) [1]	Material retained on sieve (%) [2]
>3	-	≤1
2-3	5	≤5
1-2	20	~20
0.5-1	25	~30
0.25-0.5	50	~24
0-0.25		≥20

[1] Taken from Dehont (2006), [2] Taken from Payne (2006)

Although fine material is required for briquette production, costs associated with size reduction must also be taken into account to ensure feasibility of the process.

2.3.3. Initial moisture content

Surface moisture may be utilised as lubricant or even binding material during the briquetting process (Kaliyan & Morey, 2009). There is an optimum initial moisture content for the coal fines when considering briquettability as well as mechanical strength of the resultant briquettes (Waters, 1969; Mangena *et al.*, 2004; Dehont, 2006). The surface moisture softens the finer particles, increasing their amenability to briquetting. Dehont (2006) found that briquettes produced from fines containing 2 – 3% surface moisture exhibited the highest compressive strength, while moisture above 5 – 6% created handling difficulties post production. Mangena *et al.* (2004) observed a direct correlation between briquette

compressive strength and percentage moisture added to the fines up to 6%, with further increases resulting in a reduction in compressive strength.

2.3.4. Coal rank

All coals are amenable to briquetting, but the overall briquetting conditions highly depend on the rank of the coal in use (Waters, 1969; England, 2000). Soft coals such as brown and lignite coals can be compacted without employing high temperatures or pressures (Waters, 1969). As the rank is increased to sub-bituminous and bituminous coals, higher pressures and/or potential size reduction and binder addition is required. Briquetting anthracite coal requires the use of elevated temperatures as well as the addition of binding material to ensure acceptable mechanical strength of the resulting briquettes (Waters, 1969; England, 2000).

2.3.5. Coal maceral composition

Macerals are organic elements found in various combinations within coal and are divided into three main categories, namely inertinite, liptinite and vitrinite (Mangena, 2001; Kidena *et al.*, 2002). Briquettability of coal is dependent on, amongst other things, the plasticity of the coal; a characteristic that can be allotted to the vitrinite content of the coal (Kidena *et al.*, 2002). During their study on the agglomeration of several South African coals, Mangena and du Cann (2007) microscopically observed the distortion and subsequent linking of the reactive macerals into joined masses at the surface of the briquette with pressure, thereby increasing its strength – a phenomenon observed to a lesser extent for inertinite-rich coals. Woods *et al.* (1963) concluded that the inertinite concentration varied indirectly with the mechanical strength of the prepared coal char briquettes.

2.3.6. Coal clay minerals

Clays form a major part of the mineral matter contained in coal and play a vital role during binderless briquetting (Wells *et al.*, 2005; Mangena & du Cann, 2007). The presence of kaolinite, in particular, reduces the water resistance of binderless briquettes if the coal ash yield is above 15% (Mangena & du Cann, 2007). This phenomenon was found to be as a result of the plastic nature of kaolinite when submerged in water (Heckroodt, 1991; Mangena & du Cann, 2007).

2.3.7. Briquetting conditions

Thus far, the discussion on the briquettability of coal has solely been based on the nature of the coal utilised. The effect of the initial coal conditions can, to a certain degree, be overcome by employing the most suitable briquetting conditions. This manipulation of

conditions, however, is a function of processing costs (Waters, 1969). In the following section, the briquetting temperature and pressure as well as binder addition is discussed.

a. Temperature

Fine coal agglomeration (briquetting) can be achieved by means of low or high temperature briquetting (England, 2000; Kaliyan & Morey, 2009). Increasing the pressing temperature allows for plastic deformation of the coal and in turn promotes the formation of permanent bonds between particles (Kaliyan & Morey, 2009). For binderless briquetting at elevated temperatures, the thermoplastic properties of the coal provide a good indication of the required pressing temperatures in order to reach the softening point of the coal in use. The plasticity of coal is highly dependent on its maceral composition, with the reactive macerals (liptinite and vitrinite) contributing the most to the coal thermoplastic behaviour (Coetzee *et al.*, 2014). When considering binder utilisation, the increase in pressing or post-briquetting temperature is a function of the activation temperature of the specific binder in use (Finney *et al.*, 2009). England (2000) suggested that lignosulphonate, molasses and starch bound briquettes be treated at 200 -300°C to ensure the mechanical strength and water resistance of the briquettes. While investigating the effect of curing temperature on briquette strength, Blesa *et al.* (2003b) concluded that a curing temperature of 95°C produced the strongest humate-bound briquettes.

b. Pressure

During briquetting, the application of pressure brings fine particles in enough proximity to each other to initiate particle interlocking and short-range forces causing the particles to adhere to each other (Kaliyan & Morey, 2009). Coal hardness and plasticity determine the pressure required to manufacture mechanically strong briquettes (Waters, 1969; Mangena & du Cann, 2007). Softer coals, such as lignites, require moderate pressures compared to harder coals during briquette production (Waters, 1969). Pressing pressures of 150 and 232 MPa were found suitable for the binderless agglomeration of lignite and bituminous/sub-bituminous coals, respectively (Waters, 1969; Ellison & Stanmore, 1981). The briquetting pressure largely influences the resultant briquette density and therefore strength, up to a certain extent – which is determined by the material type, moisture content, PSD as well as the pressing temperature implemented (Rhén *et al.*, 2005; Stelte *et al.*, 2011; Wongsiriamnuay & Tippayawong, 2015). During their investigation of the amenability of South African coals to binderless briquetting, Mangena and du Cann (2007) found a direct correlation between briquetting pressure and agglomerate compressive strength. While pelletizing a variety of biomass derived materials, Stelte *et al.* (2011), observed a significant

increase in pellet density at pressing pressures below 250 MPa, above which minor density increases were noted.

c. Binders

The addition of binders during briquetting becomes a necessity when the manipulation of other process variables (initial moisture content, particle size distribution and briquetting conditions) fails to yield briquettes that meet the minimum requirements (Finney *et al.*, 2009). Generally when briquetting hard coals such as sub-bituminous, bituminous and anthracite, binder addition is required, depending on the plasticity of the coal (Waters, 1969; Mangena *et al.*, 2004; Mangena & du Cann, 2007). Binders that have been investigated for coal briquetting separately or in various combinations include (Mills, 1908; Waters, 1969; Mishra *et al.*, 2000; Dehont, 2006):

- *Clay*

   Clay, more specifically bentonite, was one of the first materials to be considered for its binding abilities (Waters, 1969; England, 2000; Dehont, 2006). Briquettes produced using clay as binder, were found to be mechanically weak and required heat treatment to increase handling capabilities (Mills, 1908). Clay produces thermally stable briquettes, but adds to the ash yield of the final product (Mills, 1908; Waters, 1969). In order to ensure the water resistance of briquettes, the clay must be added in low concentrations due to its plasticity in the presence of water (Heckroodt, 1991). Although affordable, clay was found to be more suitable when used as a binder in the production of low grade fuel briquettes (Mills, 1908).

- *Coal tar pitch*

   Pitches have been utilised as coal binding agents due to their enhancement of mechanical strength and water resistance of briquettes (Mills, 1908). Coal tar pitch can either be added in the granular or molten state (Waters, 1969; Dehont, 2006). In order to initiate binding, the pitch (hard or soft) requires melting and re-solidification within the coal (Waters, 1969). Due to its carcinogenic nature and high smoke propensity, coal tar pitch has generally been replaced with bitumen which produces less harmful gases during utilisation (Mills, 1908; Waters, 1969; England, 2000).

- *Petroleum bitumen*

   Bitumen possesses similar binding capabilities as coal tar pitch with lower toxic gas emissions (England, 2000). The main difference between bitumen and pitch bound

briquettes is the susceptibility of bitumen briquettes to heat, causing them to weaken during the early stages of utilisation (Waters, 1969).

- *Cow dung*

The utilisation of biowaste material such as cow manure has enjoyed great attention under the coal/biomass co-firing topic over the years (Mishra *et al.*, 2000; Sweeten *et al.*, 2003; Sanchez *et al.*, 2009; Emerhi, 2011). In the past, dried cow manure was used as a source of energy in poor households (Idah & Mopah, 2013). Although affordable for household use, previous studies have shown that the use of animal manure as a fine coal binder does not enhance the calorific value or the mechanical strength of the resultant briquettes (England, 2000; Mishra *et al.*, 2000; Sweeten *et al.*, 2003).

- *Starch (maize, corn or potato)*

Organic compounds such as starch are mostly known for their low smoke characteristic. Although starch can significantly increase the mechanical strength of coal briquettes, it does not enhance the water resistance of the briquettes (Mills, 1908). In order for starch to be an effective binder, moisture addition is required during the briquetting process with subsequent heat treatment of the briquettes (Waters, 1969; Kaliyan & Morey, 2009).

- *Molasses (beet or sugarcane)*

Another hydrophilic organic compound investigated for its binding abilities is molasses (Waters, 1969). Classified as a matrix type binder, molasses is required in high concentrations in order to promote maximum solid bridge formation between particles during binding (Blesa *et al.*, 2003a). For appropriate activation, Blesa *et al.* (2003a) found that curing molasses-bound briquettes at $200\circ$C for 2 hours produced mechanically strong briquettes.

- *Lignosulphonates (paper mill residue)*

Investigated for their binding properties also are lignosulphonate and kraft lignin, derived from lignin, which is the strengthening agent in plants and trees (Boudet, 2000; Ekeberg *et al.*, 2006). This complex polymer requires heat treatment in order to soften the lignin, creating solid bridges which in turn enhance briquette mechanical strength (England, 2000; Kaliyan & Morey, 2009; Halt & Kawatra, 2014). Lignosulphonate is a hydrophilic compound, which requires addition of hydrophobic

compounds or heat treatment to ensure the water resistance of briquettes (England, 2000; Halt & Kawatra, 2014).

When selecting a suitable binder, consideration needs to be given not only to the end-use of the briquettes, but also the cost implications associated with purchasing and utilising the binder.

Similar to their ROM coal counterparts, briquettes have a wide range of uses both in a household and industrial context. In Section 2.4 the various processes for which briquetting could be ideal are discussed.

2.4. Utilization of briquettes

In Sections 2.4.1 and 2.4.2 the feasibility of fine coal briquetting for household and industrial use is discussed. The product requirements and possible testing techniques will also be provided for each of the uses.

2.4.1. Household usage

Post 1994, the South African Department of Energy embarked on the Integrated National Electrification Programme (INEP) which has resulted in the electrification of 87% South African households (Department of Energy, 2012). Despite these efforts, low-income homes continue to use alternative fuels such as coal, gas, wood and paraffin for cooking and heating purposes – as substitution or reduction of electricity usage (Department of Energy, 2012; Matinga *et al.*, 2014). The burning of coal, wood and/or paraffin may lead to health complications such as respiratory illness, cancer and even death (Matinga *et al.*, 2014; Pieters & Focant, 2014). Studies have shown that the indoor use of these alternative fuels bares greater influence on health than pollutants emitted industrially (Barnes *et al.*, 2009; Klausbruckner *et al.*, 2016). Parallel to mitigating industrial pollution from fossil fuel utilisation, there has been a great drive to reduce the effects of indoor use of solid fuels in low-income households over the past two decades (Matinga *et al.*, 2014).

Methods investigated for indoor pollution reduction include low-smoke fuel production and the Basa Njengo Magogo (BNM) ignition technique (Mangena & de Korte, 2004; Matinga *et al.*, 2014). When applying the BNM ignition technique, which is the cheapest process to implement, the majority of the coal is placed below the wood and paper and the rest on top. That way the volatiles emitted by the coal are burned by the wood and paper (Mangena & de Korte, 2004). This, however, does not prevent the indoor emission of cancer causing heavy metals from the coal such as lead and mercury (Matinga *et al.*, 2014).

During their low-smoke fuel production analysis, Mangena and de Korte (2004) reviewed studies by Tait and Lekalakala (1993), Horsfall (1994) and England (1993). Tait and Lekalakala (1993) manufactured briquettes consisting of coal duff and cement for use in coal stoves. Emissions tests showed a reduction in smoke during combustion, however, the briquettes shattered during use. Consequently, stove temperatures were reduced as a result of fuel bed blockages. Tait and Lekalakala (1993) managed to enhance the thermal stability of the briquettes by adding $CaCO_3$, however, the question of ignition time and combustion temperatures was not addressed during testing (Mangena & de Korte, 2004).

England (1993) investigated the feasibility of producing binderless, smokeless briquettes from bituminous waste for export purposes. The investigation entailed beneficiation of ultra-fine coal using pneumatic cells, briquetting the flotation product and finally devolatilising the briquettes at 500 – 750°C for 2 hours. From an economic and technical perspective, the project was deemed a success. Pilot scale production of the briquettes was required to not only certify that British standards for domestic fuels were met, but also to ensure the acceptance of the briquettes by the end-users (England, 1993). No further details were found on the implementation of this research.

Horsfall (1994) investigated the production of low-smoke fuel by washing and devolatilising discard coal. On laboratory scale, the process could result in the production of up to 50 kg/day of fuel using a muffle oven. The fuel contained 12% volatile matter, was easy to ignite, thermally stable and produced low smoke during combustion. The required capacity for testing the briquettes in the townships was 5 – 50 tonnes of briquettes. The process was therefore scaled up using a stoker char unit, resulting in the production of fuel containing 5% volatile matter. This fuel was difficult to ignite and slow to react, and was consequently not accepted by the community (Mangena & de Korte, 2004).

Mangena and de Korte (2004) filtered and dried ultra-fine coal beneficiated through froth flotation. The dried fines were agglomerated using a roller press, and the briquettes were subsequently devolatilised at 500°C. The final product resulted in the least particulate emissions and compared well with raw coal when considering fuel ignition time. The low-smoke briquettes did, however, have the lowest heating value compared to anthracite and raw coal. The initial estimation of costs associated with this process yielded a product cost feasible for the domestic fuel market. Community trials were still required to affirm the target market acceptance, as well as technical and economic feasibility on pilot scale (Mangena & de Korte, 2004). No further research on the implementation of this study was found.

Key parameters that address the convenience and health implications associated with using the produced low-smoke fuel need to be tested. These include; ignition time, heating value,

time to boil a pot of water, and gas/particulate emissions (le Roux, 2003). While analysing these key parameters, Kühn (2015) found that devolatising coal at 550°C produced low-smoke fuel exhibiting a good balance between fuel usability and reduction of harmful emissions.

2.4.2. Industrial usage (Gasification)

Technologies available for gasification include entrained flow, fluidized bed and fixed bed gasifiers and this study is focussed on the latter. The fixed-bed dry bottom (FBDB) gasification process is described along with the chemical and physical characteristics required for the gasifier feed. This is followed by a discussion of various models that can be used to describe char reactivity during gasification. This section is concluded with test methods available for analysing the suitability of briquettes for industrial use.

a. Process

During gasification, carbonaceous material such as coal, biomass, agricultural and/or municipal solid waste is converted into synthesis gas in the presence of a gasifying agent. The coal gasification process can generally be divided into two steps, namely pyrolysis followed by gasification of the resultant char (Liu *et al.*, 2015). Devolatilisation of coal in fixed bed gasifiers can occur at temperatures ranging between 400 and 900°C, to form chars which are reacted in the presence of the gasifying agent (Laurendeau, 1978). Air, carbon dioxide, oxygen and steam can be used as gasifying agents either separately or in various combinations (Schobert, 2013).

A typical feed scheme of the Sasol-Lurgi FBDB gasifier can be seen in Figure 2.2. 5 – 70 mm coal lumps are fed at the top of the gasifier as illustrated in the figure. The reactant gases (oxygen and steam) flow counter current to the coal through the voids between the coal particles. This flow pattern creates a temperature profile within the reactor, creating four reaction zones in the FBDB gasifier, i.e. the drying, devolatilisation, reduction, and combustion zones. In the drying zone, moisture is removed from the coal and as the temperature of the dried coal reaches 350 – 400°C, it enters the devolatilisation zone where pyrolysis takes place and char is produced. After pyrolysis, the char enters the reduction zone, where the rate limiting, endothermic reactions take place. This zone is also known as the gasification zone. The last reaction zone in the gasifier is the combustion zone, where the exothermic oxidation reaction takes place and the char is combusted to ash. This bottom section in the gasifier also contains the ash bed (Bunt & Waanders, 2008). Due to the counter current flow configuration in the gasifier, the hot ash comes into contact with cold oxygen and steam entering the bottom of the gasifier, while the hot raw gas comes into

contact with the cold coal lumps fed at the top, resulting in a cooler raw gas stream. This feeding scheme results in the improvement of thermal efficiency and lowers steam consumption (van Dyk *et al.*, 2006).
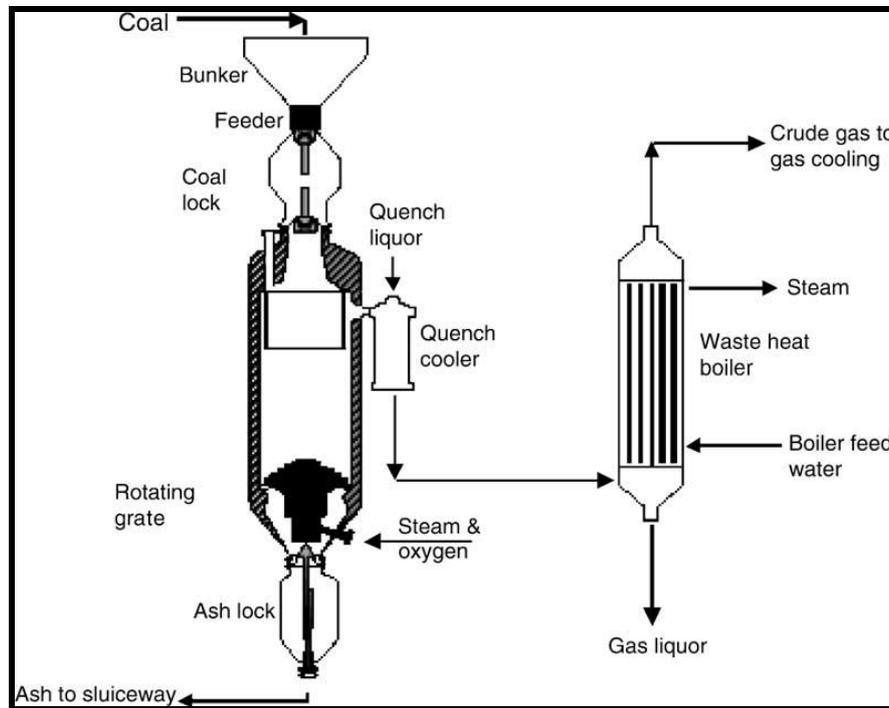
Figure 2.2 Sasol-Lurgi FBDB gasifier feed scheme taken from van Dyk *et al.* (2006)

Factors influencing char reactivity during gasification have been found to include the parent coal rank, char pore structure as well as the conditions at which the char was produced, and these are briefly discussed below (Molina & Mondragon, 1998; Liu *et al.*, 2000; Liu *et al.*, 2015).

- *Coal rank*

  The maturity of coal – coal rank – has a great influence on the chemical structure of the coal, and therefore its reactivity during utilisation (Laurendeau, 1978). Upon reviewing factors influencing char reactivity during gasification, Miura *et al.* (1989) found that coal rank was indirectly proportional to the gasification reaction rate for steam gasification and the same could be deduced for carbon dioxide and oxygen gasification. In lower ranked coals (with carbon content below 80%), the collation of the various reactivity data yielded a scattered relation between rank and reactivity (Miura *et al.*, 1989). The presence of alkali metals, such as calcium, potassium and sodium, was found to be the most influencing factor; increasing the gasification reaction rate through catalysis (Miura *et al.*, 1989; Coetzee *et al.*, 2013). Higher ranked coal, on the other hand, showed less variation in reactivity; which was

influenced more by the concentration of active sites within the coal. Overall, reactivity was observed to reduce with increasing coal rank (Miura *et al.*, 1989).

- *Pore structure*

Various investigators have drawn contradicting conclusions on the pore size in which the gasification reaction occurs. The high surface area available in micropores and the concentration of active sites prevalent in macropores have both been factors considered while determining whether the gasification reaction rate is dependent on micro- or macropore surface area (Miura *et al.*, 1989; Molina & Mondragon, 1998). Nonetheless, a direct correlation between char porosity and reactivity has been established for the gasification process. An upper limit does, however, exist for the increase in surface area and in turn coal char reactivity, which has been observed in the range of 20 – 60% carbon conversion (Cai *et al.*, 1996; Molina & Mondragon, 1998). The conditions at which the char has been formed also have a great effect on its reactivity as discussed below.

- *Devolatilisation conditions*

The devolatilisation temperature, pressure and heating rate all play a crucial role in the char reactivity (Cai *et al.*, 1996; Molina & Mondragon, 1998). During their study, Cai *et al.* (1996) found that an increase in pyrolysis temperature or pressure showed a decrease in the gasification reaction rate. The former was attributed to the ordering of the carbon structure, reducing the microporosity and subsequently the surface area available for reaction (Cai *et al.*, 1996; Lu *et al.*, 2002). A reduction in the hydrogen to carbon ratio was also observed with increasing pyrolysis temperature (Cai *et al.*, 1996). Increasing the devolatilisation pressure suppresses formed tars, preventing the opening of pores and thereby reducing the resultant char reactivity (Sha *et al.*, 1990). The later increase in char reactivity observed by Cai *et al.* (1996) with increased H_2 pressure during devolatilisation was mainly due to the char conversion in the presence of the excess H_2. An increase in pyrolysis heating rate, on the other hand, was found to increase the char reactivity up to a certain extent, after which no change in reactivity was observed. This increase has been attributed to the release of condensable tars, resulting in an increase in surface area and subsequently, an increase in char reactivity (Cai *et al.*, 1996; Roberts *et al.*, 2003).

The rate determining step during gasification is the reaction of the formed char with CO_2 or steam (Molina & Mondragon, 1998). Maintaining a thorough kinetic understanding of these

reactions leads to better practical application. Four models considered for char reactivity analysis are discussed below.

b.   Evaluation of char reactivity

When considering gas-solid reactions, 7 steps are assumed to take place in succession, which are (Levenspiel, 1999);

1. Mass transfer of the reaction gas from the bulk fluid, through the gas film around the particle, to the surface of the solid particle
2. Diffusion of the gas through the ash layer, to the unreacted core of the solid particle
3. Adsorption of the reaction gas onto the solid particle surface
4. Chemical reaction of the reaction gas with the solid at the active site, forming gaseous products
5. Desorption of the gaseous products from the reaction site
6. Diffusion of the gaseous products through the ash layer to the particle surface
7. Penetration of the products through the gas film to the bulk fluid

The slowest step, known as the rate determining step, determines whether the process is ash layer, chemical reaction or diffusion controlled (Levenspiel, 1999). The instantaneous gasification reaction rate can be described with a model that takes into account the temperature, composition and conversion dependency of the reaction, as seen in Equation 2.1 (Everson *et al.*, 2006);

$$\frac{dX}{dt} = r_s(T, p_A) f(X) \qquad \text{[2.1]}$$

In Equation 2.1, r_s, refers to the intrinsic reaction rate and f(X) the structural model. In the case where the partial pressure is 1 (100% reagent gas), Equation 2.1 simplifies to (Laurendeau, 1978);

$$\frac{dX}{dt} = k(T) f(X) \qquad \text{[2.2]}$$

The intrinsic rate constant (k) depends on temperature according to the Arrhenius equation as given in Equation 2.3 (Laurendeau, 1978):

$$k(T) = A e^{-\frac{E}{RT}} \qquad \text{[2.3]}$$

In Equation 2.3, A refers to the pre-exponential factor; E is the activation energy; R is the universal gas constant; and T the temperature.

Various structural models have been developed to describe the gasification reaction over the years. The structural models considered in this study are;

- *Homogenous Model (HM)*

  In contrast to more complex structural models, the HM is a simplistic model that does not account for structural changes that occur as the gasification reaction progresses. The HM is based on the assumption that the reaction gas is dispersed throughout a porous particle, continuously reacting not only on the particle surface, but also inside the entire particle (Levenspiel, 1999). This assumption reduces the heterogeneous gasification reaction to a homogeneous reaction (Molina & Mondragon, 1998). The reaction rate is given by:

  $$\frac{dX}{dt} = k(1 - X)$$ [2.4]

  where X is the conversion at time t.

- *Shrinking Unreacted Core Model (SUCM)*

  The SUCM neglects structural changes and assumes that the particle is a non-porous spherical grain. The solid-gas reaction therefore takes place from the surface of the particle, inwards. As the reaction progresses, the unreacted core reduces in size, leaving behind the reacted material known as the ash layer. As a result of this process, the SUCM assumes the reaction to be controlled by diffusion of the gas through the gas film, chemical reaction between the gas and the unreacted particle surface, or diffusion of the gas through the ash layer (Levenspiel, 1999; Molina & Mondragon, 1998). The SUCM expressions for time (t), applicable at isothermal reaction conditions, and reaction rate ($\frac{dX}{dt}$) can be seen in Table 2.2.

Table 2.2 SUCM equations (Njapha, 2003; Gbor & Jia, 2004)

Rate controlling step	Time	Reaction rate	
Ash Diffusion	$t = \frac{1}{k}\left[1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X)\right]$	$\frac{dX}{dt} = \frac{k}{(1 - X)^{-\frac{1}{3}} - 1}$	[2.5]
Chemical Reaction	$t = \frac{1}{k}\left[1 - (1 - X)^{\frac{1}{3}}\right]$	$\frac{dX}{dt} = k(1 - X)^{\frac{2}{3}}$	[2.6]
Gas Film Diffusion	$t = \frac{X}{k}$	$\frac{dX}{dt} = k$	[2.7]

The constants k seen in Table 2.2 are a summary of diffusion and chemical reaction kinetic constants and are therefore assumed to give an indication of the reaction rate. Equations for the SUCM rate constants can be seen in Table 2.3.

Table 2.3 SUCM rate constants (Njapha, 2003; Gbor & Jia, 2004)

Rate controlling step	Reaction constant
Ash Diffusion	$k = \dfrac{3bD_e C_{Ab}}{\rho R_p}$
Chemical Reaction	$k = \dfrac{3bk_1 C_{Ab}^n}{\rho R_p}$
Gas Film Diffusion	$k = \dfrac{3bk_g C_{Ab}}{\rho R_p}$

Multiple variations of Equations 2.5 – 2.6 can be applicable when utilising the SUCM (Levenspiel, 1999).

- *Random Pore Model (RPM)*

During the development of the RPM, Bhatia and Perlmutter (1980) suggested that particles consist of pores that randomly overlap each other, therefore reducing the surface area available for the gas-solid reaction (Molina & Mondragon, 1998). The pores are assumed to vary in size, and evolve with subsequent coalescence or collapse as the reaction progressed. With further investigation of the RPM, Gavalas (1980) assumed that particles contain straight cylindrical pores of infinite length, for which surface area and volume change could be approximated for the duration of the reaction (Molina & Mondragon, 1998). The RPM therefore takes structural changes of the char during the reaction, into account. The dimensionless structural parameter (Ψ), representing the initial char pore structure, formed part of the reaction rate expression as shown in Equation 2.8 (Molina & Mondragon, 1998);

$$\frac{dX}{dt} = \frac{r_s(1-X)S_o\sqrt{1-\varphi\ln(1-X)}}{(1-\varepsilon_o)} \qquad [2.8]$$

where r_s is the intrinsic reaction rate, and S_0 and ε_0 are the initial char surface area and porosity, respectively. The structural parameter is given as (Molina & Mondragon, 1998):

$$\varphi = \frac{4\pi L_o (1 - \varepsilon_o)}{S_o^2}$$ [2.9]

When φ > 2, pore growth is prominent during the initial stages of the reaction. This is also evident in the experimental data, with a maximum peak observed in the reaction rate versus carbon conversion (reactivity) curve. φ < 2 is an indication of pore coalescence with the reactivity curve showing no maximum peak (Irfan *et al.*, 2011).

- *Wen Model*

The Wen model forms part of a series of semi-empirical models developed to account for the wide variety in reactivity of various coals and chars as a result of differences in pore structure (Dutta *et al.*, 1977; Molina & Mondragon, 1998). An expression of the Wen model can be seen in Equation 2.10 (Wen, 1968).

$$\frac{dX}{dt} = k(1 - X)^m$$ [2.10]

A new parameter, m, was introduced as the order of the reaction. When m = 1, the Wen model shows a similar fit to the HM. An m value of 2/3 predicts data similar to the SUCM. Simultaneous estimation of the rate constant (k) and reaction order (m) ensures that the model is more robust, fitting a wider variety of reactivity data (Wen, 1968).

c. Briquette mechanical testing

Similar to their lump coal counterparts, the manufactured briquettes need to show a certain calibre of strength. Physical testing methods have been detailed by Richards (1990), Mangena *et al.* (2004), and Kaliyan and Morey (2009) to evaluate the mechanical strength of briquettes, and are detailed below.

- *Compressive strength test*

The dry compressive strength of briquettes is analysed in order to simulate the pressure experienced by a single briquette during bucket-filling or transportation by means of a conveyer belt. As per the Japanese Standard, JP JIS Z 8841-1993, described by England (2000), briquette compressive strength is analysed by placing a single briquette between 2 flat, parallel plates with surface areas larger than that of the briquette being tested. An increasing force is subsequently applied to the briquette until it cracked or broke, and this breaking force was recorded as the maximum compressive strength that the briquette could withstand (Richards, 1990).

The breaking force recorded was converted to a pressure (σ) by means of Equation 2.11 (Richards, 1990; Mangena *et al.*, 2004).

$$\sigma = \frac{F_{\max}}{A_b}$$ [2.11]

In Equation 2.11, $F_{\max}$ is the maximum force the briquette can withstand and A_b is the cross-sectional area of the plane of fracture. Richards (1990) established that the minimum compression pressure fuel briquettes should be able to withstand is 375 kPa, which is generally taken as the minimum requirement for the dry- and wet-strength of manufactured briquettes.

- *Drop test*

Various methods exist for evaluating the friability of lump coal and manufactured briquettes (Richards, 1990; Speight, 2005; Kaliyan & Morey, 2009). One such method entails dropping a sample of 23 kg twice from a 1.85 m height onto a concrete floor. The shattered material is subsequently screened to determine the average particle size, which can be expressed as a fraction of the original sample size (ASTM D-440).

- *Water resistance*

The determination of the briquette water resistance is very end-use specific. A method proposed by Mangena *et al.* (2004) entailed weighing the briquettes prior to submerging in water for 2 hours. Upon removal from the water, the briquettes were air-dried and weighed over a period of time, until no further significant mass loss was observed (Mangena *et al.*, 2004). The wet strength of the briquettes was also determined by conducting compressive strength analysis on the immersed briquettes, and this value was compared to the minimum compressive strength proposed by Richards (1990).

- *Thermal fragmentation*

When inertinite-rich coal is heated to the elevated temperatures and heating rates experienced during gasification, it may undergo thermal fragmentation depending on the initial particle size (van Dyk *et al.*, 2006; Bunt & Waanders, 2008). The creation of fine particles during fragmentation can result in pressure losses within the reactor, causing unstable operation at the top of the gasifier (Keyser *et al.*, 2006; van Dyk *et al.*, 2006; Bunt & Waanders, 2008). As no standard procedure for thermal

fragmentation was available, van Dyk (2001) proposed pre-heating a muffle oven to 100˚C prior to inserting coal with a pre-determined particle size distribution. Upon inserting the coal, the furnace was heated to 700˚C and subsequently cooled to room temperature. The thermal fragmentation test was completed using nitrogen gas under atmospheric pressure. The particle size distribution of the cooled sample was then evaluated (according to the ASTM D4749 procedure) in order to determine the percentage reduction in the Sauter diameter. The average Sauter diameter was determined using Equation 2.12 (van Dyk *et al.*, 2001);

$$\bar{d}_p = \frac{1}{\sum \dfrac{x_i}{d_{p,i}}}$$ [2.12]

where x is the mass fraction on screen i and d_p, the diameter of screen i.

The agglomeration of coal fines has created a niche market for domestic and industrial briquette utilisation locally (Mangena & de Korte, 2004; Mangena et al., 2004). Various authors have investigated fine coal agglomeration with and without the use of a binder, with great technical success (Mills, 1908; Waters, 1969; Mishra et al., 2000; Mangena et al., 2004; Dehont, 2006; Kaliyan & Morey, 2009). Chapters 3 and 4 focus on applying these existing technologies to manufacture and test coal briquettes using various binders, for use in fixed-bed gasification.

2.5. Summary

Coal mining processes result in the formation of significant amounts of coal fines. Due to the handling difficulties associated with fine coal, these fines continue to be discarded into slurry ponds and underground workings. The briquetting process presents an opportunity to utilise fine discard coal in technologies that require lump coal. Binderless briquettes prepared from inertinite-rich coal fines have yielded mechanically weaker and less water resistant briquettes compared to their vitrinite-rich counterparts. Briquetting of South African inertinite rich, high ash yield fine discard coal in the presence of a suitable binder is still poorly understood. To ensure suitability of briquettes for fixed-bed gasification, the mechanical strength, water resistance, thermal stability and reactivity of the briquettes need to be studied. The stipulated minimum requirements for coal briquettes are not end-use specific, therefore comparison between ROM coal and the manufactured briquettes is necessary.

List of Symbols

A	Pre-exponential factor (min^{-1})
A_b	Cross-sectional area of plane of fracture of the briquette (m^2)
b	Moles of solid consumed per mole of gas reacted (-)
C_{Ab}	Concentration of gas in the bulk fluid ($mole/m^3$)
$\bar{d}_p$	Average Sauter diameter (mm)
$d_{p,i}$	Screen i diameter (mm)
D_e	Effective diffusion coefficient of gas through ash layer (m^2/s)
E	Activation energy
F	Friability (%)
F_{max}	Force applied to fracture or break a briquette (N)
k_1	Reaction rate constant ($mole^{(1-n)}m^{(3n-2)}/s$)
k_g	Mass transfer coefficient of the gas in the liquid film (m/s)
L_o	Pore length at t = 0
m	Wen model reaction order (-)
M_f	Weight of the largest piece after dropping a briquette (g)
M_i	Initial weight of a briquette (g)
n	SUCM model reaction order (-)
p_A	Gas partial pressure in bulk fluid (Pa)
r_s	Intrinsic reaction rate (min^{-1})
R	Universal gas constant (J/mol.K)
R_p	Solid particle radius (m)
S_o	Initial char surface area (m^2)
T	Temperature (K)
x_i	Mass fraction on screen i (-)
X	Conversion (-)
dX/dt	Conversion rate (min^{-1})

ε_o	Initial char porosity (%)
σ	Compressive strength (MPa)
φ	RPM structural parameter (-)

Chapter 2 Bibliography

BARNES, B., MATHEE, A., THOMAS, E. & BRUCE, N. 2009. Household energy, indoor air pollution and child respiratory health in South Africa. *Journal of Energy in Southern Africa*, 20(1):4-13.

BLESA, M.J., MIRANDA, J.L., IZQUIERDO, M.T. & MOLINER, R. 2003a. Curing temperature effect on mechanical strength of smokeless fuel briquettes prepared with molasses. *Fuel*, 82(8):943-947.

BLESA, M.J., MIRANDA, J.L., IZQUIERDO, M.T., MOLINER, R., ARENILLAS, A. & RUBIERA, F. 2003b. Curing temperature effect on mechanical strength of smokeless fuel briquettes prepared with humates. *Energy & Fuels*, 17(2):419-423.

BOUDET, A.M. 2000. Lignins and lignification: Selected issues. *Plant Physiology and Biochemistry*, 38(1):81-96.

BP GLOBAL. 2015. Statistical Review of World Energy. http://www.bp.com Date of access: 17 September 2015.

BP GLOBAL. 2016. Statistical Review of World Energy. http://www.bp.com Date of access: 17 September 2016.

BUNT, J.R. & WAANDERS, F.B. 2008. An understanding of lump coal physical property behaviour (density and particle size effects) impacting on a commercial-scale Sasol-Lurgi FBDB gasifier. *Fuel*, 87(13-14):2856-2865.

CAI, H.Y., GÜELL, A.J., CHATZAKIS, I.N., LIM, J.Y., DUGWELL, D.R. & KANDIYOTI, D.R. 1996. Combustion reactivity and morphological change in coal chars: effect of pyrolysis temperature, heating rate and pressure. *Fuel*, 75(1):15-24.

CHUNG, F.H. 1991. Unified theory and guidelines on adhesion. *Journal of Apploed Polymer Science*, 42(5):1319-1331.

COETZEE, S., NEOMAGUS, H.W.J.P., BUNT, J.R. & EVERSON, R.C. 2013. Improved Reactivity of Large Coal Particles by K_2CO_3 Addition during Steam Gasification. *Fuel Processing Technology*, 114:75-80.

COETZEE, S., NEOMAGUS, H.W.J.P., BUNT, J.R., STRYDOM, C.A. & SCHOBERT, H.H. 2014. The transient swelling behaviour of large (-20 + 16 mm) South African coal particles during low-temperature devolatilisation. *Fuel*, 136:79-88.

DEHONT, F. 2006. Coal briquetting technology. Date of access: 1 August 2013. <http://www.sahutconreur.com>

DEPARTMENT OF ENERGY. 2012. A survey of energy-related behavior and perceptions in South Africa: The residential sector 2012. Date of access: 15 February 2016. <http://www.energy.gov.za/files/publications>

DEPARTMENT OF ENERGY. 2016. Basic Electricity. http://www.energy.gov.za/files/electricity Date of access: 17 March 2016.

DUTTA, S., Wen, C.Y. & BELT, R.J. 1977. Reactivity of coal and char. 1. In carbon dioxide atmosphere. *Industrial & Engineering Chemistry Process Design and Development*, 16(1):20-30.

EKEBERG, D., GRETLAND, K.S., GUSTAFSSON, J., BRATON, S.M. & FREDHEIM, G.E. 2006. Characterisation of lignosulphonates and kraft lignin by hydrophobic interaction chromatography. *Analytica Chimica Acta*, 565(1):121-128.

ELLISON, G. & STANMORE, B.R. 1981. High strength binderless brown coal briquettes Part I. Production and properties. *Fuel Processing Technology*, 4(4):277-289.

EMERHI, E.A. 2011. Physical and combustion properties of briquettes produced from sawdust of three hardwood species and different organic binders. *Advances in Applied Science Research*, 2(6):236-246.

ENGLAND, T. 1993. *The development of binderless, smokeless briquettes from bituminous colliery waste*. Master of Science, University of the Witwatersrand.

ENGLAND, T. 2000. *The economic agglomeration of fine coal for industrial and commercial use*. Report for Coaltech 2020.

EVERSON, R.C., NEOMAGUS, H.W.J.P., KASAINI, H. & NJAPHA, D. 2006. Reaction kinetics of pulverized coal-chars derived from inertinite-rich coal discards: Gasification with carbon dioxide and steam. *Fuel*, 85(7):1076-1082.

FALCON, R. & HAM, A.J. 1988. The characteristics of Southern African coals. *The Southern African Institute of Mining and Metallurgy*, 88(5):145-161.

FINNEY, K.N., SHARIFI, V.N. & SWITHENBANK, J. 2009. Fuel Pelletization with a Binder: Part I - Identification of a Suitable Binder for Spent Mushroom Compost - Coal Tailing Pellets. *Energy and Fuels*, 23(6):3195-3202.

GBOR, P.K. & JIA, C.Q. 2004. Critical evaluation of coupling particle size distribution with the shrinking core model. *Chemical Engineering Science*, 59(10):1979-1987.

HALT, J.A. & KAWATRA, S.K. 2014. Review of organic binders for iron ore concentrate agglomeration. *Minerals & Metallurgical Processing*, 31(2):73-94.

HECKROODT, R.O. 1991. Clay and clay materials in South Africa. *Journal of the Southern African Institute of Mining and Metallurgy*, 91(10):343-363.

IDAH, P.A. & MOPAH, E.J. 2013. Comparative assessment of energy values of briquettes from some agricultural by-products with different binders. *IOSR Journal of Engineering*, 3(1):36-42.

IRFAN, M.F., USMAN, M.R. & KUSAKABE, K. 2011. Coal gasification in CO_2 atmosphere and its kinetics since 1948: A brief review. *Energy*, 36(1):12-40.

JEFFREY, L.S. 2005. Characterization of the coal resources of South Africa. *The Journal of The South African Institute of Mining and Metallurgy*, 105(2):95-102.

KALIYAN, N. & MOREY, R.V. 2009. Factors affecting strength and durability of densified biomass products. *Biomass and Bioenergy*, 33(3):337-359.

KEYSER, M.J., CONRADIE, M., COERTZEN, M. & VAN DYK, J.C. 2006. Effect of coal particle size distribution on packed bed pressure drop and gas flow distribution. *Fuel*, 85(10):1439-1445.

KIDENA, K., KATSUYAMA, M., MURATA, S., NOMURA, M. & Chikada, T. 2002. Study on plasticity of maceral concentrations in terms of their structural features. *Energy Fuels*, 16(5):1231-1238.

KLAUSBRUCKNER, C., ANNEGARN, H., HENNEMAN, L.R.F. & RAFAJ, P. 2016. A policy review of synergies and trade-offs in South African climate change mitigation and air pollution control strategies. *Environmental Science & Policy*, 57:70-78.

KÜHN, M.J. 2015. *Low-smoke fuel production via low temperature pyrolysis of lump coal*. Masters dissertation, North West University, Potchefstroom.

LAURENDEAU, N.M. 1978. Heterogeneous kinetics of coal char gasification and combustion. *Progress in Energy and Combustion Science*, 4(4):221-270.

LE ROUX, L.J., CILLIERS, K.F.P. & VAN VUUREN, D.S. 2004. Low-Smoke fuels Standard Testing and Verification. Final Report to the Department of Minerals and Energy. CSIR Report No. 86DC / HT776.

LEVENSPIEL, O. 1999. *Chemical Reaction Engineering (Third Edition)*. New York: Wiley & Sons.

LIU, G., BENYON, P., BENFELL, K.E., BRYANT, G.W., TATE, A.G., BOYD, R.K., HARRIS, D.J. & WALL, T.F. 2000. The porous structure of bituminous coal chars and its influence on combustion and gasification under chemically controlled conditions. *Fuel*, 79(6):617-626.

LIU, L., CAO, Y. & LIU, Q. 2015. Kinetics studies and structure characteristics of coal char under pressurized CO_2 gasification conditions. *Fuel*, 146:103-110.

LU, L., KONG, C., SAHAJWALLA, V. & HARRIS, D. 2002. Char structuralm ordering during pyrolysis and combustion and its influence on char reactivity. *Fuel*, 81(9):1215-1225.

MANGENA, S.J. 2001. *The Amenability of some South African bituminous coals to binderless briquetting*. Magister Technologiae dissertation, Technikon Pretoria.

MANGENA, S.J. & DE KORTE, G.J. 2004. *Development of a process for producing low-smoke fuels from coal discards*. Report, Division of Mining Technology, CSIR.

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*, 85(15):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 of coal properties on binderless briquetting. *International Journal of Coal Geology*, 71(2):303-312.

MATINGA, M.N., CLANCY, J.S. & ANNEGARN, H.J. 2014. Explaining the non-implementation of health-improving policies related to solid fuels in South Africa. *Energy Policy*, 68:53-59.

MILLS, J.E. 1908. *Binders for coal briquets; investigations made at the fuel-testing plant, St, Louis, Missouri (No. 343)*. Government Printing Office.

MISHRA, S.L., SHARMA, S.K. & AGARWAL, R. 2000. Briquetting of lignite for domestic fuel. *Science and Industrial Research*, 59(5):413-416.

MIURA, K., HASHIMOTO, K. & SILVESTON, P.L. 1989. Factors affecting the reactivity of coal chars during gasification, and indices representing reactivity. *Fuel*, 68(11):1461-1475.

MOLINA, A. & MONDRAGON, F. 1998. Reactivity of coal gasification with steam and CO_2. *Fuel*, 77(15):1831-1839.

NJAPHA, D. 2003. *Determination of the kinetic models and associated parameters for the low temperature combustion and gasification of high-ash coal chars*. Doctoral dissertation, North West University, Potchefstroom.

PAYNE, J.D. 2006. Troubleshooting the pelleting process. *Feed*. Singapore.

PIETERS, R. & FOCANT, J.F. 2014. Dioxin, furan and PCB serum levels in a South African Tswana population: Comparing the polluting effects of using different cooking and heating fuels. *Environment International*, 66:71-78.

RADLOFF, B., KIRSTEN, M. & ANDERSON, R. 2004. Wallerawang colliery rehabilitation: The coal tailings briquetting process. *Minerals Engineering*, 17(2):153-157.

RHÉN, C., GREF, R., SJÖSTRÖM, M. & WÄSTERLUND, I. 2005. Effects of raw material moisture content, densification pressure and temperature on some properties of Norway spruce pellets. *Fuel Processing Technology*, 87(1):11-16.

RICHARDS, S.R. 1990. Physical testing of fuel briquettes. *Fuel Processing Technology*, 25(2):89-100.

ROBERTS, D.G., HARRIS, D.J. & WALL, T.F. 2003. On the effects of high pressure and heating rate during coal pyrolysis on char gasification reactivity. *Energy and Fuels*, 17(4):887-895.

SAMI. 2015. South African Mineral Industry. Date of access: 20 February 2016. <http://www.dmr.gov.za/publications/south-africas-mineral-industry-sami>

SANCHEZ, M.E., OTERO, M., GÓMEZ, X. & MORÁN, A. 2009. Thermogravimetric kinetic analysis of the combustion of biowastes. *Renewable Energy*, 34(6):1622-1627.

SANEDI. 2011. Release of the coal roadmap. Date of access: 17 March 2016. <http://www.sanedi.org.za/coal-roadmap>

SASTRY, V.S. 1991. *Pelletization of fine coals*. (No. DOE/PC/89766-T4). California Univ., Berkeley, CA (United States). Dept. of Materials Science and Mineral Engineering.

SCHOBERT, H.H. 2013. Chemistry of fossil fuels and biofuels. Cambridge: Cambridge University Press.

SHA, X.Z., CHEN, Y.G., CAO, J., YANG, Y.M. & REN, D.Q. 1990. Effects of operating pressure on coal gasification. *Fuel*, 69(5):656-659.

SPATH, P.L. & DAYTON, D.C. 2003. *Preliminary screening - technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas.* (No. NREL/TP-510-34929). National Renewable Energy Lab Golden Co.

SPEIGHT, J.G. 2005. Handbook of coal analysis. New Jersey: John Wiley & Sons, Inc.

STELTE, W., HOLM, J.K., SANADI, A.R., BARSBERG, S., AHRENFELDT, J. & HENRIKSEN, U.B. 2011. Fuel pellets from biomass: The importance of the pelletizing pressure and its dependency on the processing conditions. *Fuel*, 90(11):3285-3290.

SWEETEN, J.M., ANNAMALAI, K., THIEN, B. & MCDONALD, L.A. 2003. Co-firing of coal and cattle feedlot biomass (FB) fuels. Part I. Feedlot biomass (cattle manure) fuel quality and characteristics. *Fuel*, 82(10):1167-1182.

VAN DYK, J.C., 2001. Development of an alternative laboratory method to determine thermal fragmentation of coal sources during pyrolysis in the gasification process. *Fuel*, 80(2):245-249.

VAN DYK, J.C., KEYSER, M.J. & COERTZEN, M. 2006. Syngas production from South African coal sources using Sasol-Lurgi gasifiers. *Coal Geology*, 65(3):243-253.

VAN DYK, J.C., KEYSER, M.J. & VAN ZYL, J.W. 2001. Suitability of feedstocks for the Sasol-Lurgi fixed bed dry bottom gasification process. (*In* Gasification Technologies Conference. San Francisco. pp. 1-11).

WATERS, P.L. 1969. *Binders for fuel briquettes: a critical survey*. Division of Mineral Chemistry, Commonwealth Scientific and Industrial Research Organization.

WELLS, J.J., WIGLEY, F., FOSTER, D.J., LIVINGSTON, W.R., GIBB, W.H. & WILLIAMSON, J. 2005. The nature of mineral matter in a coal and the effects on erosive and abrasive behaviour. *Fuel Processing Technology*, 86(5):535-550.

Wen, C.Y. 1968. Noncatalytic heterogeneous solid-fluid reaction models. *Industrial & Engineering Chemistry*, 60(9):34-54.

WONGSIRIAMNUAY, T. & TIPPAYAWONG, N. 2015. Effect of densification parameters on the properties of maize residue pellets. *Biosystems Engineering*, 139:111-120.

WOODS, M.F., HABBERJAM, G.M., ELSWORTH, K. & BENNETT, S. 1963. The effect of maceral compostion on the binderless briquetting of hot char. *American Chemical Society Division of Energy and Fuels Preparation*, 7(2):125-144.

WORLD ENERGY COUNCIL. 2013. World Energy Resources: 2013 Survey. https://www.worldenergy.org/publications Date of access: 20 February 2014.

CHAPTER 3.

Manufacturing and testing of briquettes from inertinite-rich low grade coal fines using various binders

Nthabiseng T. Modiri, John R. Bunt, Hein W.J.P. Neomagus, Frans B. Waanders, Christien A. Strydom

The mechanical strength of briquettes derived from inertinite-rich, low grade coal was investigated in this chapter. Briquette compressive strength, drop shatter resistance and water resistance were evaluated, while adding 12 binders at four concentrations.

Abstract

As a result of coal mining processes, approximately 11% of South African run-of-mine coal is classified as fine and ultrafine and continues to be discarded. The South African Department of Energy promotes the utilisation of fine discard coal through techniques such as briquetting for use in technologies that require lump coal. Binderless agglomeration of vitrinite-rich coal has previously shown great potential, producing mechanically stronger and more water resistant briquettes as compared to briquettes produced from inertinite-rich coal. Fine coal briquetting, while making use of a suitable binder, enhances agglomeration and therefore reduces briquetting (pressing) temperatures and pressures, paving the way for producing durable products to be utilised in industrial applications. In this study, inertinite-rich, low grade coal was used along with 12 binders: clays (attapulgite and bentonite), bio char, cow dung, granulated medium tar pitch, coal tar sludge, flocculant, fly ash, lignosulphonates, polyester resin and 2 South African coal tar pitches in order to produce mechanically strong and water resistant briquettes. The binders were added in various concentrations, and the compressive strength, friability and water resistance of the resultant briquettes were determined. The briquettes manufactured using lignosulphonate and resin as binders resulted in the strongest briquettes, with compressive strengths of 16 and 12 MPa respectively at a 7.5 wt% binder concentration. Cured and uncured, with and without binder addition, the briquettes all retained their shape and size during drop tests, but none proved to be water resistant. Paraffin and wax were therefore used as waterproofing agents after pressing and curing. The produced briquettes showed sufficient strength, friability and water resistance for industrial application.

Keywords

Agglomeration, binders, coal fines, compressive strength, inertinite, waterproofing

3.1. Introduction

Coal is one of the highest contributors to revenue generated by primary mineral commodities in South Africa through domestic trade and export (SAMI, 2015). To produce coal that meets market specifications, run-of-mine (ROM) coal is processed by means of crushing, screening as well as washing (Radloff *et al.*, 2004). As a result, 11% of South African ROM coal becomes classified as fine (-0.5 mm) and ultrafine (-0.1 mm), which continues to be discarded into slime dams and underground workings (England, 2000; SANEDI, 2011). One method of utilising the fine coal locally is through agglomeration for use in technologies that require lump coal, which include chain grate stokers and fixed-bed gasifiers.

There are several techniques for agglomerating fine coal, which include pelletisation, flocculation and briquetting (Sastry, 1991), and in this paper the focus will be on the latter. Briquetting of coal has been practiced since the 18th century and reached an ultimate high in the 1960's, after which a decrease was observed due to the increase in oil and gas usage (England, 2000). Currently, declining coal reserves and environmental legislations have led to the re-visiting of coal briquetting as a form of fine discard coal utilisation in coal dependent countries (Mangena *et al.*, 2004; Waters, 1969).

The suitability of coal briquettes for industrial use is determined by the mechanical strength, water resistance and thermal stability of the manufactured briquettes (Waters, 1969; Richards, 1990). Richards (1990) established that the minimum compression strength that fuel briquettes should be able to withstand is 375 kPa, which takes into account the pressure exerted during transportation on conveyor belts or during bin storage. In order for briquettes to endure everyday handling, including loading and off-loading from trucks and dropping from conveyor belts, a minimum friability of 80% is required (Kaliyan & Morey, 2009). The water resistance is a paramount factor during stockpiling and transportation, and a maximum allowable water absorption of 5 wt% is acceptable for fuel briquettes to be classified as water resistant (Richards, 1990). Wet briquettes should also be able to withstand the minimum break pressure of 375 kPa, as stipulated by Richards (1990).

While considering binderless briquetting, Waters (1969), Mangena *et al.* (2004), Mangena and du Cann (2007) and Motaung *et al.* (2007) summarised the properties affecting the mechanical strength of briquettes as the: i) initial moisture content of the coal, ii) briquetting conditions, more specifically pressure when briquetting by force, iii) particle size distribution, iv) rank, v) maceral composition, and vi) mineral matter content. Upon reviewing the initial moisture content of the coal fines, Waters (1969), Mangena *et al.* (2004) and Mangena and du Cann (2007) found that the highest briquette compressive strengths can be achieved below 7 wt% moisture content; thereafter the initial moisture content of the fines inversely

affects the dry strength of the briquettes. Mangena and du Cann (2007) reported a direct correlation between the pressing force used to manufacture the briquette and the briquette compressive strength. The higher and lower limits for the pressing pressure are determined by equipment constraints and the rank of the coal utilised, respectively. Soft coals, such as lignite, require moderate forces for briquette production compared to higher ranked coals, which may result in lower briquetting costs (Waters, 1969). Fines with a smaller particle size produce briquettes that are mechanically stronger, due to the enhanced binding induced by an increase in particle-to-particle contact (Motaung *et al.*, 2007; Waters, 1969). This was observed by Motaung *et al.* (2007), where briquettes manufactured from coal of a finer nature reached compressive strengths up to 600 kPa above those manufactured with coarser material.

Binderless agglomeration of vitrinite-rich coal has shown great potential, producing mechanically stronger and more waterproof briquettes as compared to inertinite-rich coal (Mangena *et al.*, 2004; Mangena & du Cann, 2007; Motaung *et al.*, 2007). According to Mangena *et al.* (2004), briquettes produced from vitrinite-rich coal could withstand compression pressures over 1000 kPa, while inertinite-rich briquettes produced at the same pressing conditions by Mangena and du Cann (2007) could only tolerate compression pressures up to 720 kPa. This was mainly attributed to the distortion and subsequent linking of the reactive macerals into joined masses at the surface of the briquette with pressure, thereby increasing its strength – a phenomenon observed to a lesser extent for inertinite-rich coals (Mangena & du Cann, 2007). Mangena *et al.* (2004), Mangena and du Cann (2007) and Motaung *et al.* (2007) found that briquettes produced from binderless agglomeration of inertinite-rich coal resulted in products with a reduced wet strength, mainly as a result of the kaolinite mineral matter in conjunction with high ash yield (> 15 wt%). Water resistance analysis of inertinite-rich, low grade coals by Mangena *et al.* (2004) and Mangena and du Cann (2007) resulted either in the disintegration of the briquettes in water or lowered wet strengths as compared to their vitrinite counterparts.

Although binderless briquetting is the most economic form of briquetting, binder utilisation becomes paramount when briquetting inertinite-rich, low grade coals (England, 2000; Mangena, 2001; Woods *et al.*, 1963). A binder functions as a coherent or adhesive medium between the fine coal particles, and binding agents are desired for their ability to enhance agglomeration through various mechanisms, depending on their properties.

A suitable binder is required to produce mechanically strong, thermally stable and water resistant briquettes in a cost-effective manner (Mills, 1908; Waters, 1969). Coal tar pitch is known to produce mechanically strong and waterproof briquettes (Dehont, 2006; Waters,

1969). The pitch can be added to the coal fines in granular form or in a molten state. As a result of the carcinogenic nature of coal tar pitch, it has generally been replaced with bitumen, possessing similar binding characteristics, but producing less harmful fumes (England, 2000). The more environmentally friendly binders, such as starches and molasses, produce good quality, low smoke briquettes, but require more intensive thermal post-treatment. The main setback with regards to utilising these binders is the increased processing costs (Dehont, 2006; Waters, 1969). Investigated for their binding properties also are lignosulphonate and kraft lignin, derived from lignin, which is the strengthening agent in plants and trees (Boudet, 2000; Ekeberg *et al.*, 2006).

Inorganic compounds, such as clays, have also been investigated for their suitability as binders. These compounds produce stronger and more water resistant briquettes at low concentrations and low initial moisture contents of the binder-coal mixture (Gul *et al.*, 2015; Mangena *et al.*, 2004). Materials such as cow manure and municipal solid waste have also been investigated for their binding abilities and were found to increase the reactivity of the resulting briquettes at specific binder concentrations (Massaro *et al.*, 2014; Mishra *et al.*, 2000). These binders, although affordable, require complex pre- and post-treatment, thereby increasing processing costs.

South African coal fields are mostly comprised of inertinite coal and this study is therefore aimed at exploring methods of producing mechanically strong and waterproof briquettes from a South African inertinite-rich, low grade coal. The effect of various binders and waterproofing agents will be determined by means of compressive strength, drop shatter and water submersion tests.

3.2. Materials and Methods

3.2.1. Coal

A South African, medium rank-C, low grade, inertinite-rich discard coal (filter cake) from the Highveld area is used. The particle size distribution of the filter cake indicates that 80% of the sample is below 100 µm and can therefore be classified as ultra-fine. The chemical, mineralogical and petrographic analyses of the coal fines are given in Table 3.1. The proximate and X-ray diffraction (XRD) analysis indicate an ash yield of 23 wt% with high levels of kaolinite. The inertinite content of the coal is 56 wt% as seen from the petrographic analysis. Oven drying the sample at 105°C indicates a surface moisture of 20 wt% (ar) for the filter cake. For comparison of mechanical strength, the run-of-mine (ROM) coal from the same colliery is obtained.

Table 3.1 Coal properties

Proximate Analysis (wt%, adb[a])	
Inherent moisture	4.9
Ash yield	23.1
Volatile matter	26.3
Fixed carbon	45.7
Ultimate Analyses (wt%, dafb[b])	
Carbon	79.2
Hydrogen	4.8
Nitrogen	2.2
Oxygen	12.6
Total sulphur	1.2
Petrographic Analysis (vol%, mmb[c])	
Vitrinite	27.7
Liptinite	5.4
Inertinite	56.1
Visible minerals	10.8
Total Reactive macerals (vol%)	63.8
Reflectance properties (%)	
Mean vitrinite random reflectance (Rr)	0.65
Rank (Bituminous)	Medium Rank C
Mineralogical XRD Analysis (wt%, graphite basis)	
Calcite	1.9
Dolomite	2.6
Graphite	59.8
Gypsum	2.8
Kaolinite	22.3
Muscovite	2.0
Pyrite	0.6
Quartz	8.0

[a]adb – air-dried basis, [b]dafb – dry, ash-free basis [c]mmb – mineral matter basis

Table 3.2 Origin and pre-treatment requirements of the binders and water proofing agents utilised

Binder	Abbreviation	Origin/Supplier	Pre-treatment
Clays (attapulgite and bentonite)	A/B	Yellowstone bentonite mine near Koppies, South Africa	Milling
Bio char	BC	Sunflower husks from a farm in the North West province	None
Cow manure	CM	From a farm in the North West province	Grating
Magnifloc (high molecular weight flocculant)	F	South African mining chemicals supplier	Pre-mix 24 hours prior to pressing
Lignosulphonate and Kraft lignosulphonate	LS/KL	Paper mill by-product from Mpumalanga	Milling
NCS 991 PA MV Polyester resin	R	NCS Resins	None
Coal tar pitch - (55/59) **Coal tar pitch - (68/73)**	CTP1 CTP2	South African petrochemical industry	Milling
Crystallised medium tar pitch	MTP	South African petrochemical industry	Milling
Coal tar sludge	CT	South African petrochemical industry	None
Fly ash	FA	South African petrochemical industry	None
Paraffin	P	Hardware store in the North West	None
Wax	W	Low temperature Fischer-Tropsch Process in South African petrochemical industry	None

3.2.1. Additives

The binders used are summarised in Table 3.2. The clays, lignosulphonate, kraft lignosulphonate, pitches as well as the granulated medium tar pitch (MTP) were milled using a ball mill to a particle size below 1 mm, prior to blending with the coal sample. The cow manure was subjected to a size reduction using a grater prior to being added to the coal fines. The flocculant granules were added directly to the coal fines and left for a 24 hour period before pressing. Paraffin and wax, also presented in Table 3.2, were used to improve the water resistance of the briquettes.

3.2.2. Briquetting process

The briquettes were produced by means of a 13 x 13 mm cylindrical die using a Lloyd LRX Plus Press. The binders were each added in weight concentrations of 2.5, 5.0, 7.5 and 10%, but due to the sticky nature of the coal-flocculant mixture, the flocculant was only added up to 4 wt%. The coal-binder mixture was prepared using a Heidolph RZR 2041 mechanical agitator, maintained at 194 rpm for 5 minutes. Samples of 2.5 g were prepared and pressed with a force of 1.5 – 4.0 kN (11 – 30 MPa) to determine the optimum pressing conditions. The mechanical test results of the briquettes produced with the various binders were compared to those of the binderless briquettes, as well as to ROM coal ground and smoothed into 13 x 13 mm cylinders.

3.2.3. Curing

Optimum curing process conditions were found to be 100°C and 3 hours for the binderless briquettes. These curing conditions were utilised for the briquettes containing the binders.

3.2.4. Test procedures

The physical testing methods as detailed by Mangena *et al.* (2004), Richards (1990) and Kaliyan and Morey (2009) were used to evaluate the mechanical strength of the briquettes.

- *Compressive strength test*

  As per the JP JIS Z 8841-1993 standard described by England (2000), a briquette was placed between 2 flat, 50 mm diameter parallel plates. An increasing force was applied to the briquette until it cracked or broke, and this breaking force was recorded as the maximum compressive strength that the briquette could withstand (Richards, 1990). The Lloyd LRX Press Plus was used to compress the briquettes and the breaking force recorded was converted to a pressure by means of Equation 3.1.

$$\sigma = \frac{F_{\max}(N)}{A_b(133mm^2)} \qquad\qquad [3.1]$$

- *Drop test*

  The ASTM D-440 standard method was modified by dropping only one briquette during a test. Each briquette was dropped twice from a 1.85 m height onto a concrete floor and the largest remaining piece was weighed (Kaliyan & Morey, 2009). The friability of the briquettes was then determined by means of Equation 3.2.

  $$F = \frac{M_f(g)}{M_i(g)}$$ [3.2]

- *Water resistance*

  In order to determine the water resistance of the briquettes, the briquettes were submerged in water for 2 hours, weighed, and then air-dried with subsequent weighing until no further significant mass loss was observed (Mangena *et al.*, 2004). The wet strength of the briquettes was also determined by conducting compressive strength analysis on the immersed briquettes.

- *Microscopic surface imaging*

  High definition, microscopic images of the surface of the briquettes were obtained and investigated through light microscope imaging using a Nikon SMZ-1 Light Electron Microscope.

3.3. Results and Discussion

The various mechanical evaluations conducted on the coal briquettes are discussed in Section 3. The results are separated into two subsections, namely (i) binderless and (ii) binder addition, and within each subsection the cured and uncured briquette results are discussed.

3.3.1. Binderless

Increasing the agglomeration pressure during briquette production, increased the compressive strength of the binderless briquettes as indicated in

Table 3.3. An optimum pressing pressure of 30 MPa was utilised for briquette production.

Table 3.3 Effect of agglomeration pressure on briquette compressive strength

Agglomeration Pressure (MPa)	Compressive Strength (MPa)
11	0.579
23	0.689
30	0.875

Table 3.4 summarises the compressive strength and friability results of the cured and uncured briquettes manufactured with the pre-selected binders. From Table 3.4, the maximum compressive strength (MCS), binder concentration (C_{MCS}) and friability (F_{MCS}) at maximum compressive strength can be seen. Uncured, the binderless briquettes met the minimum requirements set out by Richards (1990), reaching compressive strengths up to 0.9 MPa. Upon curing, an increase of mechanical strength was observed, with the cured binderless briquettes yielding a maximum compressive strength of 4.9 MPa. This increase in compressive strength can be attributed to the uniformity in morphology as a result of curing, as also reported by Blesa *et al.* (2003a). The binderless briquettes retained their shape and size during drop shatter analysis, attaining friability of 97 and 99% for the cured and uncured briquettes, respectively.

Table 3.4 Maximum compressive strengths of cured and uncured briquettes

Binder	C_{MCS}[a] (wt%)		MCS[b] (MPa)		F_{MCS}[c] (%)	
	Uncured	Cured	Uncured	Cured	Uncured	Cured
Binderless	-	-	0.9	4.9	97	99
Attapulgite	10.0	2.5	1.1	3.3	97	98
Bentonite	7.5	2.5	1.0	5.5	98	98
Bio char	7.5	2.5	0.9	3.5	56	93
Cow manure	7.5	2.5	0.9	2.4	47	90
Flocculant	1.0	1.0	4.1	1.4	50	64
Lignosulphonate	2.5	10.0	0.6	17.0	99	97
Kraft Lignosulphonate	5.0	7.5	0.9	3.3	97	97
Polyester resin	2.5	10.0	0.9	12.3	98	100
(55/59) Coal tar pitch	10.0	7.5	1.1	5.6	97	98
(68/73) Coal tar pitch	10.0	10.0	1.1	6.4	99	98
Medium tar pitch	10.0	7.5	1.0	7.1	100	100
CT sludge	5.0	2.5	0.9	5.8	98	100
Fly ash	2.5	5.0	0.9	3.9	98	97

[a]C_{MCS} – binder concentration at maximum compressive strength, [b]MCS – maximum compressive strength, [c]F_{MCS} – Friability at maximum compressive strength

3.3.2. Binder addition

- *Uncured*

From Table 3.4 it can be seen that flocculant is the only binder significantly enhancing the mechanical strength of the uncured binderless briquettes, with 1 wt% flocculant addition resulting in a compressive strength of 4.1 MPa. Further increases in flocculant weakened the briquettes, refuting the use of flocculant as a binder at high concentrations. The addition of the other binders did not increase the mechanical strength of the briquettes considerably, yielding maximum compressive strengths between 0.9 and 1.1 MPa. The briquettes produced with bio char, cow manure and flocculant were the most friable, with cow manure yielding friability as low as 47%. The low friability was attributed to internal fractures that occurred within the briquettes as a result of the addition of this binder. The compressive strength and friability of the uncured briquettes at various binder concentrations can be seen in Table A.1 – Table A.3 within Appendix A1.

- *Cured*

Curing of the briquettes resulted either in no change or an increase in friability, as well as a significant increase in the maximum compressive strength of the various briquettes. This may be attributed to the activation of the binders at elevated temperatures, inducing interaction between the coal and the binders (Blesa *et al.*, 2003c).

Although at maximum concentration, the kraft lignosulphonate did not increase the mechanical strength of the briquettes above that of the binderless, cured briquette. This binder left the briquettes brittle after curing, causing a reduction in compressive strength. The fly ash, attapulgite, bio char, cow manure and flocculant all reduced the mechanical strength of the briquettes significantly for all binder concentrations.

Both coal tar pitches and MTP increased the compressive strength of the cured, binderless briquettes with every increase in binder concentration. These binders were well dispersed within the briquettes at higher concentrations after heat treatment, which was observed upon breaking the briquettes. On the other hand, bentonite and CT sludge both reduced the strength of the briquettes at concentrations above 2.5 wt%. The CT sludge seeped out of the briquettes at concentrations above 2.5 wt%, creating cracks at the surface of the briquettes, thereby reducing their compressive strength.
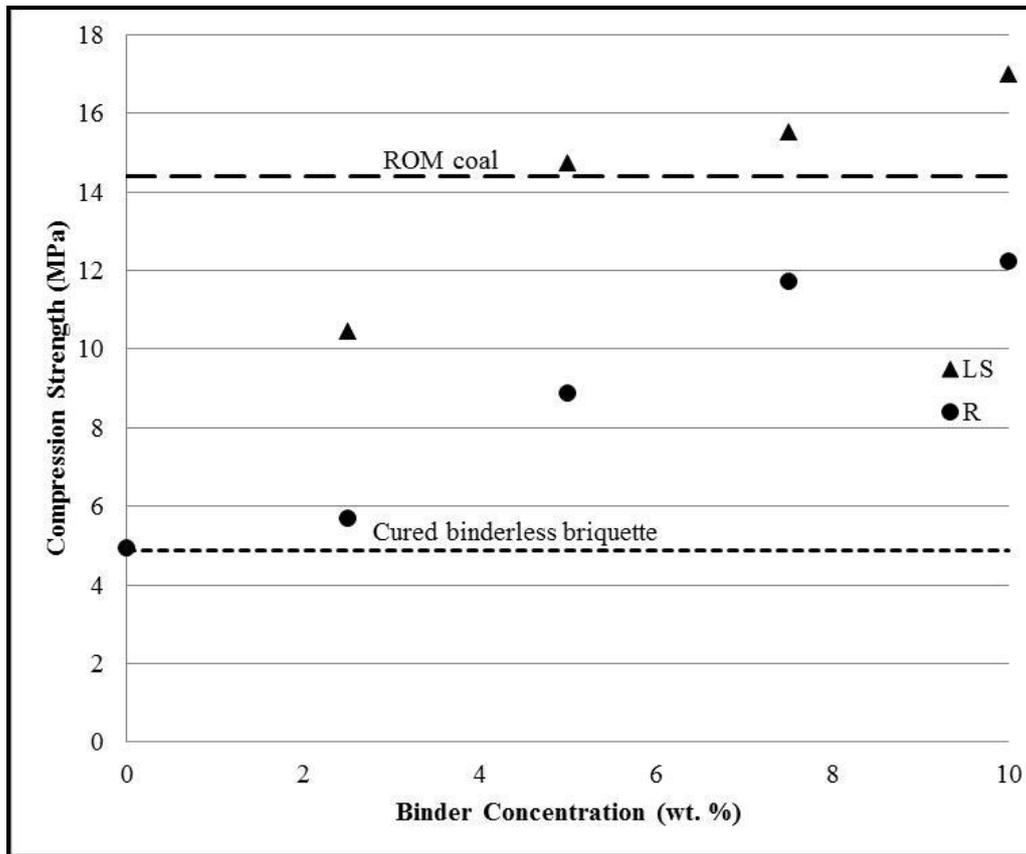
Figure 3.1 Compressive strengths of cured lignosulphonate and resin briquettes as a function of binder concentration

The most significant increase in mechanical strength was observed for lignosulphonate and resin bound briquettes, and their compressive strengths are given in Figure 3.1 as a function of the binder concentration. Figure 3.1 shows an increase in compressive strength with every increase in binder concentration. Lignosulphonate produced briquettes met the minimum requirements, even at the lowest concentration of 2.5 wt%. At concentrations above 5 wt%, the lignosulphonate briquettes could withstand pressures above 14 MPa, which was beyond the compressive strength of the ROM coal.

Lignin, the main naturally binding component in the lignosulphonate, is an amorphous thermoplastic material which undergoes plastic deformation at low compaction pressures and temperatures within its glass transition temperature (Back & Salmén, 1982), which Irvine (1984) found to be in the range of 60 and 90°C. Curing the lignosulphonate-bound briquettes at 100°C provided the desired glass transition conditions wherein the cell content of the lignin was activated or "softened". The glass transition conditions may also have reduced the viscosity and thus increased the mobility of the binding components in the lignosulphonate (Finney *et al.*, 2009). This would result in the diffusion of polymer chains and chain ends from one fibre into the proximity of an adjacent fibre, thereby increasing the bonding area. Upon

cooling, these bonds are consolidated, resulting in the formation of hardened solid bridges (Kaliyan & Morey, 2010).

Another binder producing strong briquettes was the polyester resin, with compressive strengths above the minimum requirement observed from 2.5 wt% binder addition. With every increase in resin concentration, an increase in compressive strength was observed, as illustrated in Figure 3.1. Although highly viscous at ambient temperature, the mobility of the resin was further enhanced upon curing, as a result of the decrease in viscosity. This may have resulted in the formation of solid bridges upon cooling, thereby increasing the mechanical strength of the resulting briquettes (Kaliyan & Morey, 2010). The compressive strength and friability of the cured briquettes at various binder concentrations can be seen within Table A.4 to Table A.6 in Appendix A1.

The lignosulphonate and resin bound briquettes were further investigated by light microscope imaging which provided a better visualisation of the surface morphology of the briquettes. The light microscopic images are presented in Figure 3.2 and show a significant difference between the binderless briquettes and the briquettes manufactured with the use of lignosulphonate and resin as binders. The cracks visible in the binderless briquette contribute largely to its low mechanical strength as compared to the lignosulphonate and resin bound briquettes. The resin bound briquette exhibits less voids as compared to the binderless briquette, which also becomes apparent in the mechanical strength differences between the two briquettes. The lignosulphonate bound briquette has a more uniform surface, exhibiting the least amount of voids; which validates the compressive strengths attained by the lignosulphonate bound briquettes.
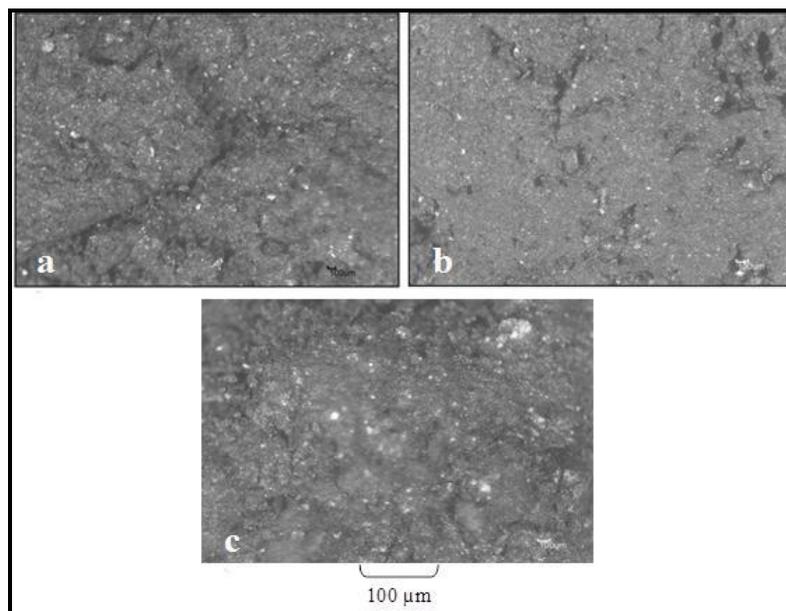

Figure 3.2 Light microscope micrographs of the surface of briquettes containing a) no binder, b) lignosulphonate as a binder and c) resin as a binder

3.3.3.   Water resistance tests

The binderless briquettes and briquettes manufactured with the various binders all disintegrated within seconds in the presence of water, which was attributed to the high kaolinite clay content and ash yield (Table 3.1). Mangena *et al.* (2004) found that kaolinite significantly reduces the water resistance of binderless briquettes when the ash yield of the parent coal is above 15 wt%. This is due to the softening and swelling nature of the kaolinite clay mineral in the presence of water.

To ensure that manufactured briquettes are comparable to their ROM coal counterparts during storage and utilisation, the strongest two briquettes were selected for waterproofing. The only additives considered to improve the water resistance of the briquettes were paraffin and wax due to their hydrophobic nature. Consequently, these additives were investigated for their use as waterproofing agents for the lignosulphonate and resin bound briquettes, yielding the highest compressive strength results.
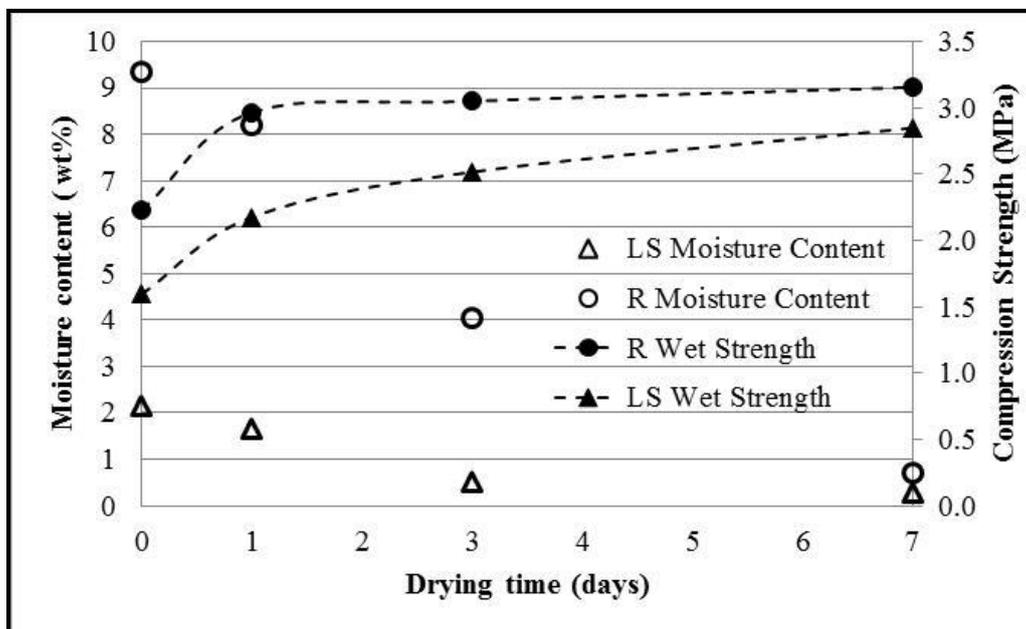
Figure 3 Moisture contents and wet strengths of briquettes as a function of air-drying time

The wet strength and moisture content of the lignosulphonate and resin bound briquettes after waterproofing, water submersion and air-drying can be seen in Figure 3. Lignosulphonate briquettes yielded better resistance when submerged in molten wax, while the resin briquettes were more water resistant when submerged in paraffin immediately after curing. The lignosulphonate briquettes had an initial moisture intake of 2 wt%, which decreased with increasing air-drying time. Moisture absorption of 5 wt% and less was deemed acceptable by Richards (1990). Although the resin briquettes initially absorbed high amounts of moisture (9.3 wt%), both binders produced briquettes that could withstand the minimum compressive strength of 375 kPa as suggested by Richards (1990) for industrial

fuel briquettes. The lowest wet strengths attained by the lignosulphonate and resin briquettes were 1.6 and 2.2 MPa respectively, and would therefore endure weathering during stockpiling and transportation.

3.4. Conclusion

Briquetting inertinite-rich, low grade coal is viable with the use of a suitable binding and waterproofing agent. Lignosulphonate and resin proved to increase the dry strength of the briquettes to a larger extent, producing briquettes that meet the minimum dry strength requirements even at the lowest concentration of 2.5 wt% addition. Due to the high kaolinite content and ash yield of the coal, waterproofing was essential. Coating the lignosulphonate briquettes with molten wax and the resin briquettes with paraffin immediately after curing resulted in water resistant briquettes that met the minimum mechanical strength requirements. Industrial fuel briquettes are required to be mechanically and thermally stable, waterproof and economically viable, and further investigation into the reactivity and economic applicability of the manufactured briquettes is required prior to industrial application.

Nomenclature

A_b	Cross-sectional area of plane of fracture of the briquette (m^2)
C_{MCS}	Concentration at maximum compressive strength (wt%)
F	Friability (%)

F_{max}	Force applied to fracture or break a briquette (N)
F_{MCS}	Friability at maximum compressive strength (%)
MCS	Maximum compressive strength (MPa)
M_f	Weight of the largest piece after dropping a briquette (g)
M_i	Initial weight of a briquette (g)
σ	Compressive strength (MPa)

Chapter 3 Bibliography

BACK, E.L. 1987. The bonding mechanism in hardboard manufacture review report. *Holzforschung - International Journal of the Biology, Chemistry, Physics and Technology of Wood*, 41(4):247-258.

BACK, E.L. & SALMÉN, N.L. 1982. Glass transitions of wood components hold implications for molding and pulping processes. *Journal of the Technical Association of the Pulp and Paper Industry*, 65:107-110.

BLESA, M.J., MIRANDA, J.L., IZQUIERDO, M.T. & MOLINER, R. 2003a. Curing temperature effect on mechanical strength of smokeless fuel briquettes prepared with molasses. *Fuel*, 82(8):943-947.

BLESA, M.J., MIRANDA, J.L., IZQUIERDO, M.T. & MOLINER, R. 2003c. Curing time effect on mechanical strength of smokeless fuel briquettes. *Fuel Processing Technology*, 80(2):155-167.

BOUDET, A.M. 2000. Lignins and lignification: Selected issues. *Plant Physiology and Biochemistry*, 38(1):81-96.

DEHONT, F. 2006. Coal briquetting technology. Date of access: 1 August 2013. <http://www.sahutconreur.com>

DEPARTMENT OF ENERGY. 2001. Coal Resources: Discards. Date of access: 2 February 2015. <http://www.energy.gov.za/files/coal_frame.html>

EKEBERG, D., GRETLAND, K.S., GUSTAFSSON, J., BRATON, S.M. & FREDHEIM, G.E. 2006. Characterisation of lignosulphonates and kraft lignin by hydrophobic interaction chromatography. *Analytica Chimica Acta*, 565(1):121-128.

ENGLAND, T. 2000. *The economic agglomeration of fine coal for industrial and commercial use*. Report for Coaltech 2020.

FINNEY, K.N., SHARIFI, V.N. & SWITHENBANK, J. 2009. Fuel Pelletization with a Binder: Part I - Identification of a Suitable Binder for Spent Mushroom Compost - Coal Tailing Pellets. *Energy and Fuels*, 23(6):3195-3202.

GUL, A.G., SIRKECI, A.A., BOYLU, F., GULDAN, G. & BURAT, F. 2015. Improvement of mechanical strength of iron ore pellets using raw and activated bentonites as binders. *Physicochemical Problems of Mineral Processing*, 51(1):23-36.

IRVINE, G.M. 1984. The glass transitions of lignin and hemicellulose and their measurement by differential thermal analysis. *Journal of the Technical Association of the Pulp and Paper Industry*, 67(5):118-121.

KALIYAN, N. & MOREY, R.V. 2009. Factors affecting strength and durability of densified biomass products. *Biomass and Bioenergy*, 33(3):337-359.

KALIYAN, N. & MOREY, R.V. 2010. Natural binders and solid bridge type binding mechanisms in briquettes and pellets made from corn stover and switchgrass. *Bioresource Technology*, 101(3):1082-1090.

MANGENA, S.J. 2001. *The Amenability of some South African bituminous coals to binderless briquetting*. Magister Technologiae dissertation, Technikon Pretoria.

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*, 85(15):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 of coal properties on binderless briquetting. *International Journal of Coal Geology*, 71(2):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 plastic (MSW) binders. *Fuel*, 115:62-69.

MILLS, J.E. 1908. *Binders for coal briquets; investigations made at the fuel-testing plant, St, Louis, Missouri (No. 343).* Government Printing Office.

MISHRA, S.L., SHARMA, S.K. & AGARWAL, R. 2000. Briquetting of lignite for domestic fuel. *Science and Industrial Research*, 59(5):413-416.

MOTAUNG, J.R., MANGENA, S.J., DE KORTE, G.J., MCCRINDLE, R.I. & VAN HEERDEN, J.H.P. 2007. Effect of coal composition and flotation reagents on the water resistance of binderless briquettes. *Coal Preparation*, 27(4):230-248.

RADLOFF, B., KIRSTEN, M. & ANDERSON, R. 2004. Wallerawang colliery rehabilitation: The coal tailings briquetting process. *Minerals Engineering*, 17(2):153-157.

RAHMAN, A.N.E., MASOOD, M.A., PRASAD, C.S.N. & VENKATESHAM, M. 1989. Influence of size and shape on the strength of briquettes. *Fuel Processing Technology*, 23(3):185-195.

RICHARDS, S.R. 1990. Physical testing of fuel briquettes. *Fuel Processing Technology*, 25(2):89-100.

SAMI. 2015. South African Mineral Industry. Date of access: 1 September 2015. <http://www.dmr.gov.za>

SANEDI. 2011. Release of the coal roadmap. Date of access: 17 March 2016. <http://www.sanedi.org.za/coal-roadmap>

SASTRY, V.S. 1991. *Pelletization of fine coals*. (No. DOE/PC/89766-T4). California Univ., Berkeley, CA (United States). Dept. of Materials Science and Mineral Engineering.

STELTE, W, HOLM, J.K, SANADI, A.R, BARSBERG, S, AHRENFELDT, J & HENRIKSEN, U.B. 2011. A study of bonding and failure mechanisms in fuel pellets from different biomass resources. *Biomass and Bioenergy*, 2(35):910-918.

WATERS, P.L. 1969. *Binders for fuel briquettes: a critical survey*. Division of Mineral Chemistry, Commonwealth Scientific and Industrial Research Organization.

WOODS, M.F., HABBERJAM, G.M., ELSWORTH, K. & BENNETT, S. 1963. The effect of maceral compostion on the binderless briquetting of hot char. *American Chemical Society Division of Energy and Fuels Preparation*, 7(2):125-144.

CHAPTER 4.

CO$_2$ reactivity of lignosulphonate and resin bound briquettes

Nthabiseng T. Modiri[,*], Hein W.J.P. Neomagus, John R. Bunt, Frans B. Waanders

The reactivity of binderless as well as lignosulphonate and resin bound briquettes was evaluated against that of lump coal. Large particle thermogravimetric analysis was conducted on the briquettes and lump coal, while using carbon dioxide as a reagent gas.

Abstract

South Africa continues to rely considerably on coal as a source of energy and carbon derived chemicals. The country's primary coal mining processes result in the production of over 28 Mt of coal fines per annum. Industrial utilisation of fine coal will not only increase the lifespan of coal, but also the amount of coal available for export. Briquetting of inertinite-rich high ash yield coal has shown promising mechanical strength results when using lignosulphonate and resin as binders. In this study, run of mine (lump) coal and briquette chars were prepared by devolatilising samples non-isothermally up to 1000°C with a hold time of 15 min. Carbon dioxide gasification was subsequently performed at 875, 900, 925, 950 and 1000°C for the lump coal, binderless, lignosulphonate and resin bound briquette chars. During the gasification process, the chars exhibited Arrhenius-type dependency on temperature with the initial reactivity increasing with increasing reaction temperature. The addition of the two binders brought no distinct change to the reactivity of the chars, but significant differences were observed between the manufactured briquettes and the run of mine coal chars. The increase in micropore surface area development during the devolatilisation process was postulated to be the major contributor to the increased reactivity of the briquettes when compared to the lump coal chars. Using the Wen model, reactivity constants were determined for the CO_2 gasification of large particles. No significant differences were observed between the activation energy of the lump coal and manufactured briquettes, with values ranging between 216 – 229 kJ/mole. The mechanical and thermal analyses of the briquettes showed promising results for industrial application, meriting a techno-economic study prior to implementation.

Keywords

Coal, CO_2 gasification, reactivity, kinetics, briquetting, micropore surface area, porosity

4.1. Introduction

Coal continues to play an essential role in the South African economy due to its relative abundance and low cost compared to other fossil- and biofuel sources (SANEDI, 2011; SAMI, 2015). In South Africa coal mining accounts for 90% of electricity generated, over 30% of the petrol and diesel produced, as well as the synthesis of over 200 major chemicals (Spath & Dayton, 2003; van Dyk *et al.*, 2006; Department of Energy, 2016). Due to rigorous mining activities, 11% of South African run-of-mine (ROM) coal becomes classified as fine (-0.5 mm) and ultrafine (-0.1 mm), which continues to be discarded into slime dams and underground workings as a result of handling, transportation and utilisation limitations (England, 2000; SANEDI, 2011). A study by Wagner (2008) showed that typical discard coal aged up to 40 years can contain between 18 - 40% ash yield, with the lowest fixed carbon content determined as 37% (db). The finer fraction (- 1.18 mm) contained heating values as high as 21 MJ/kg (ad), and can therefore be classified as a viable source of energy (Wagner, 2008).

Depleting coal reserves coupled with the dependency of the South African economy on coal utilisation and exportation, initiated explorations into fine discard coal utilisation (Jeffrey, 2005; SANEDI, 2011). For local applications, fine discard coal can be briquetted for implementation in technologies that require lump coal, such as fixed-bed gasifiers. For large scale application, briquettes can be utilised in the fixed bed dry bottom (FBDB) gasification technology, which accounts for the conversion of over 30 million tonnes of coal into liquid fuels annually in South Africa (van Dyk *et al.*, 2006). Manufactured briquettes are expected to meet the FBDB gasifier feedstock requirements to ensure continued operation. The FBDB gasifier is designed to accommodate a variety of carbonaceous material with ash yields and moisture contents up to 35 and 30%, respectively. Although designed for a top particle size of 70 mm and a bottom size of 5-8 mm, a study conducted by Bunt and Waanders (2008) showed that the most stable thermal particle size in the FBDB gasifier is between 6.3 and 25 mm (van Dyk *et al.*, 2006; Bunt & Waanders, 2008).

Various authors have investigated the suitability of different briquette configurations (binder type and pressing conditions) for household and industrial application (Rubio *et al.*, 1999; Mishra *et al.*, 2000; Mangena & de Korte, 2004; Rosin *et al.*, 2014; Massaro *et al.*, 2014; Bunt *et al.*, 2015). Criteria for the mechanical and thermal characteristics of briquettes for use in gasification are yet to be standardised as a result of the different reactor systems available worldwide. Briquettes, similar to their ROM coal counterparts, are expected to be mechanically strong, water resistant, thermally stable and reactive (Richards, 1990; Mangena *et al.*, 2004; Bunt *et al.*, 2015). Binderless agglomeration of vitrinite-rich coal has

shown great potential, producing mechanically stronger briquettes compared to inertinite-rich coal (Mangena *et al.*, 2004; Mangena & du Cann, 2007; Motaung *et al.*, 2007). This was mainly attributed to the distortion and subsequent linking of the reactive macerals into joined masses at the surface of the briquette with pressure, thereby increasing its strength – a phenomenon observed to a lesser extent in inertinite-rich coals (Mangena & du Cann, 2007). Water resistance analysis of inertinite-rich, low grade coals by Mangena *et al.* (2004) and Mangena and du Cann (2007) resulted either in the disintegration of the briquettes in water or reduced wet strengths. This was ascribed to the kaolinite mineral matter in conjunction with high ash yield (> 15 wt%) plasticising in the presence of excess water (Mangena & du Cann, 2007).

In Chapter 3 the manufacturing and testing of briquettes from inertinite-rich low grade discard coal from a colliery based in the Highveld area is discussed. Lignosulphonate and polyester resin were identified as the most effective binders for this particular coal. The addition of 5 wt% lignosulphonate with subsequent curing increased the compressive strength of the briquettes by 9.9 MPa. The briquettes could withstand a compressive strength of 14.7 MPa, which was similar to the ROM coal from the same colliery. Adding 7.5 wt% polyester resin to binderless briquettes increased the compressive strength of the briquettes from 4.88 MPa to 11.7 MPa. Applying a molten wax and paraffin coating to the surface of the briquettes after curing rendered the briquettes water resistant.

When considering the thermal characteristics of briquettes, properties such as moisture content, calorific value, emissions and heat retention during combustion, as well as gasification reactivity have been studied (Rubio *et al.*, 1999; Mishra *et al.*, 2000; Tarasov *et al.*, 2013; Massaro *et al.*, 2014; Bunt *et al.*, 2015). The agglomerates formed should contain moisture below 30% to be suitable for FBDB gasification (van Dyk *et al.*, 2006). The additives used are expected to not significantly reduce, if not enhance, the calorific value of the raw coal (Rubio *et al.*, 1999; Mishra *et al.*, 2000). While investigating the reactivity of agglomerates from Highveld fine discard coal, Bunt *et al.* (2015) found that agglomerates showed higher CO_2 gasification reactivity compared to ROM from the same colliery.

The majority of South African coalfields consist of inertinite coal and in this study the aim is to analyse the reactivity of briquettes derived from South African inertinite-rich, low grade coal fines. The reactivity of briquettes manufactured using lignosulphonate and resin as binders, is compared to ROM coal. The study will be concluded with the description of a kinetic model to predict CO_2 gasification rates for the manufactured briquettes and ROM coal.

4.2. Experimental Procedure

4.2.1. Coal

A South African, medium rank-C, low grade, inertinite-rich discard coal (filter cake) from the Highveld area was used. The particle size distribution of the filter cake indicated that 80% of the sample was below 100 μm. For comparison, ROM coal from the same colliery was obtained, characterised and analysed similarly. The proximate and ultimate analyses of the filter cake and ROM coal are provided in Table 4.1.

Table 4.1 Coal properties

	Coal fines	ROM coal
Proximate Analysis (wt%, adb[a])		
Inherent moisture	4.9	4.7
Ash yield	23.1	18.9
Volatile matter	26.3	23.0
Fixed carbon	45.7	53.4
Ultimate Analyses (wt%, dafb[b])		
Carbon	79.2	78.6
Hydrogen	4.8	4.0
Nitrogen	2.2	2.1
Oxygen	12.6	14.7
Total sulphur	1.2	0.6
ROM coal Petrographic Analysis (vol%, mmb[c])		
Vitrinite		27.7
Liptinite		5.4
Inertinite		56.1
Visible minerals		10.8
Total Reactive macerals (vol%)		63.8
Reflectance properties (%)		
Mean vitrinite random reflectance (Rr)		0.65
Rank		Bituminous Medium Rank C

[a]adb – air-dried basis, [b]dafb – dry, ash-free basis, [c]mmb – mineral matter basis

The inertinite content of the coal was 56 wt% as seen from the petrographic analysis in Table 4.1. The XRF analysis for both the coal fines and ROM coal is presented in Table 4.2. Both the coal and coal fine mineral matter were mostly comprised of SiO_2, Al_2O_3 and CaO. The concentrations of the organic species identified in the samples are typical for South African Highveld coal (van Dyk et al, 2009; Matjie et al, 2011).

Table 4.2 XRF[a] analysis for the coal fines and ROM coal ash

	Coal Fines (wt%, LOIfb[b])	ROM Coal (wt%, LOIfb)
SiO_2	47.83	50.27
Al_2O_3	26.43	24.51
CaO	7.43	10.69
SO_3	6.20	5.63
Fe_2O_3	5.00	1.78
MgO	2.36	3.3
TiO_2	1.39	1.32
K_2O	1.12	0.62
P_2O_5	0.83	0.63
Na_2O	0.41	0.81
SrO	0.41	0.36
BaO	0.30	0.2
MnO	0.09	0.07
ZrO_2	0.07	0.07
Cr_2O_3	0.03	0.00
V_2O_5	0.03	0.02

[a]ASTM D4326 XRF; [b]Loss on ignition free basis

4.2.2. Additives

The lignosulphonate utilised was a paper-pulp by-product from Mpumalanga in South Africa. The proximate and ultimate analyses of the lignosulphonate are shown in Table 4.3.

Table 4.3 Lignosulphonate proximate and ultimate analyses

	Lignosulphonate
Proximate Analysis (wt%, adb[a])	
Inherent moisture	17.4
Ash yield	14.6
Volatile matter	65.1
Fixed carbon	2.6
Ultimate Analyses (wt%, dafb[b])	
Carbon	71.8
Hydrogen	9.8
Nitrogen	1.2
Oxygen	15.5
Total sulphur	1.7

[a]adb – air-dried basis, [b]dafb – dry, ash-free basis

Prior to utilisation, the lignosulphonate was milled using a ball mill to a particle size below 1 mm. The resin obtained was a NCS 991 PA MV polyester resin with average density and viscosity (at 25°C) of 1.11 g/cm^3 and 495 mPa.s, respectively. The resin required no pre-treatment prior to addition to the coal fines.

4.2.3. Briquetting process

The briquettes were produced by means of a 13 x 13 mm cylindrical die, using a Lloyd LRX Plus Press. The lignosulphonate and resin were each added in weight concentrations of 5.0 and 7.5%. Homogeneous coal-binder mixtures were prepared using a Heidolph RZR 2041 mechanical agitator, maintained at 194 rpm for 5 minutes. Samples of 2.5 g were pressed with a force of 4.0 kN (30 MPa). Optimum curing process conditions were found to be 100°C and 3 hours for the binderless briquettes. These curing conditions were also utilised for the briquettes containing the two binders. For comparison, cylindrical samples of the ROM coal were prepared by means of shaping lump coal using a grinder and metal file. Samples with an average weight of 2 g were selected.

4.2.4. Porosimetry

The samples were stored in an oven maintained at 105°C. The porosity and surface area of the coal briquettes and ROM coal were analysed by means of CO_2 adsorption on a Micromeritics ASAP 2020 surface area and porosity analyser. Samples of approximately 0.35 g were prepared through breakage of the cylindrical briquettes and ROM coal and were subsequently degassed at 75°C at a vacuum pressure of 300 µmHg for 24 hours. Upon completion, the sample micropore surface area was analysed with CO_2 at 0°C using an ice bath. The micropore surface area was determined with the Brunauer-Emmet-Teller (BET) and Dubinin-Radushkevich (D-R) methods. The maximum micropore volume and median diameter were determined using the CO_2 adsorption Horvath-Kawazoe (H-K) method. The sample porosity was calculated by evaluating the area underneath the D-R cumulative pore volume plot (Okolo *et al.*, 2015).

The skeletal (helium) densities were analysed using a Micromeritics Accupyc II 1340 Gas Pycnometer consisting of a 10 cm^3 sample cell and expansion chamber. The sample cell was filled to approximately 75 vol.% (3 briquettes). The cell was pressurised with helium which subsequently allowed to expand into the expansion chamber, providing 2 pressure readings per sample. The recorded pressures were converted to sample volume and used in conjunction with the known sample mass to determine the sample density (Huang *et al.*, 1995).

The particle (mercury) densities were determined by means of mercury submersion. The setup was placed inside a ventilation chamber and consisted of a Sartorius ED 4202S balance, a cell containing mercury with purity greater than 99.5%, and a particle plunger. Single particles were used per measurement. The cell was placed on the balance and the briquette and plunger were submerged into the mercury (separately and combined). The weights recorded were converted to density using Archimedes' principle (Coetzee *et al.*, 2014).

4.2.5.   Reactivity

Thermal fragmentation testing was tested in an Elite Thermal Systems Ltd tube furnace model TMH16/75/610. The furnace was pre-heated to 100°C prior to inserting the briquettes and ROM coal. After inserting the sample, the furnace was heated to 700°C at a heating rate of 5°C/min with a hold time of 1 hour prior to cooling down to room temperature. The thermal fragmentation was completed under nitrogen gas of purity greater than 99.99% (AFROX South Africa), at a flow rate of 5 nL/min.

The devolatilisation and gasification of the coal were executed separately. Devolatilisation was performed in the Elite tube furnace model TMH16/75/610. Upon inserting the coal, the furnace was heated at 5 °C/min to 1000°C with a hold time of 15 min under nitrogen gas, at a flow rate of 5 nL/min.

Gasification of the coal was performed in an in-house, large particle thermogravimetric analyser (TGA) as described by Coetzee *et al.* (2013). The TGA consists of a Lenton supplied, vertical Elite Thermal Systems Ltd furnace model TSV 15/50/180. The sample was loaded into a quartz bucket, which was placed on top of a Radwag precision PS 750/C/2 mass balance. The furnace was equipped with a K-type thermocouple to measure the temperature in the reaction zone. The sample holder was inserted into the pre-determined reaction zone of the furnace and isothermal gasification reactions were conducted at 875, 900, 925, 950 and 1000°C. Afrox supplied CO_2 gas (with purity of 99.99%) was fed at 2 nL/min for the duration of the gasification experiments using a Brooks model 0254 mass flow controller. Gasification experiments were considered complete when no further mass loss was observed.

The mass loss of the sample as well as the reaction temperatures were logged and saved with time. A polynomial curve in the form of Equation 4.1 was subsequently fitted to the logged mass loss data using the sum of the least squares method in order to filter the data.

$$m_t = a_n t^n + a_{n-1} t^{n-1} + ... + a_1 t + a_0 \qquad\qquad [4.1]$$

The conversion was then determined by (Coetzee *et al.*, 2013):

$$X = \frac{m_i - m_t}{m_i - m_{ash}}$$

[4.2]

The conversion rate was determined as:

$$\frac{dX}{dt} = -\frac{[na_n t^{n-1} + (n-1)a_{n-1}t^{n-2} + \ldots + a_1]}{m_i - m_{ash}}$$

[4.3]

4.3. Results and Discussions

During thermal fragmentation analysis, the briquettes all maintained their shape and size, merely showing cracks at the particle surface as indicated for lignosulphonate bound briquettes in Figure 4.1. Similar observations were made for binderless and resin bound briquettes. This is in agreement with the findings of Bunt and Waanders (2008) who concluded that Highveld coal/char particles below 25 mm are not prone to fragmentation during the fixed bed gasification process.
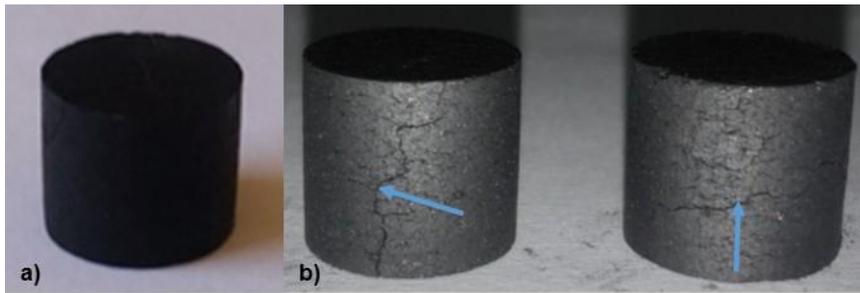

Figure 4.1 Lignosulphonate bound briquettes before (a) and after (b) thermal fragmentation

The char reactivity results for the produced briquettes as well as the ROM coal are discussed in Section 4.3. The results are separated into four subsections, namely Section 4.3.1 discussing the coal and char porosimetry, Section 4.3.2 showing the effect of reaction temperature on reactivity, in Section 4.3.3 the effect of binder addition on the char reactivity is discussed, and finally in Section 4.3.4 the kinetic modelling results are shown.

4.3.1. Porosimetry

Summarised in Table 4.4 are the CO_2 micropore surface area results consisting of the BET and D-R micropore surface areas, H-K maximum pore volumes and porosity. Table 4.4 also shows the skeletal and particle densities of the charred and uncharred briquettes and ROM coal. Prior to charring, the ROM coal micropore surface area was significantly higher than that of the manufactured briquettes. This trend was also observed in the briquette and ROM coal porosities. No significant differences were observed between median pore diameters of the briquettes and the ROM coal (with their respective chars), with a median pore diameter

of 3.96 ± 0.14 Å. The addition of lignosulphonate and resin reduced the maximum pore volume of the BL briquettes substantially. This may be as a result of the blocking of pores by the added binders (Rubio *et al.*, 1999). Upon charring, the surface area of the ROM coal reduced from 100 m^2/g to 79.6 m^2/g. This reduction can be ascribed to the possible ordering of the carbon structure, reducing the microporosity and subsequently the micropore surface area of the coal particles (Cai *et al.*, 1996; Lu *et al.*, 2002). In contrast to the ROM coal, manufactured briquettes showed an increase of micropore surface area development as a result of charring. This could be attributed to the evolution of micropores during the diffusion of the volatiles formed as a result of the pyrolysis process (Liu *et al.*, 2015). The D-R micropore surface area of the briquetted chars was found to be in the range of 184 ± 5 m^2/g. The porosity of the briquette and the ROM coal chars showed a similar trend to the BET and D-R char micropore surface area. The ROM coal porosity, on the other hand, reduced following charring. Comparison between the briquette and ROM coal char maximum pore volume showed a trend similar to porosity. The effect of binder addition was not visible after briquette devolatilisation, indicative of binder decomposition during the charring process.

Table 4.4 Properties of coal/char from CO_2 gas adsorption, helium pycnometry and mercury submersion

	ROM	ROM-C	BL	BL-C	L	L-C	R	R-C
BET (m^2/g)	100	80	64	114	55	120	48	113
D-R (m^2/g)	159	131	92	182	84	190	65	181
H-K (cm^3/g)	3.25	2.45	3.25	4.07	1.77	4.33	1.12	4.04
Porosity (%)	4.92	3.39	2.51	7.13	2.66	7.66	1.66	6.97
Skeletal Density (g/cm^3)	1.65	2.10	1.48	2.69	1.47	2.55	1.48	2.74
Particle Density (g/cm^3)	1.38	1.64	1.33	1.20	1.37	1.53	1.40	1.16

ROM – ROM coal, ROM-C – ROM coal char, BL – Binderless briquette, BL-C – Binderless briquette char, L – Lignosulphonate briquette, L-C – Lignosulphonate briquette char, R – Resin briquette, R-C – Resin briquette char

4.3.2. Effect of temperature

The conversion rate of the ROM coal char, binderless (BL), lignosulphonate (L) and resin (R) briquette chars can be seen in Figure 4.2 with carbon conversion. A decrease in the conversion rate was observed as the carbon conversion increased, with the maximum reactivity equal to the initial reactivity. This phenomenon is indicative of pore coalescence and collapse from the onset of the gasification reaction due to the low concentration of catalytic metals in the mineral matter as seen from the XRF analysis in Table 4.2 for both the

ROM coal and coal fines (Ochoa *et al.*, 2001; Kucherenko *et al.*, 2010; Coetzee *et al.*, 2013). Elevation of the reaction temperature led to an increase in the initial reactivity for the coals.
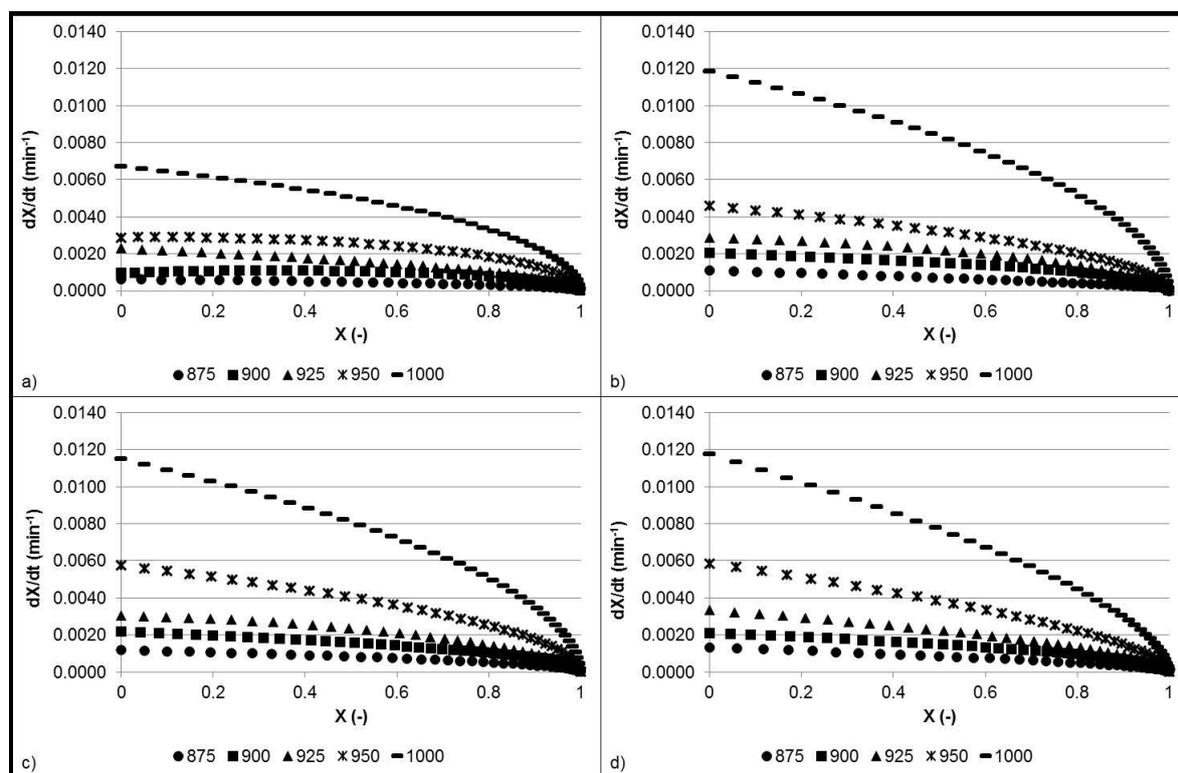

Figure 4.2 Conversion rate of (a) ROM, (b) BL (c) L and (d) R briquetted chars

4.3.3. Effect of binder addition

The effect of binder addition on the conversion rate at temperatures between 875 and 1000°C is presented in Figure 4.3. No significant difference between the reactivity of the BL, L and R briquette chars was observed at the various gasification temperatures. Brebu *et al.* (2011) determined that lignosulphonate disintegrated between 140 and 550°C, hence no significant influence in reactivity was observed subsequent to the charring process. The boiling point of polyester resin is in the range of 145 – 148°C, and is thus also removed during the charring process (NCS Composites, 2010). The addition of the two binders solely contributed to the mechanical strength of the briquettes and had no effect on briquette reactivity. The difference in CO_2 micropore surface area of the briquettes was also more pronounced prior to charring. Briquette chars exhibited D-R surface areas between 181 and 190 m^2/g, while the ROM coal char exhibited a lower D-R micropore surface area of 131 m^2/g. This is evident in the difference in char reactivity of the ROM coal and briquettes. Bunt *et al.* (2015) observed similar trends between briquette and ROM coal char reactivity. Similarly, the porosities of the BL, L and R briquette chars were higher than the ROM coal char, again substantiating the observed CO_2 char reactivities. During their analysis of pore

evolution, Liu *et al.* (2015) found that pore evolution had a great influence on micropore surface area and in turn, gasification reaction rate.
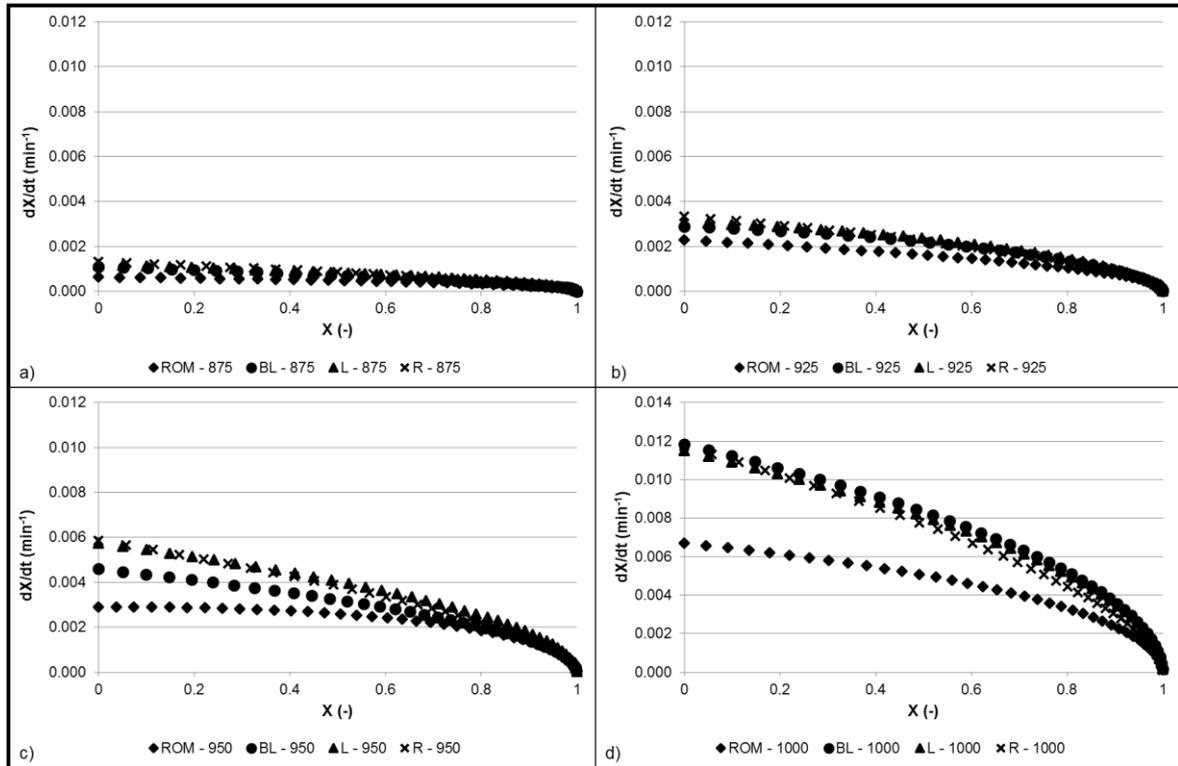
Figure 4.3 Conversion rate comparison between ROM, BL, L and R briquettes at temperatures between 875 and 1000°C

4.3.4.   Kinetic modelling

The reactivity results were modelled using the Wen model. The semi-empirical model was developed for a wider variety of pore structure evolution as a result of carbon conversion. This was achieved by introducing a second variable, the reaction order (m), as seen in Equation 4.4 (Wen, 1968):

$$\frac{dX}{dt} k_{Wen}(1-X)^m \qquad [4.4]$$

When m = 1, the Wen model assumes the same fit as that of the homogeneous model. For m = 0.667, the model predicts the SUCM fit (Wen, 1968). The Wen model reactivity predictions at 875°C are given in Figure 4.4. Reactivity predictions at 900 - 1000°C can be seen in Appendix A2.
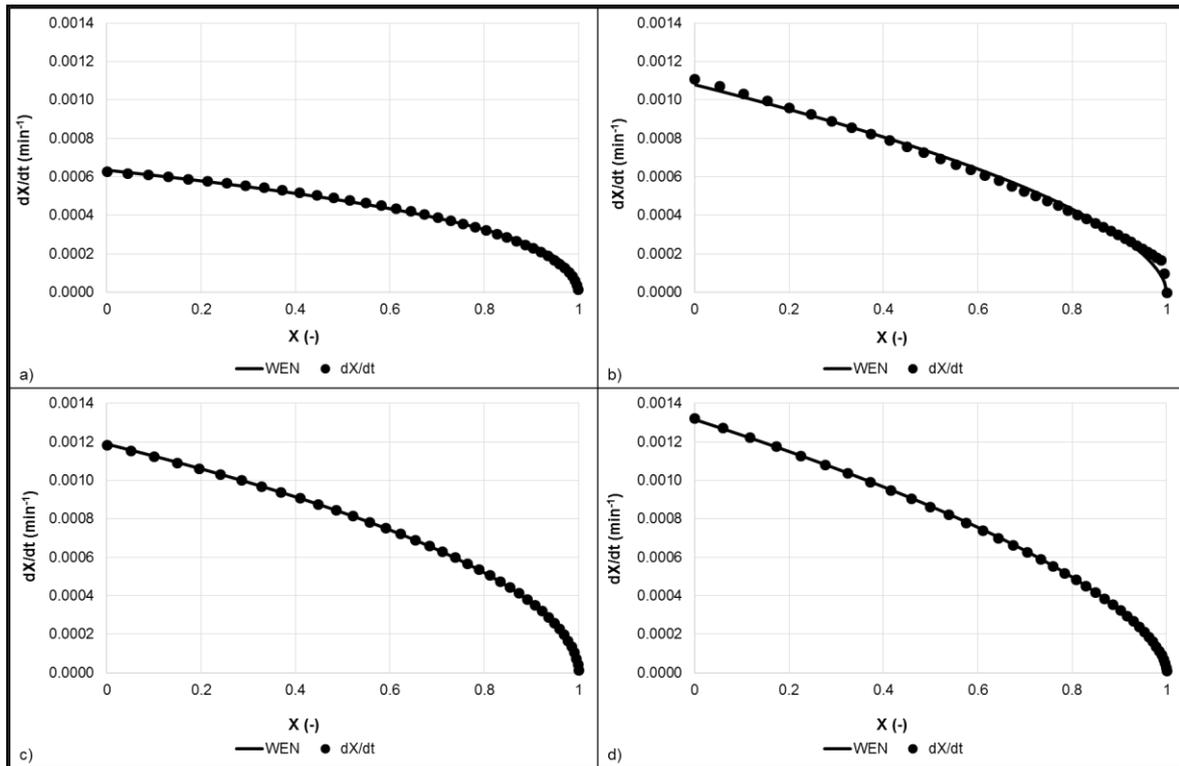
Figure 4.4 Wen model prediction of (a) ROM coal, (b) BL, (c) L and (d) R briquette char reactivity at 875°C

Table 4.5 shows the reaction order and reactivity constant values predicted using the Wen model. The reaction order showed no definitive trend with increasing temperature. An average value of 0.49 was obtained for the gasification experiments, which is similar to the assumed 0.5 for cylindrical particles when applying the shrinking unreacted core model (SUCM) in the chemical reaction controlled regime (Mahinpey & Gomez, 2016). The reaction order was generally found to be lower for ROM coal, when compared to the manufactured briquettes. The SUCM was also fitted to the reactivity data and the results can be seen in Appendix A3. Similar trends were observed in the reactivity predicted using the SUCM and Wen model. The Wen model showed more superior fit, exhibiting higher quality of fit (QOF) values compared to the SUCM.

Table 4.5 Reactivity constants and reaction orders determined using the Wen model

T (°C)	ROM		BL		L		R	
	m (-)	$k \times 10^{-3}$ (min^{-1})	m (-)	$k \times 10^{-3}$ (min^{-1})	m (-)	$k \times 10^{-3}$ (min^{-1})	m (-)	$k \times 10^{-3}$ (min^{-1})
875	0.41	0.64	0.57	1.08	0.51	1.19	0.61	1.32
900	0.29	1.19	0.45	2.08	0.42	2.13	0.48	2.09
925	0.48	2.27	0.49	3.03	0.50	3.23	0.56	3.33
950	0.36	3.18	0.51	4.61	0.51	5.76	0.60	5.84
1000	0.46	6.83	0.51	11.88	0.51	11.54	0.60	11.67
Average QOF (%)	89		94		94		98	

The reactivity constants obtained from the Wen model were used in the construction of Arrhenius plots (Figure 4.5), to further study the effect of the gasification reaction temperature.
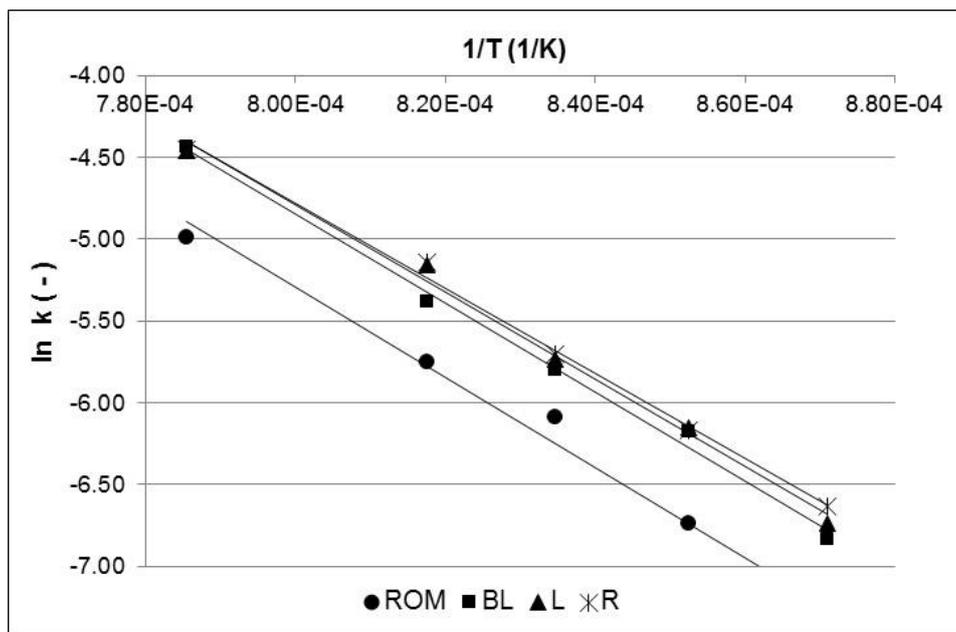
Figure 4.5 ROM, BL, L and R Arrhenius plots

A linear fit was observed for all four particles, indicating that the gasification reactions follow Arrhenius-type kinetics (Dutta *et al.*, 1977; Guizani *et al.*, 2013). Activation energy values were found to range between 216 and 229 kJ/mole as seen in Table 4.6. These values are within the range observed by Everson *et al.* (2013) during CO_2 gasification of an inertinite-rich, Highveld coal.

Table 4.6 Activation energy of ROM,BL, L and R briquette chars

	ROM	BL	L	R
$E_{a,Wen}$ **(kJ/mole)**	229	227	222	216

4.4. Conclusion

The addition of lignosulphonate and resin as binders during the briquetting of inertinite-rich coal fines proved to significantly enhance the mechanical strength of the resultant briquettes. The binders, however, brought no substantial changes to the char reactivities, due to the extensive heat the briquettes were subjected to during the devolatilisation and gasification processes. This was as a result of the disintegration of the binders during devolatilisation. The briquetting process itself brought significant changes to the char reactivity when compared to ROM coal char. The manufactured briquette chars exhibited approximately double the gasification reaction rate of the ROM coal and can therefore directly be applied to the current FBDB gasification process. Analysis of the CO_2 gas adsorption showed that briquette chars had similar micropore surface areas, which were considerably higher than the ROM coal char. The agglomeration of coal fines was found to enhance the CO_2 gasification reaction rate as a result of compaction differences between the briquette and ROM coal chars. Upon investigating various kinetic models, the Wen model was found to predict the reactivity data closely. No significant difference in the activation energy of the ROM coal and manufactured briquettes was observed. The mechanical and thermal analyses of the lignosulphonate and resin bound briquettes showed promising results for industrial application, meriting a techno-economic study to determine economic applicability.

Acknowledgements

Nomenclature

a	Polynomial coefficient (-)
E_a	Activation energy (kJ/mole)
k	Reactivity constant (min^{-1})

m	Reaction order (-)
m_{ash}	Mass of sample ash (g)
m_i	Initial sample mass (g)
m_t	Sample mass at time t (g)
n	Particle geometry form factor (-)
t_j	Time value j
X	Conversion (-)
X_j	Conversion at time t_j
dX/dt	Conversion rate (min^{-1})

Chapter 4 Bibliography

BREBU, M., CAZACU, G. & CHIRILA, O. 2011. Pyrolysis of lignin - a potential method for obtaining chemicals and/or fuels. *Cellulose Chemistry and Technology*, 45(1):43-50.

BUNT, J.R., NEOMAGUS, H.W.J.P., BOTHA, A. & WAANDERS, F.B. 2015. Reactivity study of fine discard coal agglomerates. *Journal of Analytical and Applied Pyrolysis*, 113:723-728.

BUNT, J.R. & WAANDERS, F.B. 2008. An understanding of lump coal physical property behaviour (density and particle size effects) impacting on a commercial-scale Sasol-Lurgi FBDB gasifier. *Fuel*, 87(13-14):2856-2865.

CAI, H.Y., GÜELL, A.J., CHATZAKIS, I.N., LIM, J.Y., DUGWELL, D.R. & KANDIYOTI, D.R. 1996. Combustion reactivity and morphological change in coal chars: effect of pyrolysis temperature, heating rate and pressure. *Fuel*, 75(1):15-24.

COETZEE, S., NEOMAGUS, H.W.J.P., BUNT, J.R. & EVERSON, R.C. 2013. Improved Reactivity of Large Coal Particles by K_2CO_3 Addition during Steam Gasification. *Fuel Processing Technology*, 114:75-80.

COETZEE, S., NEOMAGUS, H.W.J.P., BUNT, J.R., STRYDOM, C.A. & SCHOBERT, H.H. 2014. The transient swelling behaviour of large (-20 + 16 mm) South African coal particles during low-temperature devolatilisation. *Fuel*, 136:79-88.

DEPARTMENT OF ENERGY. 2016. Basic Electricity. http://www.energy.gov.za/files/electricity Date of access: 17 March 2016.

DUTTA, S., Wen, C.Y. & BELT, R.J. 1977. Reactivity of coal and char. 1. In carbon dioxide atmosphere. *Industrial & Engineering Chemistry Process Design and Development*, 16(1):20-30.

ENGLAND, T. 2000. *The economic agglomeration of fine coal for industrial and commercial use*. Report for Coaltech 2020.

EVERSON, R.C., OKOLO, G.N., NEOMAGUS, H.W.J.P. & DOS SANTOS, J.M. 2013. X-ray diffraction parameters and reaction rate modeling for gasification and combustion of chars derived from inertinite-rich coals. *Fuel*, 109:148-156.

GUIZANI, C., SANZ, F.J.E. & SALVADOR, S. 2013. The gasification reactivity of high-heating-rate chars in single and mixed atmospheres of H_2O and CO_2. *Fuel*, 108:812-823.

HUANG, H., WANG, K., BODILY, D.M. & HUCKA, V.J. 1995. Density measurements of Argonne Premium coal samples. *Energy & Fuels*, 9(1):20-24.

IRFAN, M.F., USMAN, M.R. & KUSAKABE, K. 2011. Coal gasification in CO_2 atmosphere and its kinetics since 1948: A brief review. *Energy*, 36(1):12-40.

JEFFREY, L.S. 2005. Characterization of the coal resources of South Africa. *The Journal of The South African Institute of Mining and Metallurgy*, 105(2):95-102.

KUCHERENKO, V.A., SHENDRIK, T.G., TAMARKINA, Y.V. & MYSYK, R.D. 2010. Nanoporosity development in the thermal-shock KOH activation of brown coal. *Carbon*, 48(15):4556-4577.

LAURENDEAU, N.M. 1978. Heterogeneous kinetics of coal char gasification and combustion. *Progress in Energy and Combustion Science*, 4(4):221-270.

LIU, G., BENYON, P., BENFELL, K.E., BRYANT, G.W., TATE, A.G., BOYD, R.K., HARRIS, D.J. & WALL, T.F. 2000. The porous structure of bituminous coal chars and its influence on combustion and gasification under chemically controlled conditions. *Fuel*, 79(6):617-626.

LIU, L., CAO, Y. & LIU, Q. 2015. Kinetics studies and structure characteristics of coal char under pressurized CO_2 gasification conditions. *Fuel*, 146:103-110.

LU, L., KONG, C., SAHAJWALLA, V. & HARRIS, D. 2002. Char structuralm ordering during pyrolysis and combustion and its influence on char reactivity. *Fuel*, 81(9):1215-1225.

MAHINPEY, N. & GOMEZ, A. 2016. Review of gasification fundamentals and new findings: Reactors, feedstock, and kinetic studies. *Chemical Engineering Science*, 148:14-31.

MANGENA, S.J. & DE KORTE, G.J. 2004. *Development of a process for producing low-smoke fuels from coal discards*. Report, Division of Mining Technology, CSIR.

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*, 85(15):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 of coal properties on binderless briquetting. *International Journal of Coal Geology*, 71(2):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 plastic (MSW) binders. *Fuel*, 115:62-69.

MATJIE, R.H., FRENCH, D., WARD, C.R., PISTORIUS, P.C. and LI, Z., 2011. Behaviour of coal mineral matter in sintering and slagging of ash during the gasification process. *Fuel Processing Technology*, *92*(8), pp.1426-1433.

MISHRA, S.L., SHARMA, S.K. & AGARWAL, R. 2000. Briquetting of lignite for domestic fuel. *Science and Industrial Research*, 59(5):413-416.

MOLINA, A. & MONDRAGON, F. 1998. Reactivity of coal gasification with steam and CO_2. *Fuel*, 77(15):1831-1839.

MOTAUNG, J.R., MANGENA, S.J., DE KORTE, G.J., MCCRINDLE, R.I. & VAN HEERDEN, J.H.P. 2007. Effect of coal composition and flotation reagents on the water resistance of binderless briquettes. *Coal Preparation*, 27(4):230-248.

NCS COMPOSITES. 2010. NCS Composites pure science. Date of access: 29 May 2016. <http://www.ncscomposites.com.au/wp-content/uploads/msdss>

OCHOA, J., CASSANELLO, M.C., BONELLI, P.R. & CUKIERMAN, A.L. 2001. CO_2 gaification of Argentinean coal chars: a kinetic characterization. *Fuel Processing Technology*, 74(3):161-176.

OKOLO, G.N., EVERSON, R.C., NEOMAGUS, H.W.J.P., ROBERTS, M.J. & SAKUROVS, R. 2015. Comparing the porosity and surface areas of coal as measured by gas adsorption, mercury intrusion and SAXS techniques. *Fuel*, 141:293-304.

RICHARDS, S.R. 1990. Physical testing of fuel briquettes. *Fuel Processing Technology*, 25(2):89-100.

ROBERTS, D.G. & HARRIS, D.J. 2007. Char gasification in mixtures of CO_2 and H_2O: Competition and inhibition. *Fuel*, 86(17):2672-2678.

ROSIN, A., SCHRÖDER, H.W. & REPKE, J.U. 2014. Briquetting press as lock-free continuous feeding system for pressurized gasifiers. *Fuel*, 116:871-878.

RUBIO, B., IZQUIERDO, M.T. & SEGURA, E. 1999. Effect of binder addition om the mechanical and physicochemical properties of low rank coal char briquettes. *Carbon*, 37(11):1833-1841.

SAMI. 2015. South African Mineral Industry. Date of access: 20 February 2016. <http://www.dmr.gov.za/publications/south-africas-mineral-industry-sami>

SANEDI. 2011. Release of the coal roadmap. Date of access: 17 March 2016. <http://www.sanedi.org.za/coal-roadmap>

SPATH, P.L. & DAYTON, D.C. 2003. *Preliminary screening - technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas.* (No. NREL/TP-510-34929). National Renewable Energy Lab Golden Co.

TARASOV, D., SHAHI, C. & LEITCH, M. 2013. Effect of additives on wood pellet physical and thermal characteristics: A review. *ISRN Forestry*, 2013:1-6.

VAN DYK, J.C., BENSON, S.A., LAUMB, M.L. and WAANDERS, B., 2009. Coal and coal ash characteristics to understand mineral transformations and slag formation. *Fuel*, *88*(6), pp.1057-1063.

VAN DYK, J.C., KEYSER, M.J. & COERTZEN, M. 2006. Syngas production from South African coal sources using Sasol-Lurgi gasifiers. *Coal Geology*, 65(3):243-253.

WAGNER, N.J. 2008. The characterization of weathered discard coals and their behaviour during combustion. *Fuel*, 87(8):1687-1697.

Wen, C.Y. 1968. Noncatalytic heterogeneous solid-fluid reaction models. *Industrial & Engineering Chemistry*, 60(9):34-54.

CHAPTER 5. CONCLUSION

5.1. Introduction

Briquettes produced from inertinite-rich, high ash yield discard coal (with the aid of various binders) were compared to ROM coal from the same origin. The Lloyd LRX Plus press was used to prepare 13 x 13 mm cylindrical briquettes. The fine coal discard and ROM coal were characterised using chemical, mineralogical, petrographic and physical analyses. The resultant briquettes and ROM coal were subjected to mechanical strength, thermal stability and reactivity assessments. The SUCM for cylindrical particles and the Wen model could describe the obtained reactivity data accurately.

5.2. Concluding remarks

Using petrographic analysis, the sample was identified as a medium rank-C coal. PSD analysis of the coal fines showed that 80% of the sample was below 100 µm, and could therefore be classified as ultra-fine. This size fraction is below the minimum acceptable particle size specified for the FBDB gasification technology. The objectives of this report are separately discussed:

- **Identify suitable binders**

The binders procured and tested in this study were:

Clays (attapulgite and bentonite) from Yellowstone bentonite mine near Koppies in the Free State. The bio char was produced from sunflower husks located at a farm in the North West province. Cow dung was also obtained at a farm in the North West province. Crystallised medium tar pitch, coal tar sludge, fly ash, and 2 coal tar pitches were sourced from a South African petrochemical company. The flocculant was supplied by a South African mining chemicals supplier. Both the lignosulphonates and kraft lignosulphonate were paper mill by-products from Mpumalanga. Polyester resin was supplied by NCS Resins.

- **Quantify the effect of binder type and concentration on the mechanical strength of the manufactured briquettes**

During the mechanical strength analysis, compressive strength and drop shatter resistance of the briquettes and ROM coal were determined. Prior to curing, the added binders had no significant influence on the mechanical strength of the briquettes. Curing binderless briquettes at 100°C for 3 hours yielded the highest mechanical strength results. These curing conditions were subsequently applied to all the briquettes containing the various binders. Once cured, briquettes containing lignosulphonate and resin could withstand the

highest compressive pressures. The compressive strength of the binderless briquettes was determined as 4.88 MPa. 7.5 wt% addition of lignosulphonate and resin increased the mechanical strength to 16 and 12 MPa, respectively. At concentrations above 5 wt%, the lignosulphonate briquettes could withstand pressures above 14 MPa, which was equivalent to the compressive strength of the ROM coal. During the drop shatter tests, the briquettes mostly maintained their shape and size. Cured briquettes prepared from flocculant yielded friability results as low as 64% due to the brittle nature of the resultant briquette.

- **Determine the effect of binder addition on the water resistance of the briquettes**

As a result of the high kaolinite content of the coal fines, the binderless briquettes were not resistant to weathering. Adding the various binders did not enhance the water resistance of the briquettes. Application of a wax or paraffin coating immediately after curing ensured that the minimum requirements for water resistance were met.

- **Assess the effect of binder addition on the thermal stability of the briquettes**

None of the briquettes significantly shattered during the thermal stability analysis. This was as a result of the briquettes being within the thermal stable particle size fraction.

- **Evaluate the effect of binder addition on the reactivity of the briquettes**

Reactivity analyses were conducted on lignosulphonate and resin bound briquettes. The reactivity of the coals was analysed using a large particle TGA at 875, 900, 925, 950 and 1000°C, with CO_2 as the reaction gas. Briquette and ROM coal chars were prepared at 1000°C. The addition of lignosulphonate and resin had no significant effect on the reactivity of the briquette chars. This was attributed to the disintegration of the binders during the charring process. The briquette derived chars showed higher reactivity compared to ROM coal char. Further investigation using CO_2 gas adsorption indicated higher micropore surface area and porosity for briquette derived chars compared to the ROM coal chars; therefore verifying trends observed during CO_2 gasification.

- **Suggest a suitable kinetic model to predict CO_2 gasification rates for the produced briquettes and ROM coal**

The Wen model predicted the reactivity data of the briquette and ROM coal chars accurately with a quality of fit of 88%. No significant differences were observed in the activation energy of the briquette and ROM coal chars.

5.3. Contribution to the coal science and technology field

From the findings of this study, the following could be identified as contributions to the field of coal science and technology;

- Suitable binders were identified for the briquetting of inertinite-rich coal fines for application in fixed-bed gasification. Production of briquettes comparable in strength to ROM coal was achieved.
- Although comparisons between briquette and ROM coal char reactivity have been investigated, this study further elaborated on the understanding of the increased briquette reactivity through CO_2 gas adsorption.
- The effect of binder addition on char reactivity was determined. It was established that the addition of lignosulphonate and resin does not influence the gasification reactivity.
- Reactivity constants were well predicted for CO_2 gasification of lignosulphonate and resin bound briquettes at 875, 900, 925, 950 and 1000°C.
- Technical feasibility of briquetting inertinite-rich, high ash coal fines for application in FBDB gasification was accomplished.

5.4. Recommendations

To enhance the results from this study, the following recommendations are made;

- Revise and confirm the drop shatter resistance analysis by determining the briquette impact resistance index (IRI).
- Although technically viable, an economic feasibility study is required to determine the applicability of the process to an existing gasification process.
- Gas emissions resulting from the addition of lignosulphonate and/or resin need to be investigated.
- A reactivity study using various combinations of steam, oxygen and carbon dioxide at higher pressures is required to better approximate the behaviour of the briquettes during industrial fixed-bed gasification.
- Pilot scale testing of the briquettes is advised.

APPENDIX A.

Additional data, not provided in Chapters 3 and 4, is provided in this section. The complete mechanical strength results are given in Appendix A1. The Wen model fit for temperatures not shown in Chapter 4 (900, 925, 950 and 1000°C) is discussed in Appendix A2. An additional model predicting the reactivity data, the SUCM, is presented in Appendix A3.

Appendix A1

Uncured

Table A.1 Compressive strength results (MPa) of uncured briquettes at various binder concentrations

Binder	Binder Concentration (wt%)			
	2.5	5	7.5	10
Attapulgite	0.99	0.96	1.01	1.06
Bentonite	0.94	0.93	0.96	0.94
Bio char	0.66	0.70	0.89	-
Cow manure	0.90	0.92	0.94	0.33
Lignosulphonate	0.63	0.63	0.45	0.41
Kraft Lignosulphonate	0.88	0.93	0.90	0.78
Paraffin	0.83	0.80	0.78	1.04
Polyester resin	0.85	0.82	0.80	0.51
Wax (cobalt catalysed)	0.92	0.82	0.87	0.85
Wax (iron catalysed)	0.91	0.82	0.79	0.77
(55/59) Coal tar pitch	0.85	0.96	1.00	1.13
(68/73) Coal tar pitch	1.01	0.91	0.99	1.05
MTP	0.99	0.91	0.99	1.02
CT sludge	0.84	0.88	0.70	0.62
Fly ash	0.88	0.81	0.73	0.59

Uncured, the binderless briquette could withstand compressive pressures up to 0.90 MPa. From Table A.1 it can be seen that adding the various binders did not significantly enhance the mechanical strength of the briquettes. Uncured, lignosulphonate resulted in a significant reduction in the mechanical strength of the briquettes.

Table A.2 Friability results (%) of uncured briquettes at various binder concentrations

Binder	Binder Concentration (wt%)			
	2.5	**5**	**7.5**	**10**
Attapulgite	97	96	96	96
Bentonite	98	96	98	98
Bio char	38	62	56	-
Cow manure	72	53	47	33
Lignosulphonate	99	98	99	98
Kraft Lignosulphonate	97	97	98	98
Paraffin	97	98	96	83
Polyester resin	98	98	98	99
Wax (cobalt catalysed)	97	98	98	98
Wax (iron catalysed)	96	97	96	97
(55/59) Coal tar pitch	96	97	97	97
(68/73) Coal tar pitch	97	98	98	99
MTP	97	99	99	100
CT sludge	98	98	97	98
Fly ash	98	99	99	35

Friability results can be seen in Table A.2. Uncured, the friability of the binderless briquette was found to be 97%. Bio char and cow manure produced briquettes with the lowest shatter resistance. Both the bio char and cow manure showed a wide particle size distribution, creating weak points within the briquettes, resulting in lowered friability.

Table A.3 Compressive strength and friability results of uncured flocculant bound briquettes

	Flocculant Concentration (wt%)			
	1	**2**	**3**	**4**
Uncured Compressive Strength (MPa)	4.03	4.06	2.26	2.18
Uncured Friability (%)	54	50	43	34

The addition of flocculant proved to enhance the mechanical strength of the uncured briquettes significantly. Above 2 wt% flocculant addition, however, the mechanical strength of the briquettes reduced. At higher concentrations, the flocculant was assumed to interact with itself instead of the coal fines; thereby producing weaker briquettes. Flocculant addition did not increase the friability of the briquettes.

Cured

Table A.4 Compressive strength results (MPa) of cured briquettes at various binder concentrations

Binder	Binder Concentration (wt%)			
	2.5	5	7.5	10
Attapulgite	3.25	2.62	2.56	2.40
Bentonite	5.47	3.32	3.24	1.82
Bio char	3.46	2.46	2.17	-
Cow manure	2.40	2.20	2.39	0.50
Lignosulphonate	10.5	14.7	15.5	17.0
Kraft Lignosulphonate	2.33	2.96	3.27	2.49
Paraffin	2.84	3.27	3.70	2.27
Polyester resin	5.70	8.89	11.7	12.3
Wax (cobalt catalysed)	5.53	3.32	3.24	2.05
Wax (iron catalysed)	2.70	1.34	1.14	1.02
(55/59) Coal tar pitch	3.94	4.42	5.57	3.02
(68/73) Coal tar pitch	2.99	4.22	5.86	6.38
MTP	2.15	6.44	7.06	5.42
CT sludge	5.77	2.11	2.42	2.23
Fly ash	1.54	3.88	3.61	0.15

Curing increased the binderless briquette mechanical strength to 4.88 MPa. In addition to lignosulphonate and resin, MTP and (68/73) coal tar pitch increased the briquette mechanical strength with increasing binder concentration. Binders enhancing mechanical strength at low concentrations include bentonite clay and CT sludge. The remainder of the binders proved to reduce the mechanical strength of the briquettes.

Table A.5 Friability results (%) of cured briquettes at various binder concentrations

Binder	Binder Concentration (wt%)			
	2.5	5	7.5	10
Attapulgite	98	99	98	96
Bentonite	98	98	97	98
Bio char	93	70	66	-
Cow manure	90	85	83	39
Lignosulphonate	99	99	99	97
Kraft Lignosulphonate	97	97	97	96
Paraffin	93	91	91	92
Polyester resin	99	99	99	100
Wax (cobalt catalysed)	97	98	99	99
Wax (iron catalysed)	97	96	98	100
(55/59) Coal tar pitch	96	97	98	98
(68/73) Coal tar pitch	96	97	99	98
MTP	98	99	100	100
CT sludge	100	100	100	98
Fly ash	95	97	97	45

Addition of the various binders did not significantly influence the friability of the cured, binderless briquette (with friability of 97%). At high concentrations, the fly ash and cow manure significantly reduced the friability of the briquettes. This was attributed to the brittle nature of the cow manure and fly ash bound briquettes at high binder concentrations.

Table A.6 Compressive strength and friability results of cured flocculant bound briquettes

	Flocculant Concentration (wt%)			
	1	2	3	4
Cured Compressive Strength (MPa)	1.38	1.03	0.50	0.20
Cured Friability (%)	64	59	35	25

Upon curing, flocculant bound briquettes were brittle and displayed low compressive strength and friability results.

Appendix A2
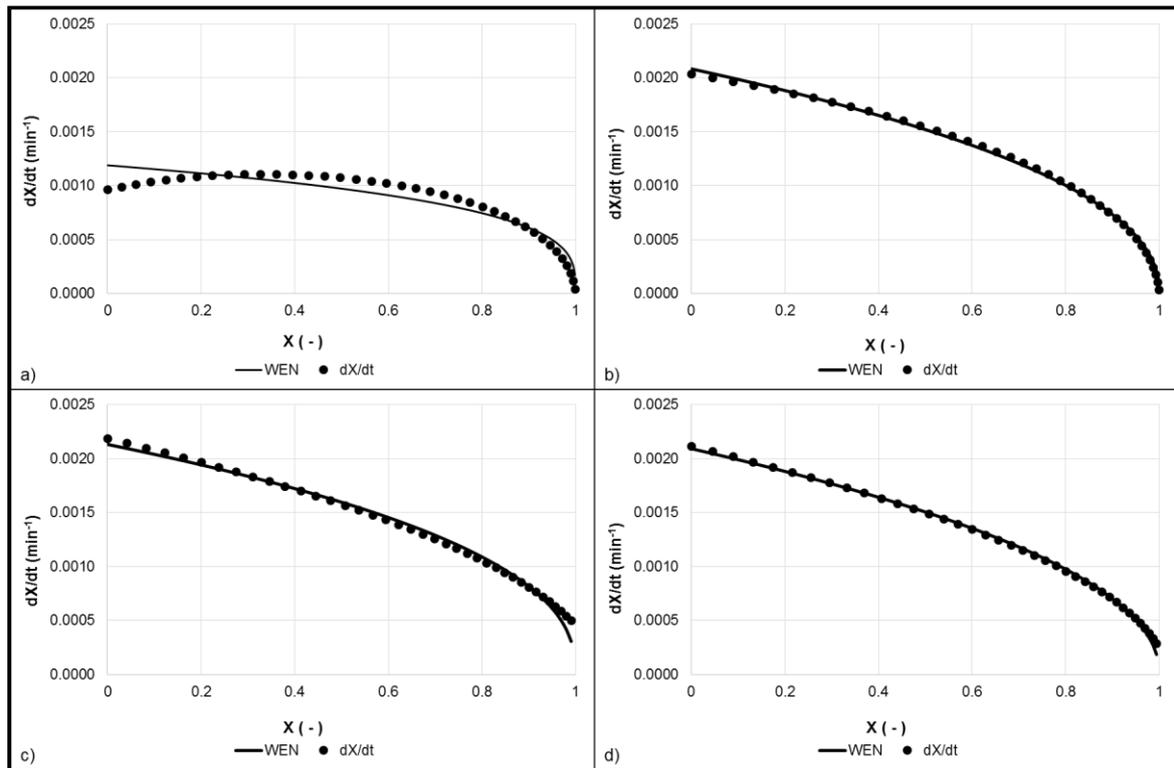
Figure A.1 Wen model prediction of (a) ROM coal, (b) BL, (c) L and (d) R briquette char reactivity at 900°C

At 900°C the Wen model predicted the briquette derived char (Figure A.1 b-c) reactivity well with an average quality of fit (QOF) of 95%. A lower QOF (77%) was obtained for the ROM coal char at this temperature as seen in Figure A.1 a.
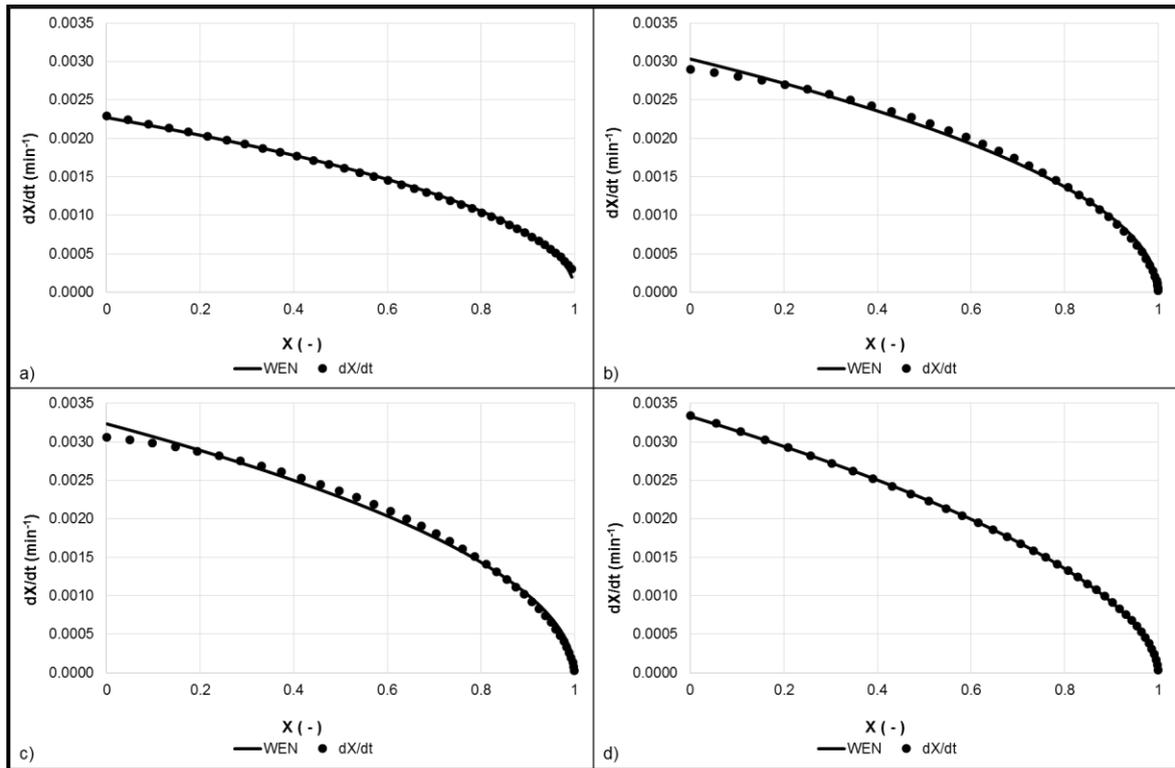
Figure A.2 Wen model prediction of (a) ROM coal, (b) BL, (c) L and (d) R briquette char reactivity at 925°C

As seen in Figure A.2, both the ROM coal and briquette char reactivities were well predicted by the Wen model, with QOF of 97 and 91% for the ROM coal and briquette chars, respectively.
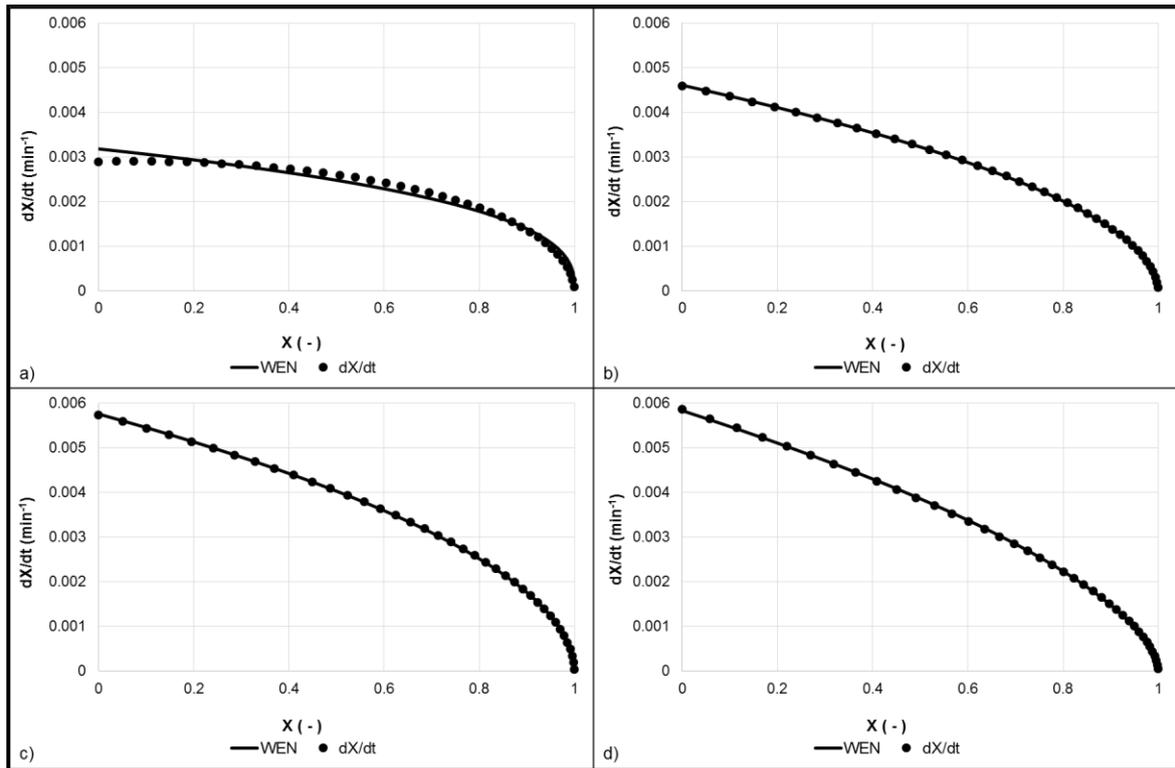
Figure A.3 Wen model prediction of (a) ROM coal, (b) BL, (c) L and (d) R briquette char reactivity at 950°C

Figure A.3 shows the Wen model predictions at 950°C. The model showed better results for the briquette chars, compared to the ROM coal char. The QOF for the ROM coal and briquette chars was 86 and 97%.
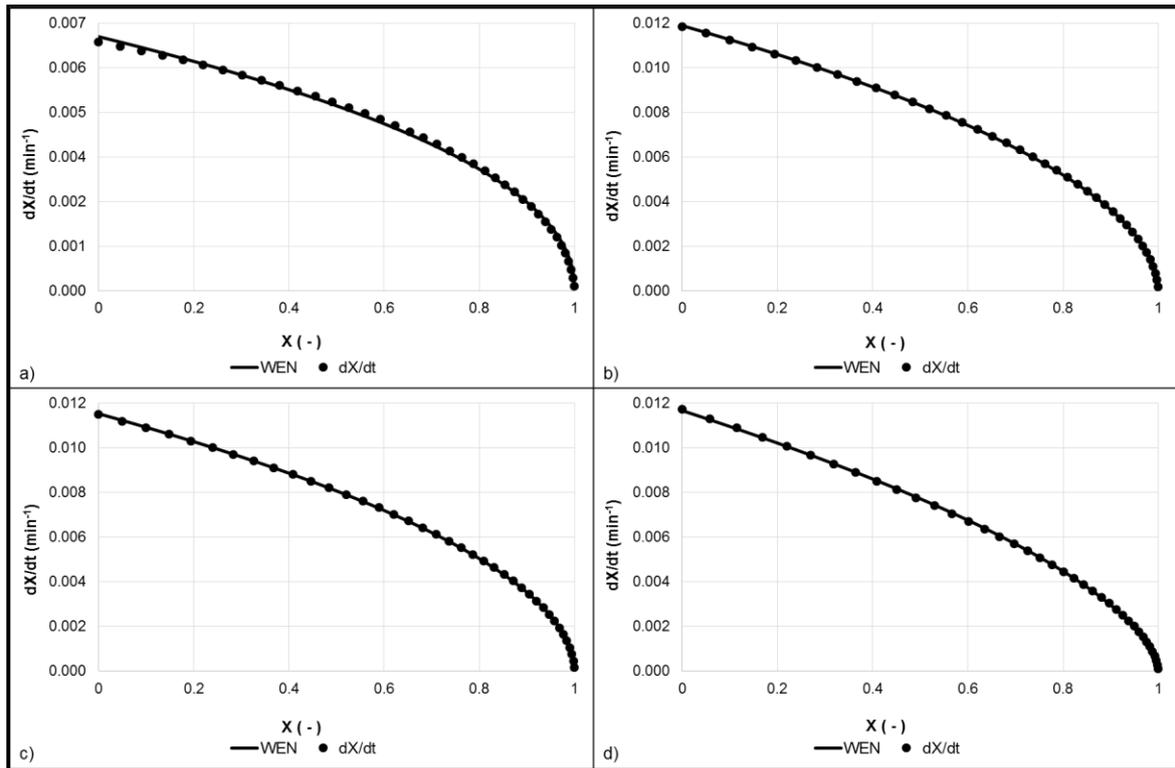
Figure A.4 Wen model prediction of (a) ROM coal, (b) BL, (c) L and (d) R briquette char reactivity at 1000°C

Similar to the above mentioned temperatures, the Wen model reactivity prediction at 1000°C for ROM coal and briquette chars was precise with QOF of 93 and 97% for the ROM and briquette derived chars.

Appendix A3

The SUCM assumes that the core of a given particle shrinks leaving an ash outer layer, while the carbon conversion takes place at the exposed, unreacted surface (Irfan *et al.*, 2011; Mahinpey & Gomez, 2016). Assuming chemical reaction control, the SUCM is given as (Mahinpey & Gomez, 2016):

$$\frac{dX}{dt} = k_{SUCM}(1-X)^n \qquad\qquad [A.1]$$

In the case of cylindrical particles n = 0.5.
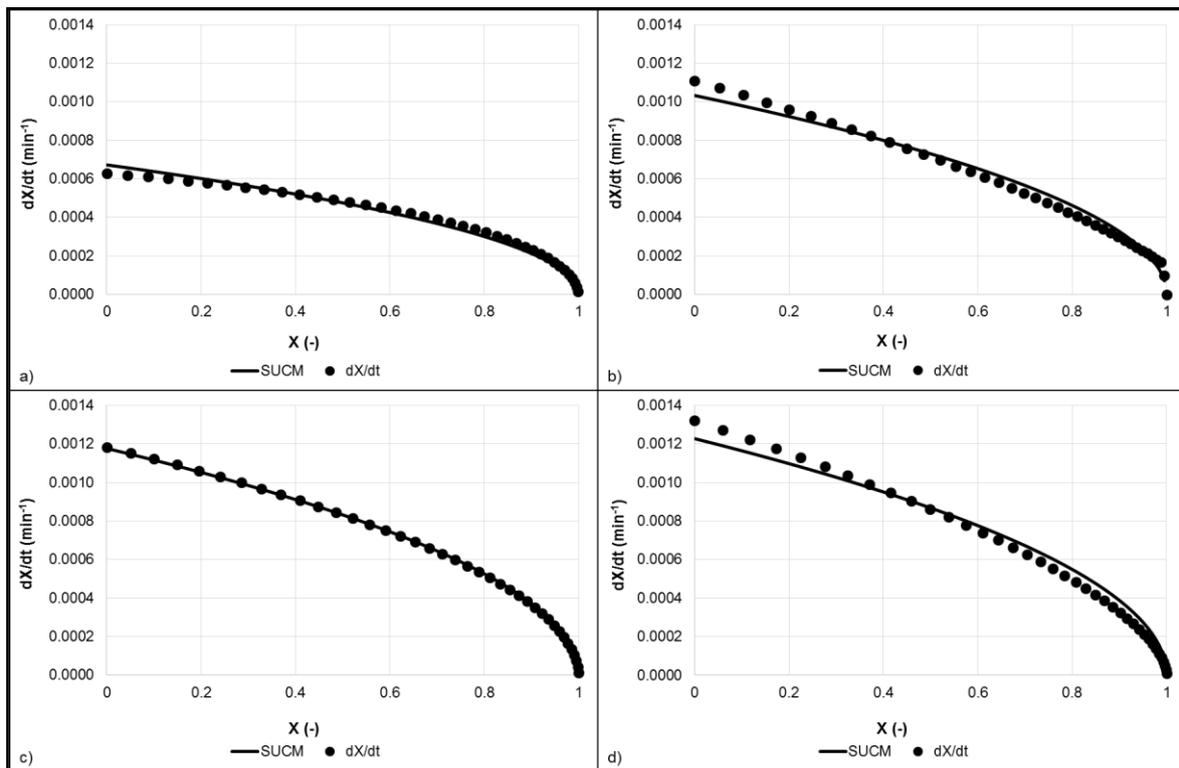
Figure A.5 SUCM fitted on (a) ROM coal, (b) BL, (c) L and (d) R briquette reactivity at 875°C

A minimum (QOF) of 79% (for R briquettes) was obtained when fitting the SUCM to the gasification reaction rate results at 875°C (Figure A.5). Comparison of the Wen model and SUCM at 875°C indicated a more precise fit by the Wen model.
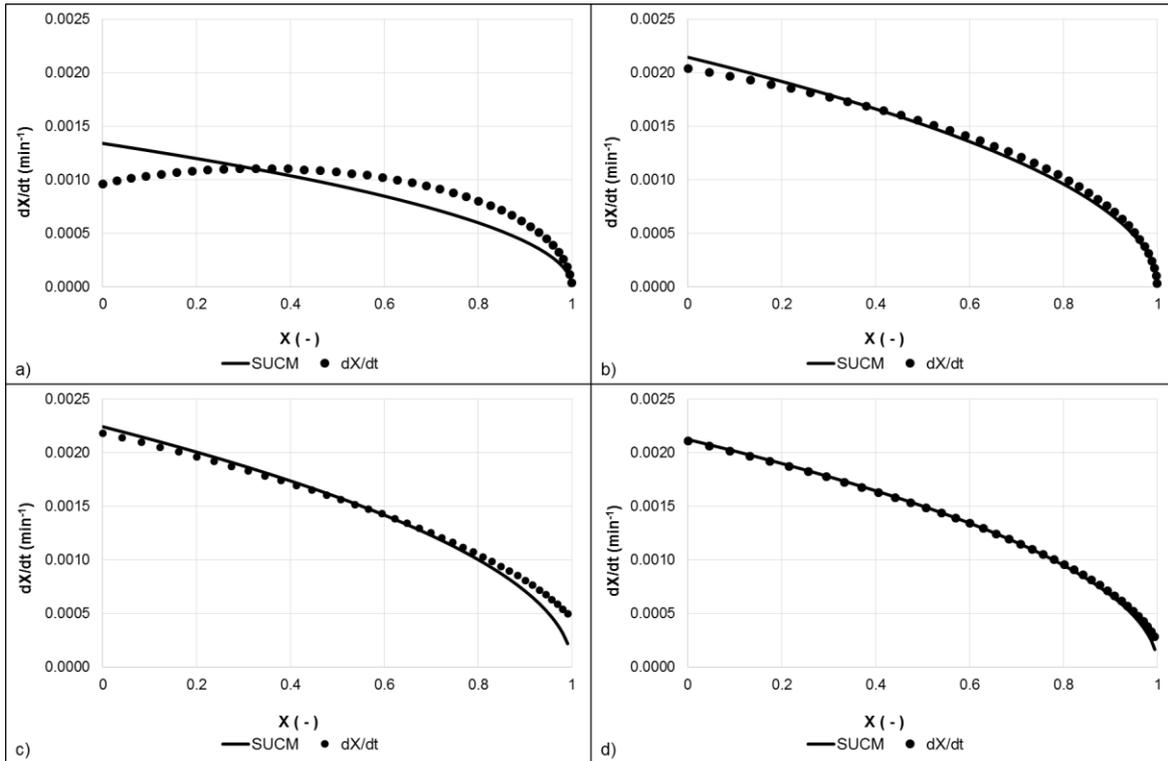
Figure A.6 SUCM fitted on (a) ROM coal, (b) BL, (c) L and (d) R briquette reactivity at 900°C

At 900°C the QOF for the ROM coal char (Figure A.6 a) was found to be 80%, while the average QOF for the briquette chars as determined as 94%. The Wen model proved to predict the reactivity data more precisely at 900°C.
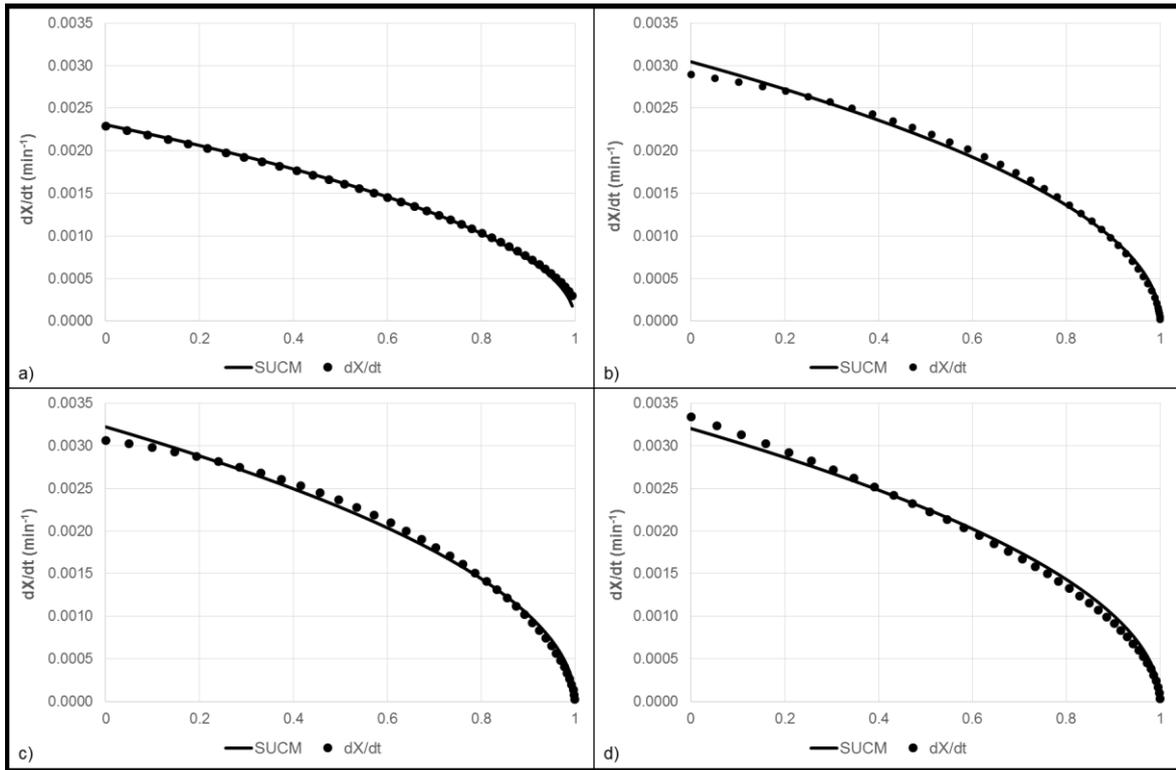
Figure A.7 SUCM fitted on (a) ROM coal, (b) BL, (c) L and (d) R briquette reactivity at 925°C

Figure A.7 shows the SUCM fit at 925°C. At this temperature, the QOF for the ROM coal and briquette chars was found to be 96 and 88%, respectively.
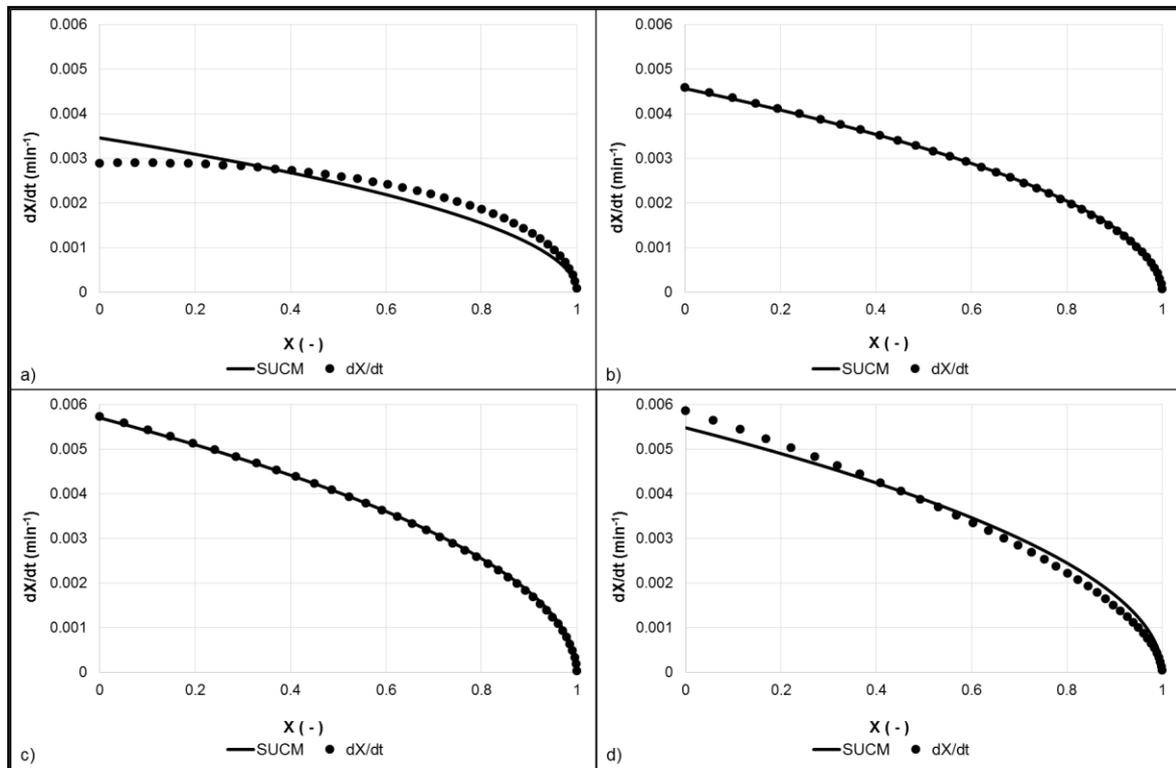

Figure A.8 SUCM fitted on (a) ROM coal, (b) BL, (c) L and (d) R briquette reactivity at 950°C

Comparison between the SUCM (Figure A.8) and Wen model (Figure A.3) at 950°C indicated a higher QOF for the Wen model.
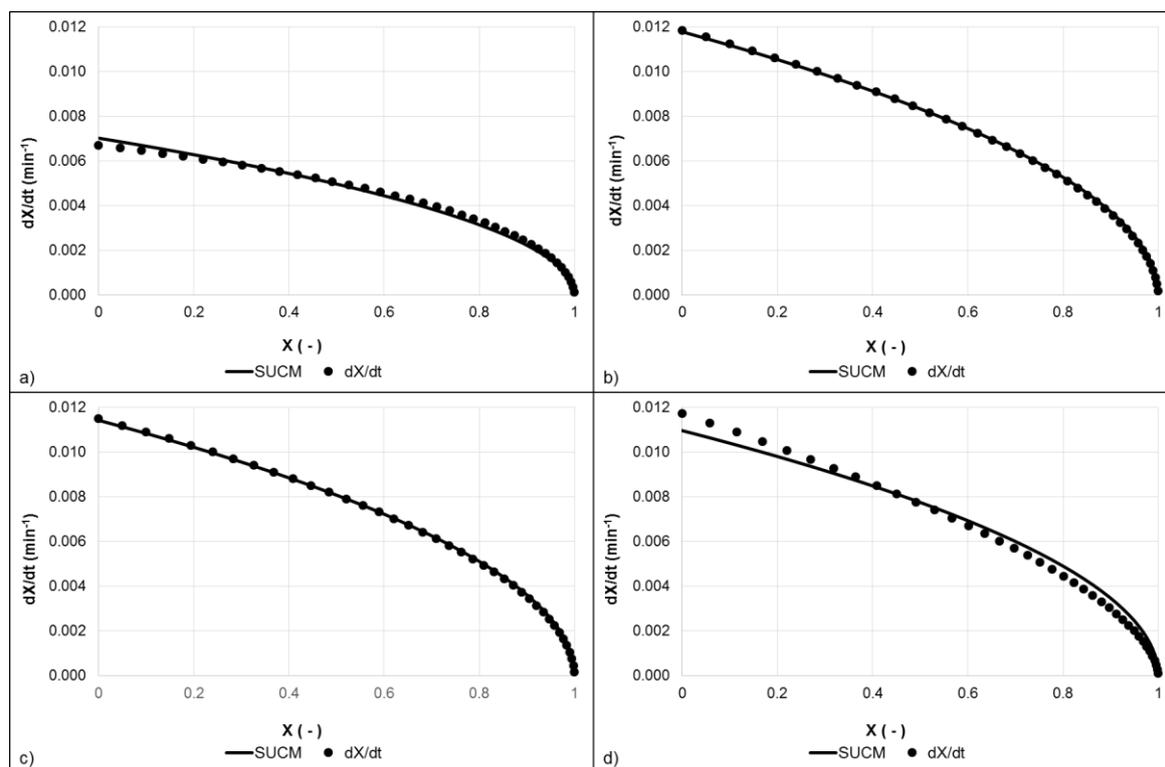

Figure A.9 SUCM fitted on (a) ROM coal, (b) BL, (c) L and (d) R briquette reactivity at 1000°C

The SUCM reactivity prediction at 1000°C is presented in Figure A.9.

A summary of the reactivity constants (k_{SUCM}) predicted with the SUCM can be seen in Table A.7, which shows an increase in initial reactivity with increasing reaction temperatures. Similar to the Wen model reactivity constants (k_{Wen}), the SUCM ROM char reactivity constants were found to be much lower than observed for the agglomerated coal chars. Generally, the QOF for the SUCM was lower than that obtained when fitting the Wen model

Table A.7 Reactivity constants determined from the SUCM

T (°C)	ROM		BL		L		R	
	k x 10⁻³ (min⁻¹)	QOF (%)	k x 10⁻³ (min⁻¹)	QOF (%)	k x 10⁻³ (min⁻¹)	QOF (%)	k x 10⁻³ (min⁻¹)	QOF (%)
875	0.67	94	1.03	92	1.18	94	1.23	79
900	1.34	80	2.14	94	2.24	92	2.13	96
925	2.31	96	3.04	90	3.22	87	3.20	88
950	3.46	87	4.56	95	5.71	92	5.48	82
1000	7.02	94	11.77	95	11.43	95	10.97	82
Average QOF (%)	90		93		92		85	