The caking and swelling of South African large coal particles

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stronger than you seem, and smarter than you think."

- A. A. Milne

Declaration

I, Sansha Coetzee, hereby declare that this thesis entitled: “***The caking and swelling of South African large coal particles”***, submitted in fulfillment of the requirements for the degree Ph.D. in Chemical Engineering is my own work and has not previously been submitted to any other institution in whole or in part. Written consent from authors had been obtained for publications where co-authors have been involved.

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	28/4/2015
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Preface

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To whom it may concern,

The listed co-authors hereby give consent that **Sansha Coetzee** may submit the following manuscript(s) as part of her thesis entitled: **The caking and swelling of South African large coal particles,** for the degree *Philosophiae Doctor in Chemical Engineering*, at the North-West University:

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Journal articles

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Coetzee S.; Neomagus H.W.J.P.; Bunt J.R.; Mathews J.P.; Strydom C.A.; Schobert H.H. Reduction of Caking Propensity in Large (Millimeter-Sized) South African Coal Particles with Potassium Carbonate Impregnation To Expand Fixed- and Fluidized-Bed Gasification Feedstock Suitability. *Energy & Fuels* **2015**, *29*, 4255-4263.

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Coetzee S.; Neomagus H.W.J.P.; Bunt J.R.; Everson, R.C. Improved reactivity of large coal particles by K_2CO_3 addition during steam gasification. *Fuel Process. Technol.* **2013***, 114*, 75-80.

Conference proceedings

Coetzee S. *(presenter)*; Neomagus H.W.J.P.; Bunt J.R.; Strydom C.A.; Schobert H.H. The transient swelling behaviour of large South African coal particles during low-temperature devolatilisation. Presented at 31st Annual International Pittsburgh Coal Conference, Pittsburgh, USA, October 6-9, 2014; Paper 54-9. ***(Oral presentation)***

Coetzee S. *(presenter)*; Neomagus H.W.J.P.; Bunt J.R.; Strydom C.A.; Schobert H.H. The reduction of swelling of large coal particles through impregnation with K_2CO_3. Presented at 31st Annual International Pittsburgh Coal Conference, Pittsburgh, USA, October 6-9, 2014; Paper 36-2. ***(Oral presentation)***

Coetzee S. *(presenter)*; Neomagus H.W.J.P.; Bunt J.R.; Strydom C.A.; Schobert H.H. The influence of K_2CO_3 on powdered and lump coals with varying swelling properties during devolatilisation. Presented at 31st Annual International Pittsburgh Coal Conference, Pittsburgh, USA, October 6-9, 2014; Paper 30-2. ***(Oral presentation)***

Coetzee S. ***(presenter)***; Neomagus H.W.J.P.; Bunt J.R.; Strydom C.A. The swelling behaviour of South African large coal particles. 18th Southern African Coal Science & Technology Indaba, Parys, South Africa, November 13-14, 2013. ***(Oral presentation)***

Nel (Coetzee) S. ***(presenter)***; Neomagus H.W.J.P.; Bunt J.R.; Everson, R.C. Catalytic steam gasification of large coal particles. Presented at International Conference on Coal Science and Technology, Oviedo, Spain, October 9-13, 2011; Paper B64. ***(Oral presentation)***

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Abstract

The swelling and caking propensity of coals may cause operational problems such as channelling and excessive pressure build-up in combustion, gasification and specifically in fluidised-bed and fixed-bed operations. As a result, the swelling and caking characteristics of certain coals make them less suitable for use as feedstock in applications where swelling and/or caking is undesired. Therefore, various studies have focused on the manipulation of the swelling and/or caking propensity of coals, and have proven the viability of using additives to reduce the swelling and caking of powdered coal (<500 µm). However, there is still a lack of research specifically focused on large coal particle devolatilisation behaviour, particularly swelling and caking, and the reduction thereof using additives. A comprehensive study was therefore proposed to investigate the swelling and caking behaviour of large coal particles (5, 10, and 20 mm) of typical South African coals, and the influence of the selected additive (potassium carbonate) thereon.

Three different South African coals were selected based on their Free Swelling Index (FSI): coal TSH is a high swelling coal (FSI 9) from the Limpopo province, GG is a medium swelling coal (FSI 5.5-6.5) from the Waterberg region, and TWD is a non-swelling coal (FSI 0) from the Highveld region. Image analysis was used to semi-quantitatively describe the transient swelling and shrinkage behaviour of large coal particles (-20+16 mm) during low-temperature devolatilisation (700 °C, N_2 atmosphere, 7 K/min). X-ray computed tomography and mercury submersion were used to quantify the degree of swelling of large particles, and were compared to conventional swelling characteristics of powdered coals. The average swelling ratios obtained for TWD, GG, and TSH were respectively 1.9, 2.1 and 2.5 from image analysis and 1.8, 2.2 and 2.5 from mercury submersion. The results showed that coal swelling measurements such as FSI, and other conventional techniques used to describe the plastic behaviour of powdered coal, can in general not be used for the prediction of large coal particle swelling.

The large coal particles were impregnated for 24 hours, using an excess 5.0 M K_2CO_3 impregnation solution. The influence of K_2CO_3-addition on the swelling behaviour of different coal particle sizes was compared, and results showed that the addition of K_2CO_3 resulted in a reduction in swelling for powdered coal (-212 µm), as well as large coal particles (5, 10, and 20 mm). For powdered coal, the addition of 10 wt.% K_2CO_3 decreased the free swelling index of GG and TSH coals from 6.5 to 0 and from 9.0 to 4.5, respectively. The volumetric swelling ratios (SR_V) of the 20 mm particles were reduced from 3.0 to 1.8 for the GG coal, and from 5.7 to 1.4 for TSH. In contrast to the non-swelling (FSI 0) behaviour of the TWD powders, the large particles exhibited average SR_V values of 1.7, and was found not be influenced by K_2CO_3-impregnation. It was found that the maximum swelling coefficient, k_A, was reduced from 0.025 to 0.015 $^oC^{-1}$ for GG, and from 0.045 to 0.027 $^oC^{-1}$ for TSH, as a results of impregnation. From the results it was concluded that K_2CO_3-impregnation reduces the extent of swelling of coals such as GG (medium-swelling) and TSH (high-swelling), which exhibit significant plastic deformation.

Results obtained from the caking experiments indicated that K_2CO_3-impregnation influenced the physical behaviour of the GG coal particles (5, 10, and 20 mm) the most. The extent of caking of GG was largely reduced due to impregnation, while the wall thickness and porosity also decreased. The coke from the impregnated GG samples had a less fluid-like appearance compared to coke from the raw coal. Bridging neck size measurements were performed, which quantitatively showed a 25-50% decrease in the caking propensity of GG particles. Coal TWD did not exhibit any caking behaviour. The K_2CO_3-impregnation did not influence the surface texture or porosity of the TWD char, but increased the overall brittleness of the devolatilised samples. Both the extent of caking and porosity of TSH coke were not influenced by impregnation. However, impregnation resulted in significantly less and smaller opened pores on the surface of the devolatilised samples, and also reduced the average wall thickness of the TSH coke.

The overall conclusion made from this investigation is that K_2CO_3 (using solution impregnation) can be used to significantly reduce the caking and swelling tendency of large coal particles which exhibits a moderate degree of fluidity, such as GG (Waterberg region). The results obtained during this investigation show the viability of using additive addition to reduce the caking and swelling tendency of large coal particles. Together with further development, this may be a suitable method for modifying the swelling and caking behaviour of specific coals for use in fixed-bed and fluidised-bed gasification operations.

Keywords: large coal particles, quantification of swelling, reduction of swelling, caking, image analysis, South African coal.

Table of Contents

Chapter 1

Introduction

In Chapter 1, the issue of coal swelling and caking is addressed and a detailed explanation behind the reasoning for investigating methods for reducing the swelling and caking propensity of coal is provided. The shortcomings of large coal particle research, specifically large coal particle swelling and caking, are also identified in this chapter. These shortcomings have been used to formulate the objectives of this investigation, which will assist in bridging the gap between fundamental research conducted on the swelling and caking behaviour of powdered coal and the actual swelling and caking behaviour of large coal particles in industrial fixed-bed and fluidised-bed operations.

1.1. Introduction and Motivation

In 2012, coal was the fastest growing fossil fuel, with 29% of the global energy expenditure derived from coal, where the coal demand continued to grow in 2013, with an increase in coal consumption of +2.4%, from +2.3% in 2012.[1,2] According to the International Energy Agency (IEA), it is projected that global coal consumption will still increase by about 2% each year until 2019.[2] Coal is known to be an effective solid fuel since it burns relatively easy, produces large quantities of energy and can be utilised for various applications,[3] where South Africa's coal-mining industry has contributed in supplying the local and global energy demand for more than a century.[4]

Globally, South Africa possesses the ninth-largest amount of retrievable coal reserves, which amount to 95% of Africa's total coal reserves.[5,6] The coal reserves comprise of approximately 96% bituminous coal, 2% metallurgical coal, and 2% anthracite.[4] Due to its limited oil and natural gas reserves, South Africa relies on the large coal deposits to meet energy demands, which account for an estimated 72% of the country's total energy consumption, as illustrated in Figure 1.1.[5]

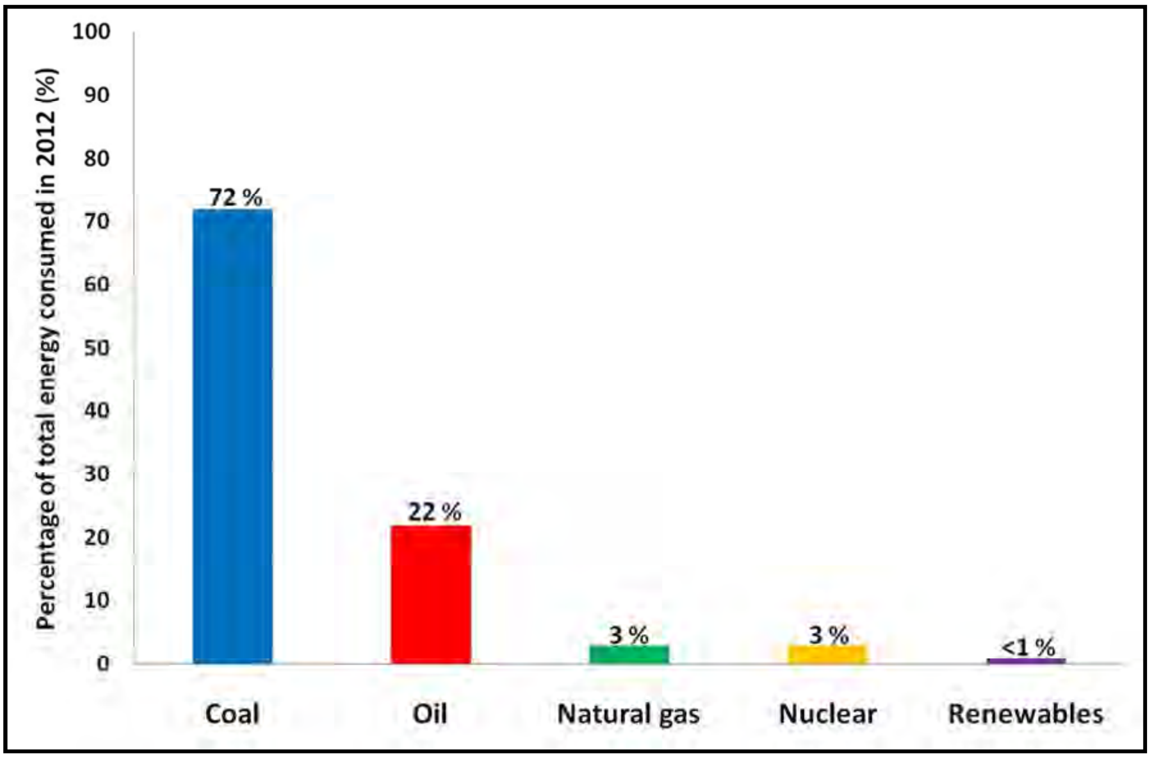

Figure 1.1: Total energy consumption in South Africa in 2012[7]

Over the past decade, South Africa's coal production/consumption levels have remained relatively unchanged. In 2012, South Africa produced an estimated 288 million short tons of coal, of which about 25% was exported.[5] South Africa mainly exports thermal coal to countries such as India, China, and Europe, and was the world's fifth-largest thermal coal exporter in 2012.[1,5] The majority of South Africa's coal production originates in the Central Basin, which includes the Witbank, Highveld, and Ermelo coalfields (as illustrated in Figure 1.2).[4] According to Eberhard,[4] coal production in the Central Basin is expected to peak in the next decade.

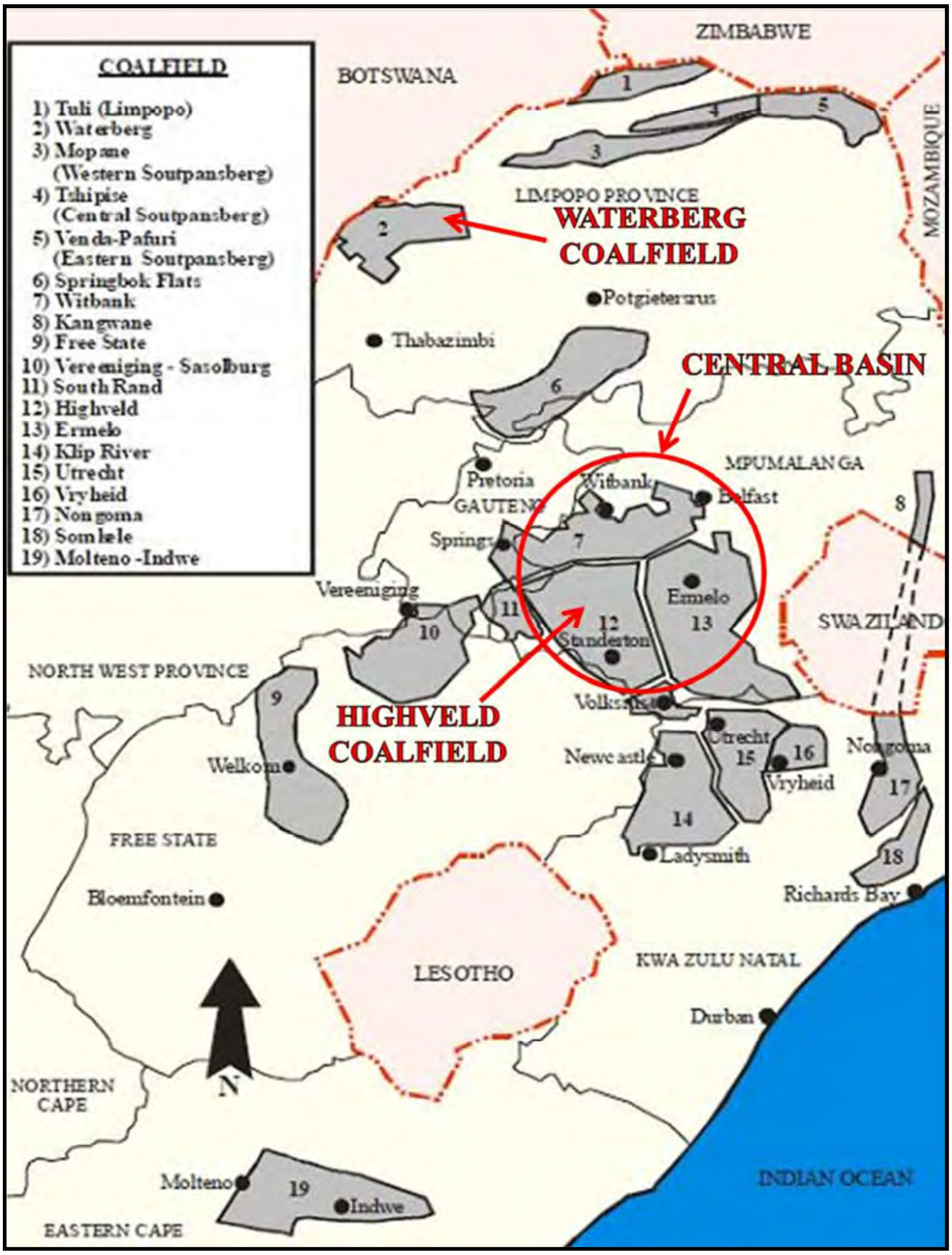

Figure 1.2: Map of South African coalfields (Adapted from Eberhard[4])

The increasing demand for coal used in energy generation and liquid fuel production, together with the exportation of high grade South African coal, will result in the depletion of South African coal reserves specifically used for fixed-bed gasification. Bituminous coal used for South Africa's petrochemical and synthetic fuels industry originates from the Highveld-Witbank region, and this area is thought to be depleted around 2050.[3,8,9] It will therefore be of strategic importance to explore other coal-supplying regions for the required coal. The Waterberg area, as well as other coal regions in South Africa such as Limpopo, are relatively unexplored and contain vast reserves of coal, which potentially can be used as feedstock until the end of the 21st century.[4,8] Waterberg coals are currently used as coking coal, feedstock for power generation, and for domestic use on a relative small scale.[10] The main concern when selecting alternative feedstocks for existing fixed-bed and fluidised-bed gasifiers is the difference in coal properties. Typically, coals mined in the Highveld region are vitrinite-rich, with relatively low ash yields compared to other South African coals.[11] The ash yield of coals mined in the Waterberg area can be as high as 65%, and export coals generally require washing to ensure ash yields <15%.[4] However, Engelbrecht *et al.*[12] showed that a low-grade high-ash coal from the Waterberg region (Grootegeluk) can be utilised in fluidised-bed gasifiers for the production of synthesis gas. Certain Waterberg coals exhibit considerable swelling and caking propensity,[13] which may be a concern when considered as an alternative feedstock for fixed-bed and fluidised-bed operations. Therefore, in order to explore the viability of using Waterberg coals as feedstock to meet the increasing demand for coal, measures will have to be taken to either modify the coal utilisation technology for operation with swelling and caking coals, or methods should be investigated to reduce the swelling and caking characteristics of these coals.

Coal utilisation processes generally involve the heating of coal, either in an oxygen atmosphere (electricity generation) or an oxidative/reductive atmosphere (steel manufacturing and gasification). Upon heating, coal is devolatilised and releases moisture and volatiles to produce a porous solid (coke or char). While all types of coal undergo chemical transformations during devolatilisation, certain bituminous coals undergo significant physical deformation as well.[13,14] Coals which are subject to physical changes during heating, such as softening and swelling, are known as caking coals. The series of physical transformations that caking coals undergo during the heating process include softening, melting, fusing, swelling and resolidifying, which occur within a specific temperature range, and are also referred to as the plastic properties.[15] The understanding of the plastic properties of coal can assist in predicting coal behaviour under specific operating conditions, and is also critical to improve and develop coal conversion technologies.[15,16]

Two phenomena largely contribute to the behaviour of coal during heating, namely particle swelling and agglomeration.[13] The swelling of a coal particle occurs during the plastic stage, when the volatile matter is released, but is trapped inside the particle due to the high fluidity of the melted or softened coal. The volatile matter cannot escape, and therefore causes the formation of single or multiple bubbles, which act as the driving force for swelling.[15,17] Various studies have been conducted to investigate the swelling phenomena, and it has been reported that factors such as heating rate, operating temperature, pressure, coal type, particle size and gas atmosphere affect the swelling behaviour of coal.[13,18,19] The swelling of coal results in the formation of coke/char with different structures, which significantly influence char combustion, gasification kinetics, and ash formation.[17] In addition to influencing the efficiency of coal conversion processes, the swelling and caking of coal during devolatilisation is also associated with numerous operational problems. Excessive swelling of the coal may result in a build-up of oven wall pressure, which leads to unsafe operating conditions,[18] while caking coals are known to agglomerate during the heating process, which makes them less suitable for use in fixed-bed and fluidised-bed gasifiers. When heat is applied, the coal becomes viscous and plastic, which causes the coal particles to form agglomerates, and can adhere to the walls of gasifiers and coking ovens and also complicate the unloading of the gasifiers.[16,20] The agglomerates may cause channelling throughout the coal bed, which will ultimately influence process efficiency.[20]

Since the swelling and caking characteristics of certain coals limit coal selection for fixed-bed and fluidised-bed operations, various studies have been conducted in order to reduce the swelling and caking propensity of caking coals. A variety of pre-treatment methods have been identified to reduce the swelling and caking tendency of such coals. It is well known that the addition of alkali and alkaline metal salts reduces the swelling and caking tendency of coal, and has been investigated extensively as a possible method which can be applied to reduce and/or eliminate coal swelling and agglomeration.[21-24] Various authors have focused on the different hypotheses aimed at explaining the mechanism of the coal-alkali interactions which are responsible for reducing the plastic behaviour of coal.[21,24-26] These studies were all conducted on powdered coal to eliminate any mass and heat transfer limitations which may arise when larger particles are used. The interaction of additives and coal/char has mostly been investigated in gasification studies, where low-ash or ash-free pulverised coals have been used to eliminate interaction between the additive and mineral matter in the coal.[27-29] Since this work is focussed on large particle (unaltered, as-received) applications, the interaction between the coal and additive was not a focus.

Studies investigating the devolatilisation behaviour of coal have mainly focused on pulverised coal samples, while millimetre sized particles are occasionally used for fluidised bed combustion studies.[30] The need to investigate coarse coal particle devolatilisation has only recently been realised, and various investigators have since studied the devolatilisation behaviour of lump coal particles, varying in size from 5 to 75 mm.[31-33] However, there still remain shortcomings with regards to research focusing on large coal particle devolatilisation behaviour, with specific focus on swelling and caking, and the reduction thereof using additives.

A comprehensive, systematic study is therefore proposed to investigate the swelling and caking of large coal particles of three typical South African coals, and to examine the influence of an effective additive on the caking and swelling propensity of these coals. Potassium carbonate was selected as additive, since Strydom *et al.*[34] showed that K_2CO_3 is the most suitable amongst other potassium based additives (KOH, KCl, CH_3COOK), for decreasing the swelling and plasticity of specifically high swelling South African coal (sample size <75 µm). The focus of this investigation is on the physical behaviour of the coals during devolatilisation, and is not aimed at investigating the mechanistic aspect of the coal-alkali interactions. The results obtained from this study will give insight into the swelling and caking behaviour of large coal particles from South African coals. The conclusions drawn from this study will also signify the viability of using additive addition to alter the unwanted swelling and caking characteristics of coal, in order to provide a suitable feedstock for fixed- and fluidised-bed gasifiers.

1.2. Aim and objectives

The aim of this project is to quantify the swelling and caking behaviour of typical large South African coal particles, and examine the influence of potassium carbonate thereon.

The objectives stipulated for this study are summarised as follows:

- To develop a method to quantify the degree of swelling of large coal particles during devolatilisation.
- To evaluate the swelling behaviour of large coal particles during low-temperature devolatilisation, and to compare the results with the Free Swelling Index of powdered coal.

- To quantify the influence of K_2CO_3 on the swelling propensity of large coal particles and powders, and to study the influence of K_2CO_3 on the transient swelling and shrinkage behaviour.

- To determine the influence of impregnation with K_2CO_3 on the caking tendency of large coal particles, and to examine the influence of the additive on the char/coke structure.

1.3. Scope and outline of this thesis

In the literature chapter, the process of devolatilisation is reviewed, with specific focus on the chemical and physical transformations which are responsible for the plastic behaviour of coal. The plasticity of coal is discussed in detail, with reference to the various theories which have been proposed on the subject of thermal coal softening and plastic coal behaviour. The phenomena of coal swelling and coal caking, which results from the plastic behaviour of coal, are also reviewed. Lastly, the reduction of coal swelling and caking through additive addition is discussed, followed by a detailed summary of previous research that has been conducted on this topic. This literature review is given in **Chapter 2**.

The first objective of this research project was to develop a quantification method to quantify the degree of swelling of large coal particles. This was followed by a systematic study of large coal particle transient swelling behaviour during devolatilisation. The swelling behaviour of -20+16 mm coal particles from three different South African coals were quantitatively and qualitatively studied, using novel approaches. Mercury submersion and X-ray computed tomography (CT) were used to quantify the degree of swelling of the large particles, while image analysis was used as a semi-quantitative approach to describe the transient swelling and shrinkage behaviour of the particles during low-temperature (up to 700 °C) devolatilisation. The main aim of this paper (**Chapter 3**) was to quantify large coal particle swelling, and compare the results obtained with swelling measurements for powdered coal obtained from conventional analyses such as Free Swelling Index (FSI).

The influence of K_2CO_3 on the swelling propensity of large coal particles was quantified, as a continuation of the investigation on large coal particle swelling. Solution impregnation was used to impregnate the large coal particles with a K_2CO_3 solution. Mercury submersion was once more used to quantify particle swelling, while image analysis was applied to determine the influence of K_2CO_3 on large coal particle swelling and shrinkage. This investigation

(**Chapter 4**) was aimed to show the feasibility of using K_2CO_3 for swelling reduction of large coal particles, which may potentially be a suitable method for reducing unwanted swelling in fixed- and fluidised-bed operations.

The influence of K_2CO_3 on the caking propensity of large coal particles from three different South African coals was determined. The same impregnation method was used as described in Chapter 4, and batch samples were used to evaluate the caking tendency of the coals during devolatilisation. During this investigation, various parameters were investigated: extent of caking, surface texture of devolatilised material, porosity, wall thickness, and bridging neck size. The overall objective of this paper (**Chapter 5**) was to determine whether or not K_2CO_3 can be used to modify the caking tendency of a coal. The results will indicate the possibility to manipulate unwanted caking tendencies of large coal particles, and may potentially lead to the selection of coal feedstocks which were previously less suitable for utilisation in fixed- and fluidised-bed gasifiers.

Chapter 6 summarises the conclusions drawn from the results obtained during this investigation. Recommendations are made based on the most important conclusions drawn from this investigation, and is aimed at assisting future research regarding the topic of large particle swelling and caking.

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Chapter 2

Literature Review

This Chapter contains a review of literature relevant to this study. This includes background on the topics of coal devolatilisation, coal swelling and agglomeration/caking, and the effect of additives on coal swelling and caking. The specific literature relevant to each paper is included in the subsequent chapters.

2.1. Introduction

The following relevant topics are reviewed in this chapter: coal devolatilisation, coal plasticity with specific focus on swelling and caking, and the influence of additives on coal swelling and caking with reference to previous studies. During devolatilisation, coal undergoes physical transformations to form char or coke, which makes the process of devolatilisation an important aspect to consider when studying coal swelling and caking. Extensive research has been focused on determining an exact mechanism for the devolatilisation process, and this has resulted in the postulation of a mechanism specifically describing the plastic behaviour of coal. Swelling and agglomeration/caking are amongst some of the plastic properties of coal which can significantly influence combustion and gasification reactivity, as well as the formation of ash. Since the plasticity of coal determines the degree of swelling and caking, it is therefore necessary to understand which factors influence this behaviour. In applications where swelling and caking are undesirable, such as fixed- and fluidised-bed gasifiers, it has become increasingly important to consider methods which can be used to alter the swelling and caking behaviour of coal during utilisation. In these instances, a suitable method will ultimately allow for the selection of alternative coal feedstocks, which may previously have been less suitable due to their swelling and caking propensity.

2.2. Coal Devolatilisation

The devolatilisation of coal, also known as pyrolysis, is the decomposition of coal in the absence of reactive media such as oxygen, steam and CO_2. The terms “devolatilisation” and “pyrolysis” are used interchangeably in literature due to the similarity of the char chemistry and volatile composition of the coal in these two processes.[1] The chemical and physical behaviour of coal during devolatilisation has been studied extensively over the years.[1-5]

The heating of coal in an inert atmosphere results in the formation of a carbonaceous, porous solid, known as coke or char, and the evolution of volatiles. The volatile products are essentially comprised of gas, ammonia, tar and light oils.[6,7] Chemically, the volatiles are composed of a mixture of hydrogen, carbon dioxide, methane and higher molecular weight hydrocarbons, and water.[7-9] The yield of liquid and gaseous devolatilisation products depend on the volatile matter content of the coal, and the temperature, heating rate and residence time of the devolatilisation process.[7,8]

2.2.1 Mechanism of coal devolatilisation

Coal devolatilisation is of great importance since it is the preliminary step in coal conversion processes, and accounts for as much as 70% of the total weight loss of the coal.[4,9] Devolatilisation is also a process which is influenced by the organic composition of the coal, consequently affecting the successive coal conversion steps. Coal behaviour such as particle swelling and agglomeration, physical char structure and char reactivity is also influenced by the devolatilisation process.[4,6,9] Since devolatilisation has such a discernible effect on conversion processes, it is crucial to understand the devolatilisation mechanism, in order to comprehend and predict the chemical and physical behaviour of coal during devolatilisation.

The mechanism of coal devolatilisation has previously been reported upon and discussed in literature.[2,3,5,10] Upon heating of the coal, the evolution of occluded gases such as methane, carbon dioxide and water occur below 200 °C.[5] Between 200 and 500 °C, decomposition of organic sulphur compounds and nitrogen compounds occur, with the evolution of hydrogen taking place between 400 and 500 °C.[5] The devolatilisation reactions are initialised by the rupture of bonds and do not occur below approximately 400 °C, since this is the least amount of energy needed to break the C-C bonds. The C-C bonds at the bridges between the ring structures are the weakest compared to other C-C bonds, specifically those in the aromatic ring structures. Devolatilisation starts with the cracking of the bridges between the ring structures to produce free radicals. The free radical groups are extremely reactive and combine with gaseous compounds in their vicinity to form aliphatics and water. The water and aliphatics mixture diffuse out of the coal particle at such a slow rate that it condenses, with the elimination of hydrogen, to produce coke. The following reactions show the typical devolatilisation reactions which occur as the temperature increases:[5]

Cracking:

$$R-CH_2-R \rightarrow R-R'+-CH_2$$

Reaction (2.1)

Saturation:

$$-CH_3+H' \rightarrow CH_4$$

Reaction (2.2)

$$-OH + H' \rightarrow H_2O$$ Reaction (2.3)

Tar production:

$$-R - CH_2 + H' \rightarrow R - CH_3$$ Reaction (2.4)

Condensation reactions (cross-linking reactions):

$$R - OH + H - R \rightarrow R - R + H_2O$$ Reaction (2.5)

$$R - H + H - R' \rightarrow R - R' + H_2$$ Reaction (2.6)

The R is a radical obtained from aromatic hydrocarbons such as benzene and naphthalene. Carbon oxides are also produced, as described by the following reaction:

$$R - COOH \rightarrow R - H + CO_2$$ Reaction (2.7)

The hydrogen present in the coal partially reacts to form water and hydrocarbons and is partially liberated as molecular hydrogen,[5] and is an important component in devolatilisation reactions, specifically considering tar production (Reaction (2.4)). According to Solomon *et al.*,[6] the tar formation is related to the viscosity of the char, and the consequent chemical and physical structure of the char, and is therefore important to char swelling and reactivity.

Various other explanations and mechanisms have been proposed to describe the process of devolatilisation. Gavalas[2] characterised the reactivity of coal during devolatilisation, hydropyrolysis and liquefaction according to different classes of functional groups, namely: hydroaromatic structures, aromatic nuclei, alkyl chains, alkyl bridges, and oxygen groups. Soloman and co-workers[10] proposed nine reaction steps to describe the devolatilisation process in terms of volatile evolution. Chermin and van Krevelen[11] described the plastic behaviour of coking coals based on the metaplast theory,[12] as depicted by the following simplified reaction mechanism as proposed by van Krevelen *et al.*:[13]

$$P \xrightarrow{k_1} M$$ Reaction (2.8)

$$M \xrightarrow{k_2} R + G_1 \qquad \text{Reaction (2.9)}$$

$$R \xrightarrow{k_S} S + G_2 \qquad \text{Reaction (2.10)}$$

where k_1, k_2 and k_3 are reaction constants, P represents the raw coal, M is the metastable intermediate product (metaplast), R denotes the semi-coke and S the coke, while G_1 and G_2 are the primary and secondary gases, respectively. For the purpose of their study, all three reactions (2.8-2.10) were initially assumed to be first order reactions. According to this theory the metaplast is responsible for the plastic behaviour of the coal, which may act as an unstable plasticiser under certain conditions. This suggests that the temperature where maximum plasticity occurs will coincide with the temperature where the metaplast concentration is at its maximum. Furthermore, Reaction (2.8) is responsible for the softening of the coal, while Reaction (2.9) is responsible for the reduction in plasticity.

Recent studies have shown that coal can be assumed to have a macromolecular network structure, to which theories incorporating cross-linked polymers can be applied. Such theories have been invaluable to better comprehend and model various coal properties such as equilibrium swelling, insolubility, viscoelastic properties, cross-linking during char formation, and coal tar formation during devolatilisation.[9]

The exact chemical transformation which coal undergoes during devolatilisation is complex, due to the heterogeneous nature of the coal.[9,14] Various investigators have studied the thermal decomposition of coal, in order to develop a general description of coal behaviour in a gasifier or combustor.[4,5,15] Serio *et al.*[4] investigated which chemical descriptors for coal and char can be applied to predict coal behaviour during the various stages of devolatilisation. These include predictions of: (i) the amount, composition and evolution rate of volatiles and gases, (ii) the amount and composition of tar, and (iii) the viscosity and reactivity of the metaplast or char phase.[4] The following schematic (Figure 2.1), which was originally proposed by Chermin and Van Krevelen,[11] was presented by Serio and co-workers,[4] and describes the different stages of devolatilisation.

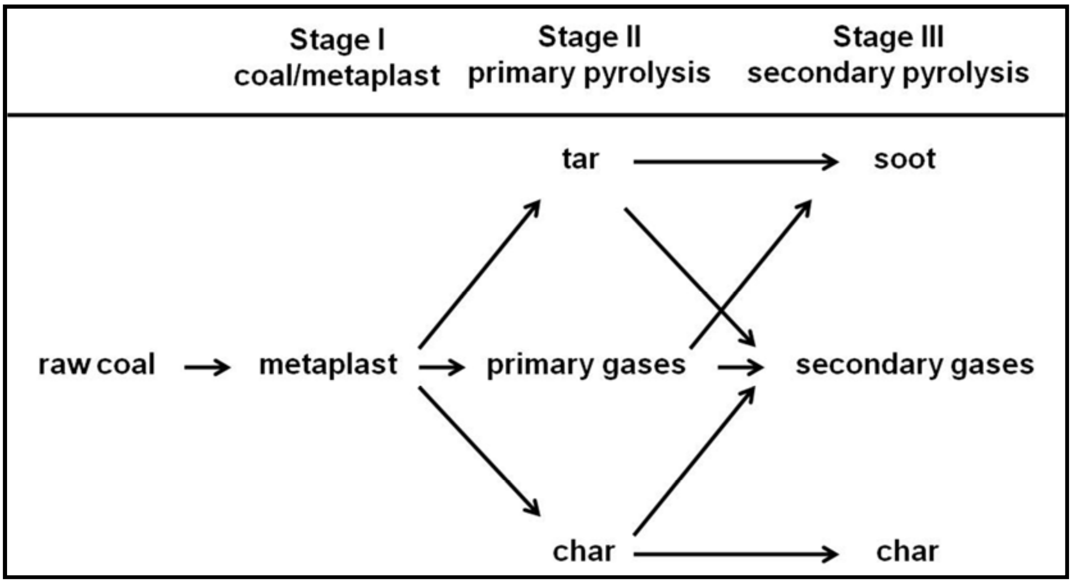

Figure 2.1: Different stages of devolatilisation (Adapted from Serio *et al.*[4])

Stage I describes the initial phase of devolatilisation of the coal, where bond-breaking reactions may occur, as well as a decrease in hydrogen bonding which can lead to melting. A number of light species, which either existed as guest molecules or formed during breakage of weak bonds, are discharged. Additional bond breaking occurs in Stage II, which leads to tar and gas evolution and char formation. During Stage III, the products formed during devolatilisation can undergo consecutive reactions to secondary products.[4]

2.3. Coal swelling and agglomeration

During devolatilisation, coal undergoes a series of chemical and physical transformations.[14,16-19] The chemical changes include the decomposition of the coal's molecular structure to form metaplast and to release volatiles, which result in char formation.[18] From a coal physical property perspective, some coals melt during devolatilisation to produce coke, while other coals leave a friable char residue.[20] The various physical transformations that bituminous coals may undergo during the devolatilisation step include: softening, melting, fusing, swelling and/or resolidifying, which occur within a specific temperature range, and which are also referred to as plastic or thermoplastic properties.[21,22] In some cases the physical transformations can also lead to morphological changes, which can produce different types of char and consequently influences the char combustion reactivity, gasification kinetics, and ash formation.[18,23,24] Therefore, the understanding of the plastic properties of coal can assist in predicting coal behaviour under specific operating conditions, and is also critical to improve and develop coal conversion technologies.[21,25]

2.3.1 Plasticity

Coal fluidity influences char formation and consequently the char reactivity during various coal utilisation processes, and therefore it is imperative to determine and understand the fluid behaviour of coals. During liquefaction, highly fluid coal tends to rapidly dissolve in the solvent which leads to subsequent liquid-liquid interactions, while non-fluid coals must first undergo slower solid-liquid reactions.[26] In combustion or gasification, the degree of fluidity determines the degree of particle swelling[27] and agglomeration, and also controls intrinsic char reactivity[4] and char fragmentation.

According to Solomon *et al.*[26] the following factors influence the fluidity of coal: (1) the fluidity of the liquid fraction of the coal, (2) the reliance of fluidity on temperature, (3) the contribution of solid char or mineral particles to the fluidity, (4) and bubble formation due to trapped gases. Coal fluidity may also be influenced by the heating rate and gas atmosphere of the utilisation process, and mineral matter in the coal.[28-30] The most important properties of melting coal, according to Saxena[5] and Gavalas,[2] are the viscosity and the pore structure of the plastic state. The pores of plastic coals tend to collapse at the onset of melting, consequently resulting in volatile transport taking place via bubble nucleation, growth and escape to the particle surface. Therefore, the viscosity of the melted coal influences the release of volatiles to a large extent. The swelling behaviour of coal, along with the residual pore structural changes occurring during devolatilisation, influences the reactivity, heat- and mass transfer during carbon conversion processes.[2,5]

The rheological properties of coal have been measured and studied extensively in order to better understand the plastic behaviour of coal.[2,5,12] The rheological properties of coal include consistency, plasticity, elasticity, liquid (simple and complex), and solid (plastic and elastic). Waters[31] observed a relationship between instantaneous weight loss and the fluidity of coal, using various rheological measurements. It was also observed that plastic coals act as Newtonian fluids which exhibit exponential temperature viscosity correlations.[31] Generally, rheological measurements such as Gieseler plastometry are conducted at low heating rates of a few degrees per minute. At these low heating rates, only bituminous coal shows signs of fluidity. At low heating rates the coals start to soften at 573 K, while maximum fluidity occurs at around 623 K. Resolidification is observable at around 773 K. The softening temperature and the duration of the plastic stage are dependent on covalent bond breaking, as well as condensation reactions and the loss of tar.[5] Fluidity is observable for coals with carbon contents (daf) in the range of 81-92%, however the carbon content is not a complete indication of the rheological properties.[2] The hydrogen and oxygen content is also a good indication of fluidity, where the fluidity decreases with increasing oxygen content, for a specific carbon content.[2] Barriocanal *et al.*[32] reported that the rank of the coal also had an influence on the coal's plastic behaviour. It was reported that an increase in coal rank resulted in an increase in temperatures of the initial softening, maximum fluidity and resolidification phases, and a decrease in the maximum fluidity.[32]

According to van Krevelen *et al*.,[13] a number of theories have been formulated on the subject of thermal coal softening and plastic coal behaviour. The oldest known hypothesis is the binding agent or bitumen theory, which proposes that coal consists of a combination of bitumina and humic substances (residual coal). Upon heating, the coal is plasticised by the melting bitumen, which acts as a binding agent and fuses the non-melting residual coal particles together. From this theory it can be logically argued that the coal will lose its coking or plastic properties if the bitumen is extracted.[13] In contrast, the homogeneous melting theory states that the coal, when heated at a sufficiently rapid heating rate, melts as a whole. The partial melting theory considers the concept of isocolloids of coal. This theory proposes that the smallest molecules present in the coal become mobile when heated, and consequently plasticises the whole mass. Lastly, the thermobitumen theory hypothesizes that the plastic behaviour of coal can only be attributed to the formation of a liquid primary product of devolatilisation.[13] Each of the above-mentioned theories address various factors related to the plastic softening of coal.

In order to describe and predict coal behaviour during devolatilisation, the physical and chemical transformations during devolatilisation have to be studied extensively. According to Dakič and co-workers[33] the entire devolatilisation process can be categorised into three phases, according to the following schematic (Figure 2.2):

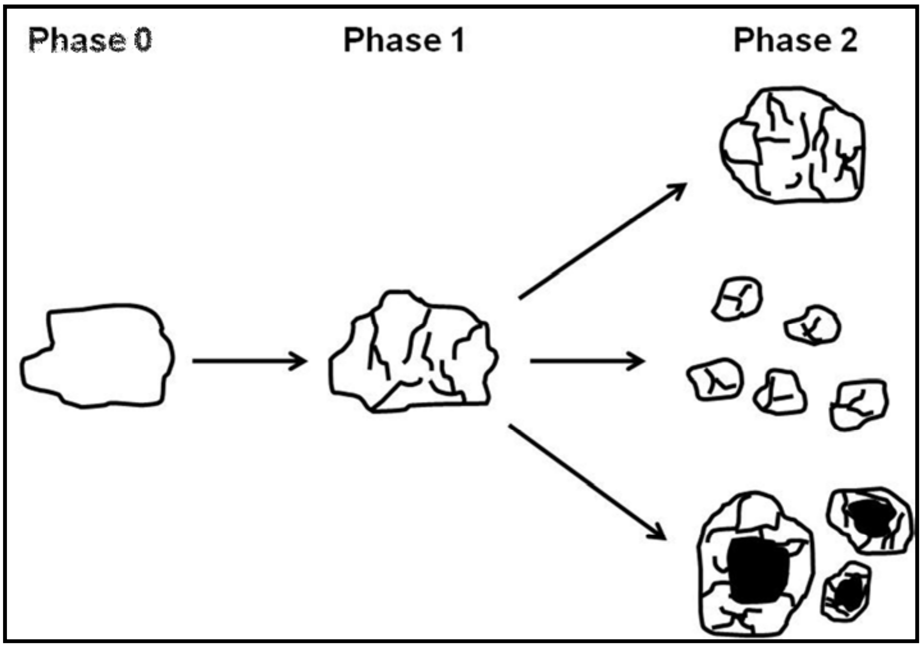

Figure 2.2: Three stages of devolatilisation (Adapted from Dakič *et al.*[33])

Phase 0 represents the parent coal particles, while Phase 1 illustrates the release of volatiles and moisture from the particle. Phase 2 shows that different coals can behave differently during devolatilisation, to form significantly different products. The following three cases are illustrated in Phase 2:[33] (1) the number of particles remain the same, and the coal particles do not change significantly in size and shape, (2) the particles fragment, but the volume remains relatively unchanged, and (3) swelling and fragmentation occurs, and the coal structure transforms dramatically during devolatilisation.

The progression from Phase 1 to Phase 2 of devolatilisation, for bituminous coals, includes a series of phase changes:[7,33] (1) at around 400 °C the coal softens and becomes fluid-like, (2) the softened coal swells as a results of pressure build-up during volatile release, (3) the swelling stops at around 500 °C when the plasticity of the coal reduces and the coal resolidifies to form a porous structure. When non-plastic coals are heated, they form a pulverant and inconsistent residue, whereas caking coals produce a coherent residue known as coke, with varying degrees of swelling and friability.[25] According to Tsai,[7] the softening of coal is purely a physical phenomenon of melting, and is independent of any reactions which occur during devolatilisation. The two most important consequences of the plastic behaviour of coal is swelling and caking.[16,23,24,34,35]

2.3.2 Swelling

According to Brewer[36] and Habermehl *et al.*,[12] swelling can be defined as the increase in volume of coal during heating under such condition that allows the plasticised or softened coal to expand freely. Swelling occurs when the released volatiles encounter resistance which is caused by the limiting transport capacity of the transforming/evolving pore structure. This causes pressure to build up in the particle, and when the pressure exceeds a certain point, the particle either breaks (fragmentation) or undergoes plastic deformation to accommodate more gases.[12,33,36] Gao and co-workers[37] observed that coal particle swelling is generally followed by rapid contraction due to bubble rupture, after which the particle resolidifies. This was also reported by Habermehl *et al.*,[12] who describes the physical transformation of coal during devolatilisation as a succession of several processes, which include softening, swelling, resolidifaction, and shrinkage after resolidification. Coal particle swelling during devolatilisation is an important occurrence, since it affects the particle size, density, porosity and reactivity of the char, and consequently the behaviour of the resulting char in coal utilisation processes.[18]

In order to investigate the degree of swelling of coal, a standardised method for powdered coal (-212 µm, ISO 501:2003) is used to characterise coal in terms of its swelling properties. This method, the Free Swelling Index (FSI) test, provides a “free swelling index”,[2,12,36] and gives a qualitative indication of the degree to which a specific coal can swell. Coals that do not display signs of plastic properties do not exhibit swelling, according to the free swelling index. The degree of swelling is influenced by factors such as the fluidity of the plastic coal, the thickness of the bubble walls formed by the gas, and the interfacial tension between the fluid and solid particles in the coal.[25]

In order to better understand coal behaviour during devolatilisation, Littlejohn[38] characterised coals according to their swelling properties, as shown in Figure 2.3.

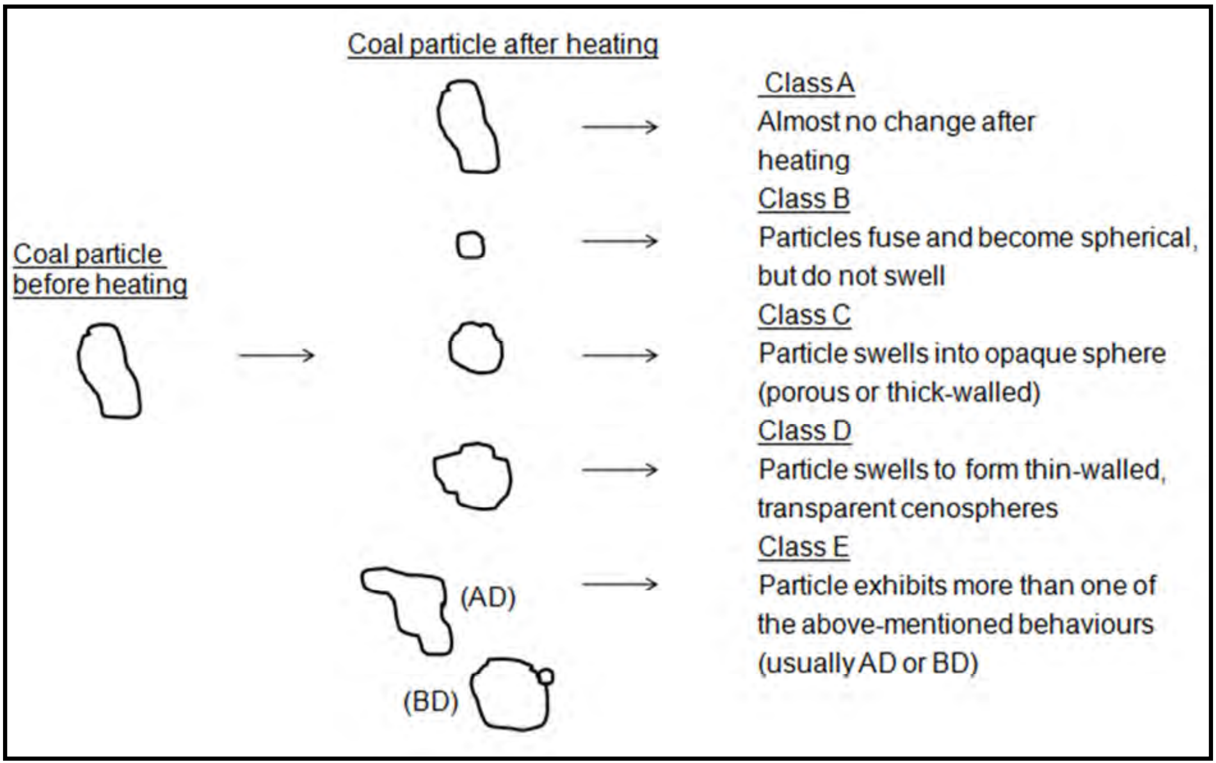

Figure 2.3: Characterisation of coal according to their swelling properties (Adapted from Littlejohn[38] and Saxena[5])

Figure 2.3 illustrates the various classes into which char particles can be characterised, according to their swelling properties. According to Littlejohn[38], class D can be further characterised in terms of the type of cenospheres formed during heating. When plastic coals are heated to high temperatures at high heating rates, the rate of volatile evolution is rapid which generates large void spaces and results in the formation of hollow char particles, known as cenospheres. Cenospheres are hollow spherical char particles, and are approximately forty times larger than the original coal particle, with minimal visible pores.[5,39]

2.3.3 Agglomeration/Caking

Agglomeration is generally defined as the formation of agglomerates or aggregates when material fuses together during heating.[40] Coal particle agglomeration is described as the softening of coal during heating, which causes the particles to adhere together to form a coalesced solid.[2,22,25,41] The term “softening” is often replaced by terms such as “agglomeration” and “caking”, while coals which generally exhibit no fluid-like tendencies are deemed as “non-plastic” or “non-caking” and “non-agglomerating” coals.[2] The degree of plasticity of a coal influences the dynamics of bubble formation, as well as the tendency of the coal to swell and coalesce.[22]

The occurrence of softening and agglomeration of coal during heating in an inert atmosphere is very complex, and is therefore necessary to understand in order to predict the agglomerating behaviour of coal.[42] Campbell *et al*.[16] investigated the agglomeration of lump coal blocks (2x2x2 cm^3), and observed that the tendency of the coal to agglomerate increased with increasing vitrinite, liptinite and volatile matter content. It was also found that a decrease in volatile matter content resulted in an increase in the tendency of the coal to crack, and a decrease in swelling propensity.[16] The findings of Campbell *et al.*,[16] as well as results obtained by Kidena *et al*.[43] and Kim *et al*.,[14] indicate that the same coal properties which seem to influence swelling, also influences coal agglomeration.

Klose and Lent[42] discussed the theory behind coal particle agglomeration based on particle bonding. Particle bonding can be categorised into bonding without and with material bridges (van der Waals, electrostatic and magnetic forces).[42,44] Klose and Lent[42] developed a kinetic model to describe the bonding mechanism of coal particle agglomeration during the softening phase. The model considered the following bonding characteristics: bonding neck growth during moderate heating rates, neck growth as a function of particle size, and the influence of viscosity on neck growth.[42]

2.4. Effect of additive addition on coal swelling and caking

As previously mentioned, coal swelling and caking are an unwanted occurrence in processes where fixed- and fluidised-bed gasifiers are used. Excessive swelling of coal particles may lead to various operational problems, such as build-up of oven wall pressure.[23,24] Coal caking or agglomeration has also been recognised as the single most serious technical complication during the development of industrial devolatilisation processes.[2,24,25,34,45] During heating, coals may become viscous and plastic, which cause the particles to form agglomerates, which can possibly adhere to gasifier or coking oven walls, and/or reduce gas permeability through the coal bed and cause channelling.[25,45] Therefore, various methods have been developed and investigated to reduce or eliminate the swelling and caking propensity of coal. Some of the pre-treatment methods which have been found to reduce the swelling and caking propensity of coals include oxidation using a gas, solution (sodium permanganate), or solid, or by applying a slow heating rate.[12,41,45-48] However, pre-oxidation of coal, to either reduce or promote coking behaviour, is not a desirable pre-treatment method, since it may reduce the thermal efficiency of the coal.[45,48] Pre-treatment is also not practical for large-scale industrial operations, where large quantities of coal is processed.

In addition to the various pre-treatment methods, the use of additives such as alkali and alkaline metal salts has been investigated in order to determine the influence of these additives on the caking and swelling of coal. Extensive research has been conducted on swelling and agglomeration reduction due to additive addition, in order to determine the most effective additives to be used, as well as to determine how the additives reduce the plasticity of the coal, and consequently the swelling and agglomerating behaviour.

Swelling can be reduced due to the promotion of cross-link formation at lower temperatures than those required for devolatilisation. Swelling may be reduced because the metal salts catalyse ether cross-link formation at around 573 K.[35] According to Mulligan and Thomas,[55] additive-coal interaction increases the permeability of the plastic phase and promotes the cross-linking reactions, which results in a reduction in coal softening and the mobility of the metaplast. Bexley *et al*.[49] and Tromp *et al*.[50] proposed that the swelling of coal is reduced due to the reaction of alkali and alkaline metal salts with the carboxylate and phenolate groups of the coal. Bexley *et al*.[49] reported the following suggested mechanisms for the interaction of additives with the coal: 1) increased methylene cross-link reaction, 2) catalysis of the dehydrogenation process which is supposed to reduce coal plasticity, and 3) conversion of the coal hydroxyl functional groups to form the corresponding metal salts. Carbonate salts such as potassium carbonate react with the carboxylate and phenolic functional groups of the coal to form corresponding alkali metal salts.[49] The functional groups of coal are involved in decarboxylation reactions, dehydroxylation reactions, condensation which results in cross-linking, and the formation of furan-like structures.[49] The formation of alkali metal salts as a result of additive-coal interaction displaces hydrogen, reducing the amount of hydrogen available during pyrolysis. Since tar is richer in aliphatic hydrogen compared to the parent coal, less hydrogen will result in lower tar yields and higher coke yields.[49,55] Looking at the physical coal properties, the formation of potassium salts will increase the coals' softening point and reduce the mobility of the lamellar and micellar units which will results in less swelling.[49,55] According to Clemens and Matheson[51] and Neavel[52], the additive depletes the donor hydrogen supply which is responsible for stabilising free radical fragments and consequently generating additional solvating species. A decrease in hydrogen donor species results in a decrease in the yield of solvating species, which influences the softening and fluidity of the coal.[51]

2.5. Research focused on modification of coal swelling/caking

Table 2.1 contains a summary of previous investigations which have focused on the reduction or elimination of coal swelling and agglomeration through additive addition. The work summarised indicates that the focus thus far has been on using powdered coal (<500 µm) to study the influence of additives on swelling and caking.

Table 2.1: Summary of studies conducted to determine the influence of additives on swelling and agglomeration

Author	Particle size (µm)	Additive
Khan and Jenkins[22]	<74	K and Ca additives
Tromp *et al.*[50]	<44, <75, 106-200, 212-400	K_2CO_3
Bexley *et al.*[49]	<212	Li_2CO_3, $NaHCO_3$, Na_2CO_3, $KHCO_3$, K_2CO_3, Na_2O, NaCl, Na_2SO_4, $NaNO_3$, KCl, $CaCO_3$, Fe_2O_3, Al_2O_3 (and others)
Crewe *et al.*[34]	<74	NaOH
Fernández *et al.*[53,54]	<212	Non-coking coals, coal tar pitch, residue from benzol distillation column, residue from tyre recycling plant
Mulligan and Thomas[55]	<500	Pitch, Na_2CO_3
Clemens and Matheson[51]	<425	Chloroform extract, decacyclene
McCormick and Jha[35]	<420	Na and Ca composites
Strydom *et al.*[56]	<75	KOH, KCl, K_2CO_3, KCH_3CO_2
Kawa *et al.*[48]	<149	Na_2CO_3, coal-hydrogenation catalysts (hepta-ammonium molybdate, stannous chloride)

Khan and Jenkins[22] investigated the influence of various calcium and potassium compounds (individually and combined) on the swelling and plasticity of a low-volatile bituminous coal. It was observed that K_2CO_3 and CaO (individually and combined) was most effective in reducing coal swelling.[22] Tromp *et al.*[50] investigated the effect of K_2CO_3 on the thermoplastic properties of a high volatile and a medium volatile coal. They found that the addition of K_2CO_3 significantly reduces the volume swelling of both coals. It was also found that the ability of K_2CO_3 to reduce swelling, decreases with increasing devolatilisation pressure.[50] The effect of additives on the swelling of coal can be attributed to an increase in the softening temperature of the coal. According to Tromp and co-workers[50] the increase in softening temperature implies that the formation of alkali salts reduces the mobility of the coal matrix, thus reducing the degree of swelling.

Bexley *et al*.[49] investigated additive-coal interactions with over 20 different additives (mostly alkali and alkaline earth metal species). It was found that most sodium and potassium compounds eliminated dilatation when 1-4% w/w was added to the coal. It was also observed that these additives altered the caking and swelling properties of the coals.[49] Crewe *et al*.[34] studied the effect of sodium hydroxide on the caking of coal, using various impregnation methods. Results showed that the caking propensity of the coal was completely destroyed when 1-2 wt.% (dry basis) sodium hydroxide was added with solution impregnation. Contrasting results were obtained for the dry mixing method, where 20 wt.% sodium hydroxide was required to reduce the caking character of the coal.[34]

Fernández *et al*.[53,54] investigated the influence of non-coking coals, coal tar pitch, residue from a benzol distillation column, and residue from a tyre recycling plant on the thermoplastic properties of a high-volatile and a low-volatile bituminous coal. It was reported that the volatile matter content of the additive determined the degree by which the thermoplastic properties were influenced. It was also found that the coal tar pitch and the residue from the Benzol distillation column increased maximum fluidity, while the tyre residue decreased maximum fluidity. Mulligan and Thomas[55] used tar pitch and Na_2CO_3 as additives, and found that the pitch increased the plastic range of the coals, whereas the Na_2CO_3 reduced the plastic range of the coals. The results were obtained from Gieseler and Dilatometry measurements. Clemens and Matheson[51] investigated the influence of a chloroform extract (obtained from Webb coal) and a radical stabiliser, decacyclene, on the Gieseler fluidity data of Webb coal. It was found that the chloroform extract lowered the softening point and increased the plastic range, while the chloroform extract/decacyclene combination increased the fluidity of the coal. The increased fluidity was attributed to the decacyclene's ability to stabilise free radicals.[51]

McCormick and Jha[35] used various sodium and calcium composites, with calcium acetate and sodium hydroxide as catalyst precursors. It was found that Na and Ca (individual and mixtures) reduced the Free Swelling Index (FSI) values of the coal, depending on the loadings. Strydom *et al.*[56] found that K_2CO_3 is the most suitable amongst other potassium based additives (KOH, KCl, KCH_3CO_2), for decreasing the swelling behaviour and plasticity of specifically high swelling South African coal. Kawa *et al.*[48] investigated the agglomeration of Rock Springs coal, by applying heating rates of 6 °C/min and 75 °C/min, respectively. It was found that coals which were slowly heated did not exhibit caking propensity, while coals which were rapidly heated were highly agglomerated.[48] Kawa *et al.*[48] also reported that the caking propensity of coal could be reduced or eliminated by the addition of alkali carbonate or hepta-ammonium molybdate.

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Chapter 3

The transient swelling behaviour of large (-20+16 mm) South African coal particles during low-temperature devolatilisation

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The transient swelling behaviour of large coal particles from three South African coals with varying swelling characteristics is investigated in this Chapter. Novel techniques were used to quantify large particle swelling, and the results were compared with conventional swelling measurements obtained from powdered coal.

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Abstract

In order to predict coal behaviour during certain utilisation processes, and to improve and develop coal conversion technologies, it is important to understand the swelling behaviour and plastic properties of coal. X-ray CT (computed tomography) and mercury submersion were used to quantitatively and qualitatively describe the swelling behaviour (N_2 atmosphere, 7 K/min) of large particles (-20+16 mm) of South African coals, and were compared to conventional swelling related characteristics for powdered coals. Three South African coals, with low, intermediate and high Free Swelling Indices (FSI) were selected. Single coal particles were devolatilised (from ambient to 700 °C at 7 K/min) in a furnace equipped with a video camera. Image analysis was conducted on the images obtained from the furnace, to describe the swelling behaviour of single coal particles as a function of devolatilisation temperature. X-ray computed tomography (X-ray CT) and mercury submersion measurements were used to analyse particles before and after devolatilisation, to quantify the degree of swelling. While the FSI, dilatometry and Gieseler results did not indicate any plastic behaviour for the TWD sample (-212 µm particles), the large particles did exhibit a significant degree of swelling during devolatilisation. The GG and TSH large coal particles started swelling at a slightly lower temperature than the initial softening temperature obtained by dilatometry for the -212 µm coal particles. Image analysis qualitatively described the swelling behaviour of large coal particles during devolatilisation, while both the X-ray CT and mercury submersion methods quantified the volumetric swelling ratio of large coal particles. The average swelling ratios obtained for TWD, GG, and TSH respectively were 1.9 ± 0.5, 2.1 ± 0.6 and 2.5 ± 0.9 from image analysis and 1.8 ± 0.4, 2.2 ± 1.0 and 2.5 ± 1.0 from mercury submersion. The anomaly found for the TWD coal is expected, since mass transfer of tar and volatiles out of the particles will influence the thermoplastic behaviour, and consequently the difference in swelling behaviour due to particle size variation. Therefore, it is hypothesised that the FSI, and other conventional techniques used to describe the plastic behaviour of small particles of coal, can in general not be used for the prediction of large coal particle swelling.

Keywords: large coal particles, swelling, low-temperature devolatilisation

3.1. Background and Introduction

During coal devolatilisation, moisture and volatiles are released to produce a porous solid (coke or char). While all types of coal undergo chemical transformations during devolatilisation, certain bituminous coals also show signs of apparent fusion and resolidification during heating,[1,2] and are termed caking coals. The series of physical transformations that caking coals undergo during the heating process include softening, fusing, swelling and resolidification, and occur within a specific temperature range.[3] The understanding of the plastic properties of coal can assist in predicting coal behaviour under specific operating conditions, and is also critical to improve and develop coal conversion technologies.[3,4]

Coal particle swelling and agglomeration are two of the phenomena which influence coal particle behaviour during heating.[1] The swelling of a coal particle occurs during the plastic stage of the sample when the volatiles are released by thermal decomposition of the coal structure, but are trapped inside the particle. The volatiles cannot escape from the softened coal particle and act as the driving force for swelling. After the resolidification of the particle, the effect of the volatiles can be perceived in the form of single or multiple bubbles or voids remaining in the solid char.[1,5,6] Various studies have been conducted to investigate thermal swelling phenomena, and it has been reported that operating conditions such as heating rate, final operating temperature, pressure, and gas composition affect the swelling behaviour.[1,7,8] In addition, coal properties such as volatile matter content, petrographic composition, and particle size also have an influence on the thermal swelling behaviour.[8-17]

The swelling of coals result in the formation of chars with different structures, which significantly influences the char combustion, gasification kinetics, and ash formation.[3] In addition to influencing the efficiency of coal conversion processes, the swelling and caking of coal during devolatilisation is also associated with numerous operational problems, specifically during coke production in the iron and steel manufacturing industries. Excessive swelling of the coal may result in a build-up of oven wall pressure, which leads to unsafe operating conditions.[7] The agglomeration characteristics of caking coals also make them less suitable for use in fixed-bed and fluidised-bed gasifiers, since softened coal particles form aggregates, which reduce the permeability of gas through the coal bed and cause channelling.[18]

Studies investigating the devolatilisation behaviour of coal, specifically the swelling behaviour, have mainly focused on pulverised coal samples, while millimetre-sized coal particles have occasionally been utilised in studies concerning fluidised bed combustion.[19] In Table 3.1, devolatilisation studies conducted to date, which have focused specifically on the particle behaviour of large coal particles, are summarised.

Table 3.1: Summary of research regarding large coal particle behaviour during devolatilisation

Author	Particle size (mm)	Temperature of devolatilisation (°C)	Investigation
Diessel[20]	25	<1000	Transformation of different macerals during devolatilisation
Kim *et al.*[21]	0.8-17.5	1000	Devolatilisation and cracking propensity of lump coal
Dakič *et al.*[22]	2-15	850	Fragmentation and swelling behaviour in a fluidised bed
Campbell *et al.*[1]	20	500-1000	Agglomeration of lump coal in an ambient pressure reactor
Minkina *et al*.[19]	20-30	300-800	Char properties and structure of lump coal after devolatilisation
Fu *et al*.[7]	2.2x2.2 - 20.5x14.3	20-1000	Swelling and shrinkage behaviour of coal during devolatilisation
Van Dyk[23]	6.7-19	100-900	Thermal fragmentation of coal during devolatilisation
Dacombe *et al*.[24]	1-6	1000-1110	Large coal particle fragmentation in a drop tube furnace
Stubington and Linjewile[25]	5-12	850	Fragmentation of large coal particles during devolatilisation
Nomura and Arima[26]	<3	1250	Inlfuence of volume change of coal during carbonization on internal pressure in a coke oven

Most of the studies involve the comparison of coals and chars before and after devolatilisation, and only limited research was conducted on the transient behaviour of large coal particle devolatilisation.[7] This emphasises the need for further studies focusing specifically on the transient swelling behaviour of large coal particles.

The aim of this study was to investigate and quantify the swelling behaviour of large coal particles (-20+16 mm) during low-temperature devolatilisation (100-700 °C), and to compare the results with values obtained from Free Swelling Index (FSI) measurements. X-ray computed tomography (X-ray CT)[27] and mercury submersion methods were used to quantify the swelling behaviour of large coal particles, while image analysis was used to monitor the transient swelling behaviour during the course of devolatilisation.

3.2. Experimental

3.2.1 Coal samples

Three different South African coals were selected based on their distinguishable FSI values, which ranged from 0 to 9. Coal TWD was a washed, medium rank-C bituminous coal, from the Highveld region. Coal GG was a washed, medium rank-C coal from the Waterberg region, while coal TSH was a medium rank-B coal from the Limpopo province. Coal TSH was sent to Bureau Veritas Testing and Inspections South Africa for density separation. The apparent density of all the coals were <1500 kg/m^3, and a -20+16 mm size fraction was obtained for each coal. Particles were selected based on their individual density (<1500 kg/m^3), as determined from mercury submersion.

3.2.2 Dilatometry and Gieseler fluidity measurements

Dilatometry measurements were conducted according to the Ruhr Dilatometer Test (SANS 6072:2009) to study the dilation/contraction of the pulverised coal samples, Gieseler fluidity (SANS 6072:2009) measurements were conducted to study the degree of fluidity of the different coals. Both of these analyses were conducted at Bureau Veritas Testing and Inspections South Africa.

3.2.3 SEM images

SEM (Scanning electron microscopy) images were acquired at the Laboratory for Electron Microscopy (LEM) at the North-West University, South Africa. The analyses were conducted using an FEI QUANTA 250 FEG ESEM analyser integrated with an Oxford X-MAX 20 EDS (energy dispersive spectrometry) system.

3.2.4 Swelling experiments

Low-temperature devolatilisation experiments were conducted in order to study the swelling behaviour of large coal particles when heated in an inert atmosphere. A coal ash fusibility

(CAF Digital/APC) furnace, supplied by Carbolite, was used for the devolatilisation experiments. Figure 3.1 is a schematic representation of the experimental set-up.

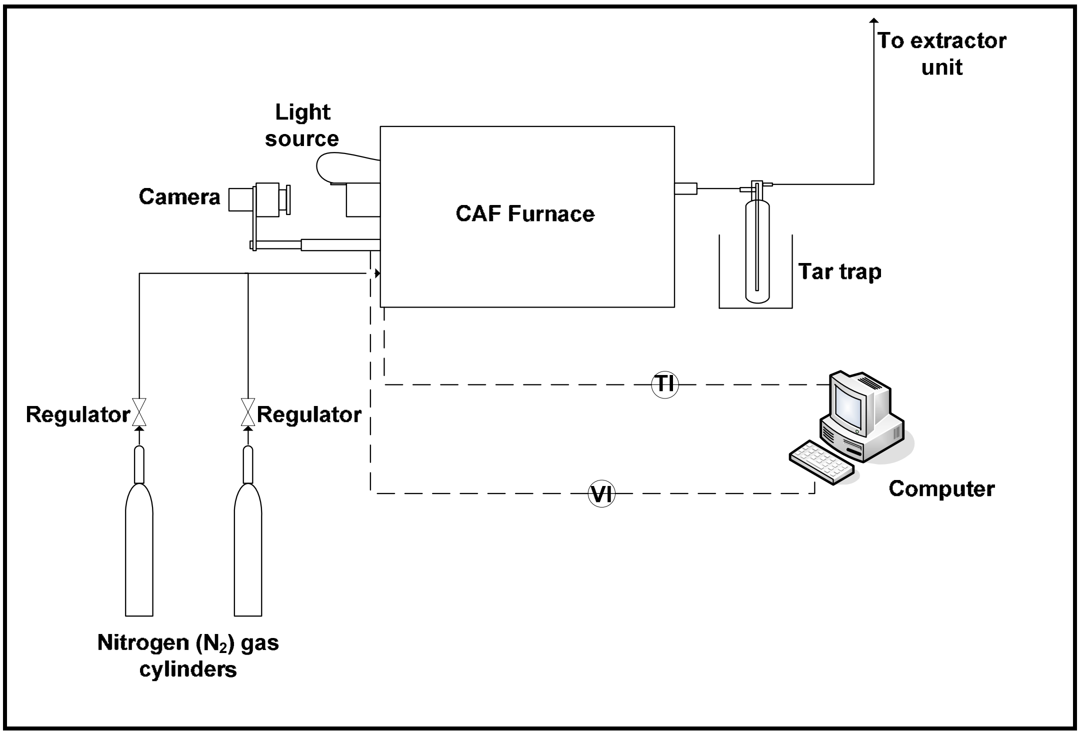


Figure 3.1: Experimental set-up

The CAF furnace is equipped with a video camera and a light source. The video camera allows real-time image capturing during experimentation, while the light source illuminates the sample and provides enhanced image clarity specifically at low operating temperatures (<700 °C). The gas outlet is connected to a tar trap, which consists of a cold trap which is cooled by ice. Specific CAF software is used to simultaneously log the temperature, time and the images captured by the camera.

Single coal particles were placed on a sample holder and inserted into the CAF furnace. A thermocouple was situated approximately 1 cm from the coal particle. -20+16 mm raw coal particles (± 5 g) were used for the devolatilisation experiments, and particles were hand-selected to ensure that near-spherical particles were used for experimentation. The coal particles were inserted into the CAF furnace at 100 °C, and heated to the specified devolatilisation temperature at a rate of 7 K/min. A flowrate of 6 l/min (STP) nitrogen gas (African Oxygen Limited, UHP grade) was used to sweep the volatile gases from the furnace. The image capturing software was initialised at the onset of the experiment, and was programmed to capture one image with every 1 K. To determine the mass loss due to moisture and volatile release, the mass of each coal particle was measured before and after devolatilisation.

3.2.4.1 Techniques used to investigate large coal particle swelling

The conventional method used to study the swelling behaviour of powdered coal samples is the test method used to determine the free swelling index (FSI). This FSI test method (Standard: ISO 501:2003) gives an empirical value, which is a good indication of the coking characteristics of the coal. However, the FSI does not quantify the extent of swelling of the coal.[11,28,29] Since large coal particles were used for this study, and only powders can be used for FSI tests, other methods were investigated and developed to study and quantify the swelling behaviour of large particles. For the X-ray CT scans and mercury submersion techniques, each measurement was repeated 10 times for a specific particle, and the uncertainty was determined for the respective methods using a 95% confidence interval. Uncertainty values of 1.4% and 0.4% were determined for mercury submersion and X-ray CT, respectively.

X-ray computed tomography

X-ray computed tomography scans were obtained at the MIXRAD facility at the South African Nuclear Energy Corporation (NECSA), using a Nikon XTH 225 ST micro-focus X-ray tomography system. The Nikon XTH 225 ST is equipped with a computerised control station, as well as an X-ray chamber which houses the samples during the acquisition of the X-ray CT scans. The volumetric swelling behaviour of a single coal particle was studied by obtaining X-ray CT scans of the particle before and after devolatilisation. The scanning parameters which were used for each scan were an X-ray tube voltage of 100 kV and an X-ray tube current of 61 µA. The volume of the particle was determined using the volume analyser function of the VGStudio Max 2.1 software. The envelope volume, defined as the sum of the volume of the solid material and the voids within the solid,[30] was determined for each particle before and after devolatilisation.

Mercury submersion

Mercury submersion analysis was used to determine the volume of the large coal particles. The volume of single large coal particles (-20+16 mm) was indirectly determined by weighing the mass increase while submerging the particle in mercury, applying Archimedes' principle. Porous particles were covered with a single layer of thin plastic film, to prevent the mercury from penetrating the particle. Results obtained from mercury submersion provide values for the envelope volume, which is defined as the sum of the volume of the solid material and the voids within the solid.[30]

Image analysis

Image analysis techniques have previously been used to study coal particle behaviour during devolatilisation.[5,7,31] The images obtained during the swelling experiments (CAF furnace) were analysed using ImageJ software. The contrast of the images was enhanced, and the perimeter of the particles was outlined in order to measure the area of the particle, before and after devolatilisation. The analyser tool of ImageJ was used to measure the relative area. The method used during image analysis is illustrated in Figure 3.2.

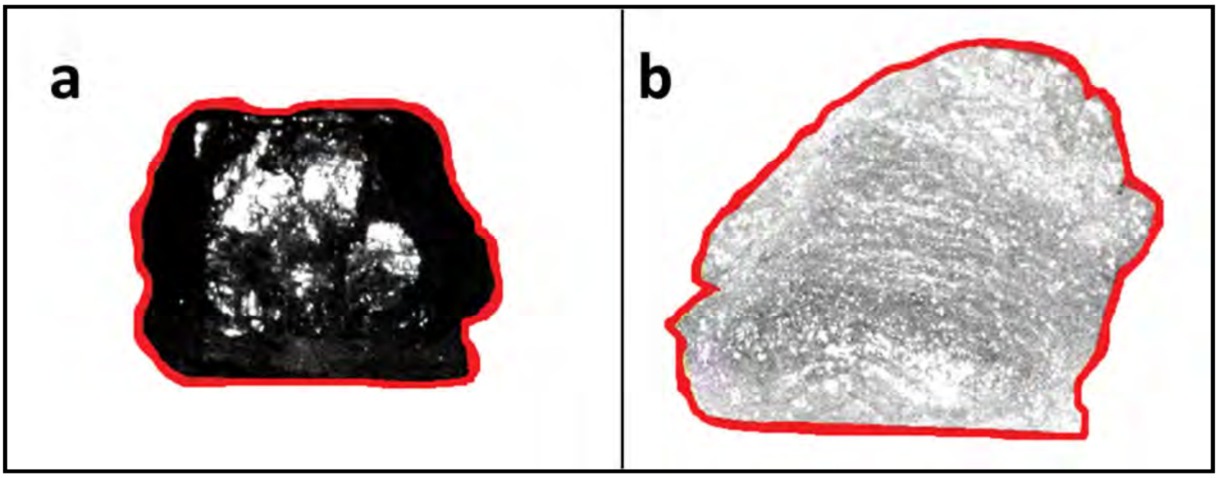


Figure 3.2: Image analysis of images obtained during devolatilisation experiments (where (a) before devolatilisation, and (b) after devolatilisation)

The image analysis method is a qualitative method, since the swelling ratios are only determined on a two-dimensional basis (area), as opposed to the X-ray CT and mercury submersion methods which provide volume-based swelling ratios.

Data processing

Results obtained from X-ray CT, mercury submersion and image analysis were used to determine the degree of swelling obtained for a single coal particle during devolatilisation. For the X-ray CT and mercury submersion methods, the swelling ratio on a volumetric basis (SR_V) is defined as:

$$SR_V = \frac{V_f}{V_i} \qquad \text{Eq. (3.1)}$$

where V_f is the final particle volume after devolatilisation, and V_i is the initial particle volume before devolatilisation. The image analysis method provides the area (2D image) of the particle before and after devolatilisation. Therefore, the swelling ratio from image analysis, SR_A, is based on area, and defined as:

$$SR_A = \frac{A}{A_i} \qquad \text{Eq. (3.2)}$$

where A is the area of the particle at a specific point during devolatilisation, and A_i is the initial area of the particle before devolatilisation. Transient swelling during devolatilisation is described using Eq. (3.2). The averages were obtained by calculating the mean of the experimental values (SR_V, SR_{Amax}), and uncertainties were determined using a 95% confidence interval.

3.3. Results and discussion

3.3.1 Coal characterisation

Results for the characterisation analyses of the three South African coals, conducted by Bureau Veritas Testing and Inspections South Africa and Petrographics SA, are given in Table 3.2. For characterisation purposes, the -20+16 mm size fraction of each coal was comminuted to the specified particle size for each analysis. Characterisation results correlate well with previously reported results for coal from the same origin.[32,33]

Table 3.2: Characterisation results of three South African coals used for devolatilisation experiments

Characterisation analysis	Standards	TWD	GG	TSH
Proximate analysis (wt.%, a.d.b)				
Inherent moisture content	SANS 5925:2007	4.8	2.5	0.6
Ash content	ISO 1171:2010	14.2	13.9	18.2
Volatile matter	ISO 562:2010	29.7	36.9	19.7
Fixed carbon	By difference	51.3	46.7	61.5
Gross calorific value (MJ/kg)	ISO 1928:2009	26.6	28.1	29.2
Ultimate analysis (wt.%, a.d.b)				
Carbon content	ISO 29541:2010	65.1	67.8	71.1
Hydrogen content	ISO 29541:2010	3.9	4.8	3.9
Nitrogen content	ISO 29541:2010	1.7	1.4	1.7
Oxygen content	By difference	9.3	8.1	4.0
Total sulphur	ISO 19579:2006	1.0	1.5	0.6
Free swelling index, FSI	ISO 501:2003	0	6.5	9.0
Gieseler fluidity (°C)	ISO 10329:2009			
Initial softening temperature		not observed	400	420
Maximum fluid temperature		not observed	430	467
Solidification temperature		not observed	457	508
Maximum fluidity (ddpm)		not observed	50	1209
Dilatation (°C)	SANS 6072:2009			
Softening temperature		not observed	371	386
Temperature of maximum contraction		not observed	418	425
Temperature of maximum dilatation		not observed	435	488
Maximum contraction (%)		not observed	33	24
Maximum dilatation (%)		not observed	14	103
Petrographic analysis (vol.%, m.m.f.b.)	ISO 7404-3:1994			
Total vitrinite		59	86	82
Total liptinite		4	6	0
Total inertinite		37	8	18
Reflectance properties				
Mean vitrinite random reflectance (Rr)	ISO 7404-5:1994	0.63	0.68	1.35
Mean Maceral reflectance (Rsc)		1.01	0.70	1.54
Rank	ISO 11760:2005	Medium Rank C	Medium Rank C	Medium Rank B

As seen from Table 3.2, all three coals have relatively low ash values for South African coals (<20 wt.% a.d.b.), and varying volatile matter contents ranging between 19.7 and 36.9 wt.% (a.d.b.). The most significant difference between the coals is the free swelling index (FSI), 0 for the TWD coal, 6.5 for the GG coal, and 9 for the TSH coal. In addition, the coals also exhibited different plastic behaviour according to the Gieseler fluidity and dilatation analyses. The TSH coal showed the highest degree of fluidity while the TWD coal showed insignificant signs of fluidity (Table 3.2). According to Speight[4] and Solomon and Hamblen,[34] the degree of fluidity of the coal often influences the degree of particle swelling. Therefore, the lack of fluid behaviour of the TWD coal may explain the absence of any swelling behaviour. The oxygen content of the coal is also a good indication of its fluidity, where the fluidity decreases with increasing oxygen content.[29] As indicated in Table 3.2, TSH coal has the lowest oxygen content and the highest degree of fluidity, while TWD coal has the highest oxygen content but shows insignificant fluid behaviour.

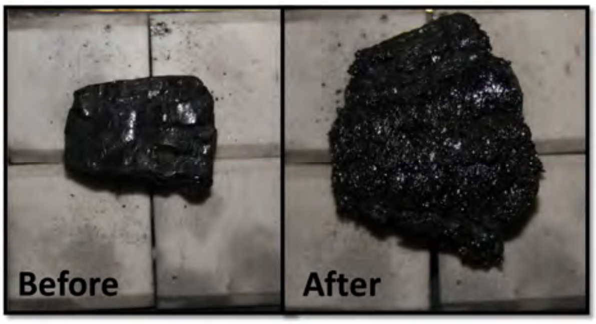
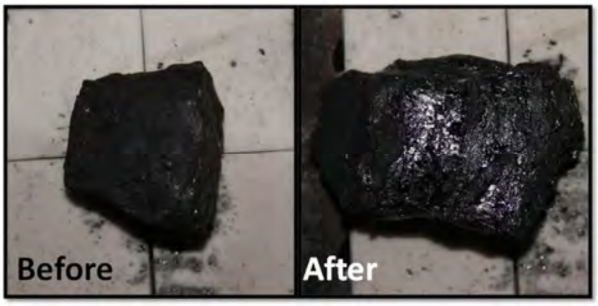
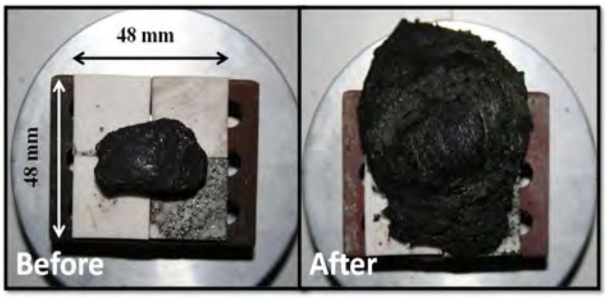
The petrographic results, Table 3.2, indicate that the GG and TSH coals are rich in vitrinite, while the TWD coal has noticeably more inertinite. This can also explain the lack of fluidity exhibited by the TWD coal sample, since inertinite-rich macerals exhibit little to no fluidity during devolatilisation.[17] The mean vitrinite random reflectance (Rr) characterised coals TWD and GG as medium rank-C bituminous coals, while TSH was characterised as a medium rank-B bituminous coal. The petrographic analysis results can also be used to explain the plastic behaviour of different coals. The softening temperature of coal depends largely on the petrographic composition of the coal, where an increase in vitrinite content results in a decrease in softening temperature.[11,13] Upon comparing the TSH and GG coals, it is evident that an increase in vitrinite content from 75% (TSH) to 81% (GG) results in a decrease in softening temperature from 386 to 371 °C (Gieseler fluidity), and from 420 to 400 °C (dilatation). From Table 3.2, it can also be seen that the plastic range, as determined from the Gieseler fluidity measurements, increases from the lower bituminous (medium rank C) GG coal to the higher bituminous (medium rank B) TSH coal.

3.3.2 Swelling

3.3.2.1 Visual observations

Examples of images of coal particles, before and after devolatilisation up to 700 °C, are shown in Table 3.3, and a description of the appearance of the char is given. Before and after images of a single particle of each coal are shown; however, the description of the char is typical to all 9 particles (from a specific coal source) used for experimentation.

Table 3.3: Images and visual observations of multiple large coal particles after devolatilisation (700 °C)

Sample	Before/After images	Visual Observations
TWD		• Signs of melting on some areas of the particles • Char particles have a more uneven surface • Cleat and crack formation visible on some particles
GG		• Melting of entire particle • Maceral bands (shiny/dull) visible • Hard, without signs of brittleness • Char particles have more rounded edges
TSH		• Very brittle and porous • Shiny surface • All chars are completely deformed in comparison to raw coal particles

SEM images were taken of the coal particles before and after devolatilisation to study the change in microscopic structure during devolatilisation. The difference between the microscopic structure of the raw coal and the char (devolatilised up to 700 °C) is shown in Figure 3.3.

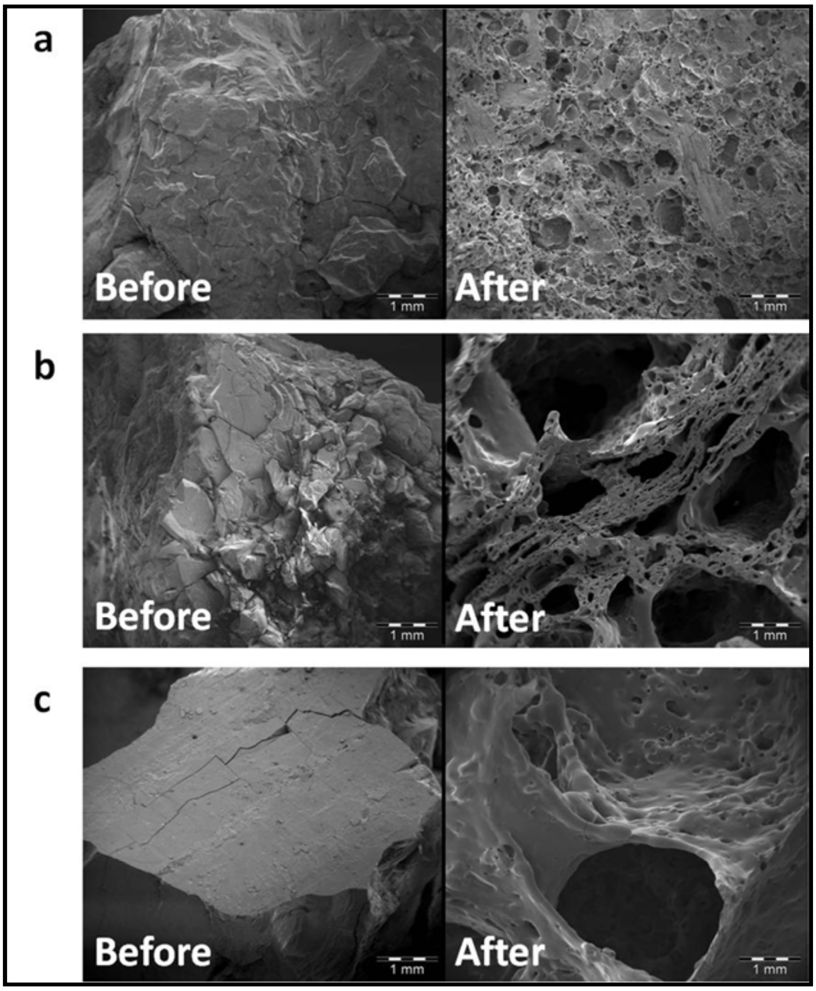


Figure 3.3: SEM images of a) TWD, b) GG, and c) TSH particles before and after devolatilisation up to 700 °C

As seen from Figure 3.3, all three chars have different structures compared to the raw coal. In Figure 3.3a, it is shown that the TWD char is more porous than the raw coal with very thick walls, and contains signs of small bubbles which were formed due to volatile release. The GG char (Figure 3.3b) is more porous compared to the TWD char, with thinner walls and larger bubbles visible in the SEM image. The formation of large bubbles, in comparison to the TWD char's small bubbles, can be attributed to a higher degree of fluidity achieved by the GG coal during volatile release. In contrast, the TSH char (Figure 3.3c) is a thin-walled char with visible large bubble formation. According to Wall *et al.*,[35] the different chars shown in Figure 3.3 can be classified as follows: TWD is classified as a group III char – a dense char with low porosity, GG is classified as a group II char – a thick-walled char with medium porosity, and TSH is classified as a group I char – a thin-walled char with high porosity. From the SEM images it is evident that the three different coals form significantly different chars. This can be attributed to the different maceral concentrations of the different coals which influence the plastic behaviour of the coal, as well as the amount and rate at which the volatiles are released during devolatilisation.[11,35-37]

3.3.2.2 Measurement of degree of coal swelling

X-ray CT scans and mercury submersion measurements were used to measure the swelling of single large coal particles after heating in an inert atmosphere. The degree of swelling is described by the swelling ratio (SR_V), as defined in Eq. (3.1). The initial volume (V_i) was determined with scans (X-ray CT) and measurements (mercury submersion) of a particle before devolatilisation (ambient temperature). The final volume (V_f) was determined with scans (X-ray CT) and measurements (mercury submersion) of a particle after devolatilisation (having been exposed to the specified maximum temperature of devolatilisation). GG and TSH coal particles were heated to the initial softening temperatures obtained by Gieseler fluidity measurements (400 °C for GG, 420 °C for TSH), while a temperature of 500 °C was selected for the TWD coal particles, which did not exhibit plastic properties according to conventional analyses. This was done to ensure that the swelling was measured before the coal particles reached maximum fluidity and lost its structural integrity, and to avoid the possible occurrence of shrinkage. The results are shown in Table 3.4.

Table 3.4: Swelling ratios (SR_V) obtained using Hg-submersion and X-ray CT

Sample	SR_V Hg-submersion	SR_V XCT scans
TWD1	1.5	1.6
TWD2	1.8	2.1
TWD3	1.9	n.a.
TWD4	1.9	n.a.
TWD5	2.1	n.a.
GG1	1.7	1.7
GG2	1.7	1.7
GG3	2.4	n.a.
GG4	2.8	n.a.
GG5	2.7	n.a.
TSH1	3.2	3.3
TSH2	2.3	2.5
TSH3	2.9	2.9
TSH4	2.0	2.1
TSH5	2.3	2.4

n.a.- not available

The mercury submersion and X-ray CT techniques are volume-based, and take into account the three-dimensional swelling of a particle. The most noteworthy observations made from these results are the SR_V values for TWD coal, which indicate significant swelling for the large coal particles, and are in contrast to the swelling behaviour of the powders. In Figure 3.4, the parity for the SR_V obtained from mercury submersion and X-ray CT is shown, and it can be concluded that they compare well.

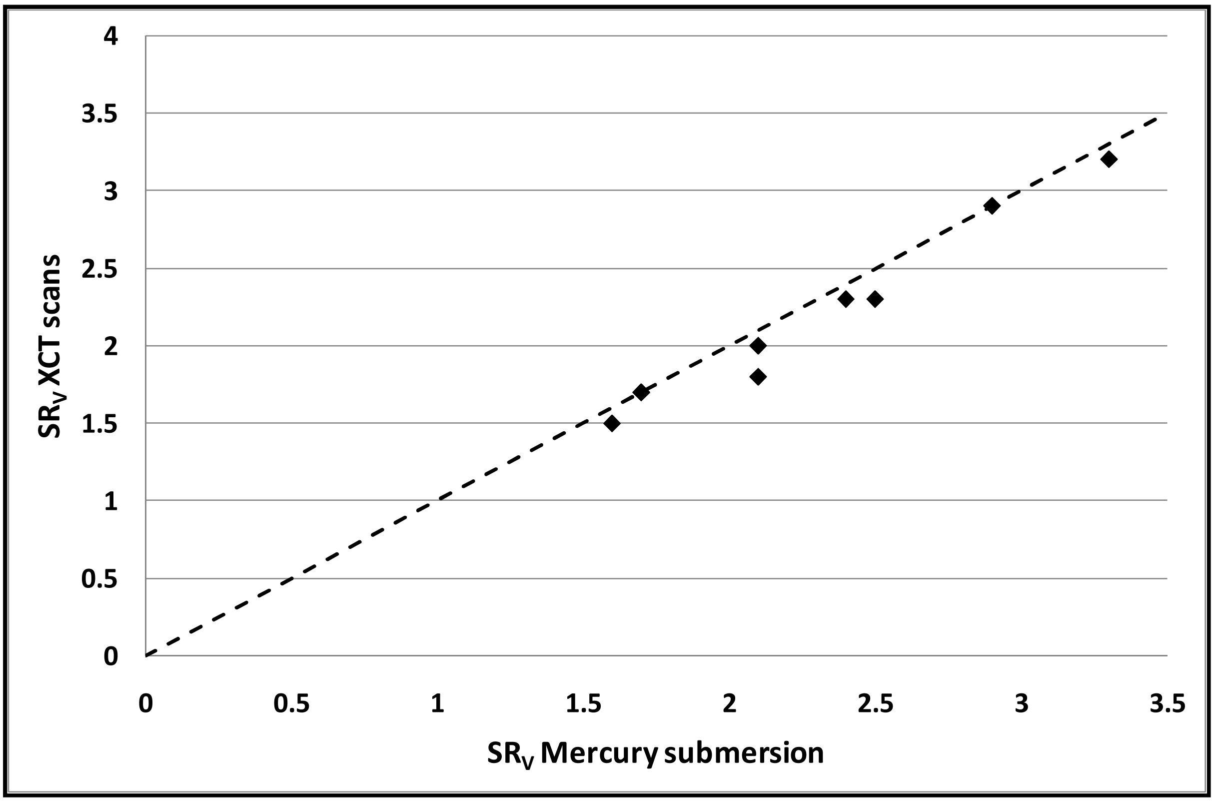


Figure 3.4: Parity between SR_V determined from mercury submersion and X-ray CT

Nomura and Arima[26] also successfully measured the volume change of coal during carbonisation in a coke oven using X-ray CT scans, and concluded that X-ray CT scans can be used to qualitatively predict the swelling behaviour of large coal particles. Mathews *et al*.[38] utilised X-ray CT to quantify the shrinkage of lump coal during thermal drying.

3.3.3 Coal swelling as a function of temperature

3.3.3.1 Visual observation of transient swelling

The swelling behaviour of the large coal particles was continuously monitored during experimentation. Figure 3.5 shows images of the coal particles at various temperatures throughout devolatilisation.

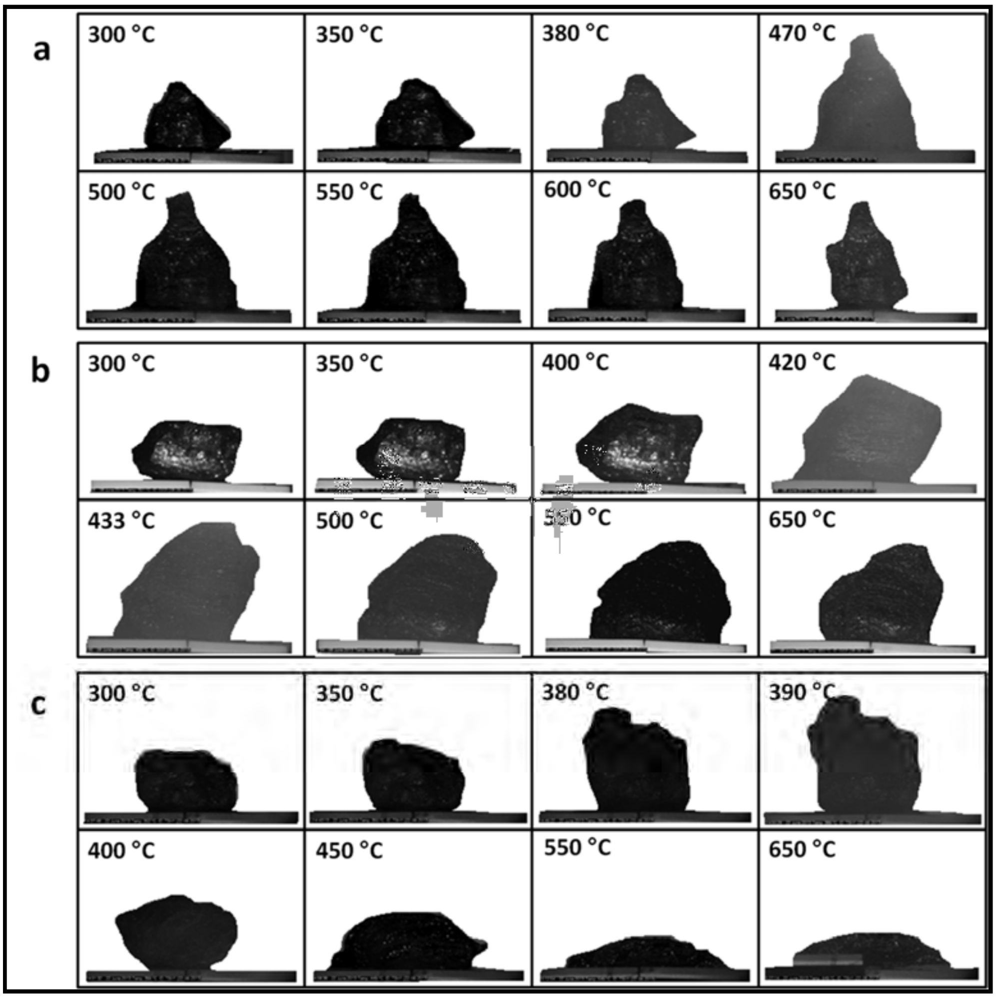


Figure 3.5: Progress of large coal particle swelling behaviour during devolatilisation. a) TWD, b) GG, and c) TSH

The images (Figure 3.5) illustrate the swelling behaviour of the coal particles from 300 to 650 °C. The swelling behaviour of a TWD coal particle is illustrated in Figure 3.5a. Initial swelling of the coal particle can be observed at 380 °C. Figure 3.5b shows the swelling of a GG coal particle, where initial swelling is observed at 400 °C. The GG coal particle reached maximum swelling at 433 °C, after which slight shrinkage is observed. The swelling behaviour of a TSH coal particle (Figure 3.5c) indicates that the particle started to swell at 350 °C, and reached maximum swelling at 390 °C. Shrinkage of the coal particle is visible at

400 and 450 °C. The most significant observation made from Figure 3.5c, which is not observed for the TWD and GG particles, is that the particle became completely fluid and flowed over the sample holder (550 and 650 °C).

3.3.3.2 Devolatilisation experiments

Figure 3.6 illustrates the swelling behaviour of TWD large coal particles during devolatilisation, in comparison to the dilatation and contraction data of the powder.

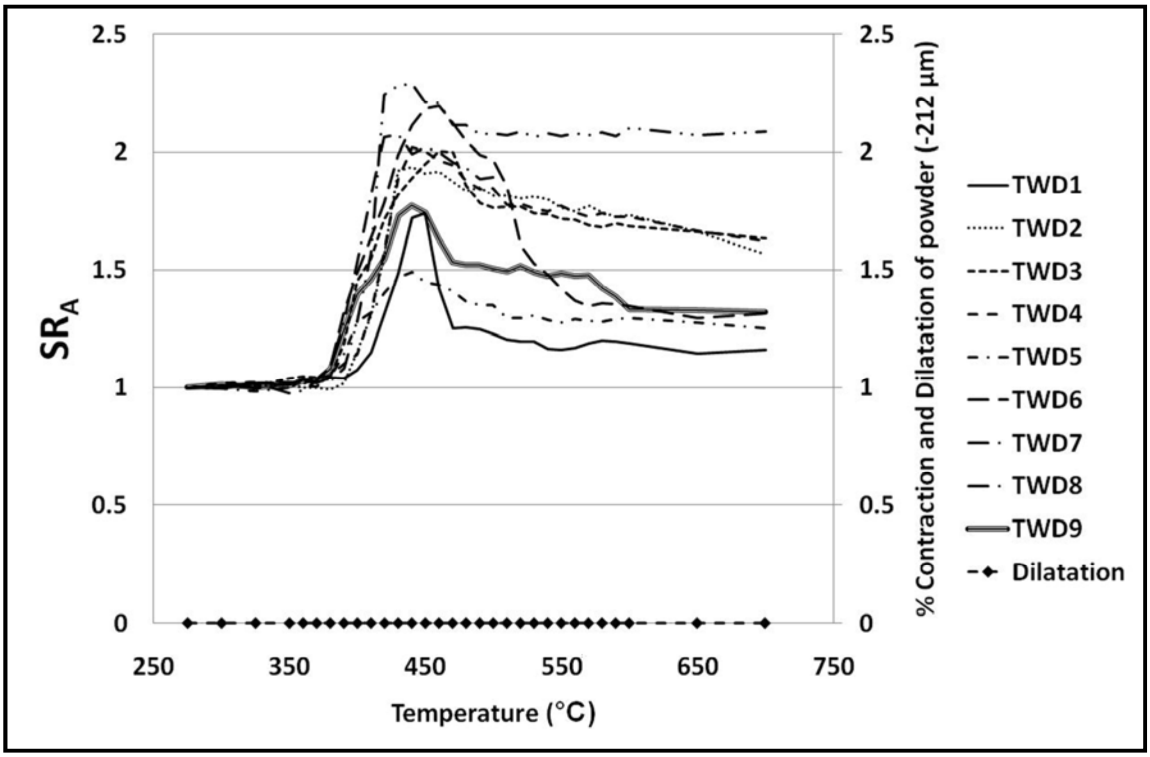


Figure 3.6: Swelling behaviour of individual TWD large coal particles during devolatilisation and contraction/dilatation of pulverised coal

The most significant observation made from the results given in Figure 3.6 is the swelling behaviour of the large TWD coal particles in comparison to the powdered coal. The FSI, Giesler and Dilatometry results, as shown in Table 3.2, indicate that the -212 µm TWD sample did not display any swelling or plastic behaviour. However, the -20+16 mm TWD particles (Figure 3.6) exhibited significant swelling. Since particle size influences the transportation of tars, and consequently the swelling behaviour of the coal, the particle size of the coal needs to be taken into consideration as a factor in swelling and notably in the application of data from conventional analyses using small particles and powders. From Figure 3.6 it can also be observed that the initial swelling temperature of the particles was between 380 and 390 °C. Shrinkage of the particles occurs between 460 and 550 °C, after which the size of the particles did not change significantly. An average shrinkage of 34% was determined for the 9 particles. The plastic behaviour of the TWD coal particles is also illustrated in Figure 3.6, whereby the particles swell until a maximum, after which the particles shrink. All particles exhibited the same swelling trend, which was also observed by Fu *et al.*[7] for two Chinese coals, where they used raw and processed coal blocks to study the transient swelling behaviour during devolatilisation. As seen from the swelling behaviour results, not all of the TWD particles exhibited the same degree of swelling. A similar spread was reported by Van Niekerk *et al.*[39] for solvent swelling of 2-4 mm coal particles.

Table 3.5 includes the maximum swelling ratio (SR_{Amax}) obtained for each particle, the temperature (T_{max}) at which maximum swelling was obtained, and the mass loss of each particle during devolatilisation.

Table 3.5: SR_{Amax}, T_{max}, and mass loss obtained for TWD coal particles during devolatilisation

Sample	SR_{Amax}	T_{max} (°C)	Mass loss (wt.%)*
TWD1	1.7	450	32.2
TWD2	1.9	440	29.6
TWD3	2.0	460	33.6
TWD4	2.0	440	38.4
TWD5	1.5	440	31.8
TWD6	2.2	450	31.4
TWD7	2.0	450	24.2
TWD8	2.3	440	34.6
TWD9	1.8	440	37.6

***- air dry basis**

From Table 3.5 it can be observed that the maximum swelling ratio obtained for the selected TWD large coal particles was between 1.5 and 2.3, and that this maximum swelling was obtained between 440 and 460 °C. The mass loss obtained during devolatilisation does not correlate with the degree of swelling. Fu and co-workers[7] also reported that no correlation could be found between volatile matter content and swelling and shrinkage ratios of raw and processed coal.

The swelling behaviour of GG large coal particles as a function of temperature is illustrated in Figure 3.7.

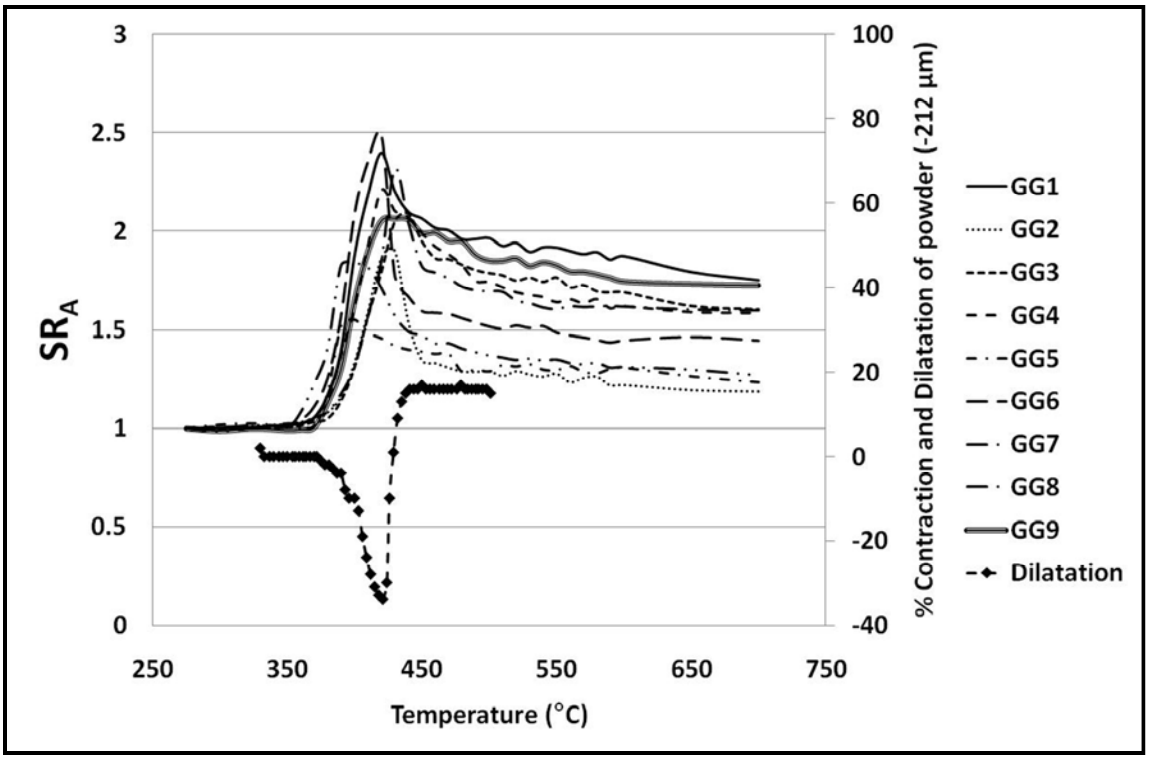


Figure 3.7: Swelling behaviour of individual GG large coal particles during devolatilisation and contraction/dilatation of pulverised coal

As can be seen from Figure 3.7, the GG coal particles follow the same trend as the TWD particles (swelling and shrinkage), which is a common trend observed for swelling coals during the initial (swelling) and final stages (shrinking) of devolatilisation.[7,40,41] In comparison to the dilatation results it can be observed that the large GG coal particles show signs of swelling at around 360 °C, a slightly lower temperature than the initial softening temperature (371 °C) determined from dilatometry (for -212 µm sample). An average shrinkage of 43% was determined, and shrinkage of the coal particles occur between 400 °C and 430 °C up until 550 °C, after which the size of the particles do not change considerably. Measurements for SR_{Amax} and T_{max} obtained for the GG large coal particles are summarised in Table 3.6.

Table 3.6: SR_{Amax}, T_{max}, and mass loss obtained for GG coal particles during devolatilisation

Sample	SR_{Amax}	T_{max} (°C)	Mass loss (wt.%)*
GG1	2.4	420	34.6
GG2	2.1	440	34.1
GG3	2.2	420	24.2
GG4	2.5	420	32.1
GG5	1.6	410	36.5
GG6	1.9	430	33.2
GG7	2.3	430	33.5
GG8	1.9	400	28.8
GG9	2.1	430	32.3

***- air dry basis**

From Table 3.6 it can be seen that a maximum swelling ratio of 1.6 – 2.5 was obtained for GG coal, and that the SR_{Amax} for all particles was obtained between 400 and 440 °C. The results indicate that mass loss was not correlated with the swelling ratio, as was also observed for the TWD coal.

The swelling behaviour of the TSH large coal particles is illustrated in Figure 3.8. The TSH coal particles reached a point of maximum swelling, after which the particles became completely fluid and lost their structural integrity. Therefore, the swelling behaviour was only reported up to the maximum swelling ratio.

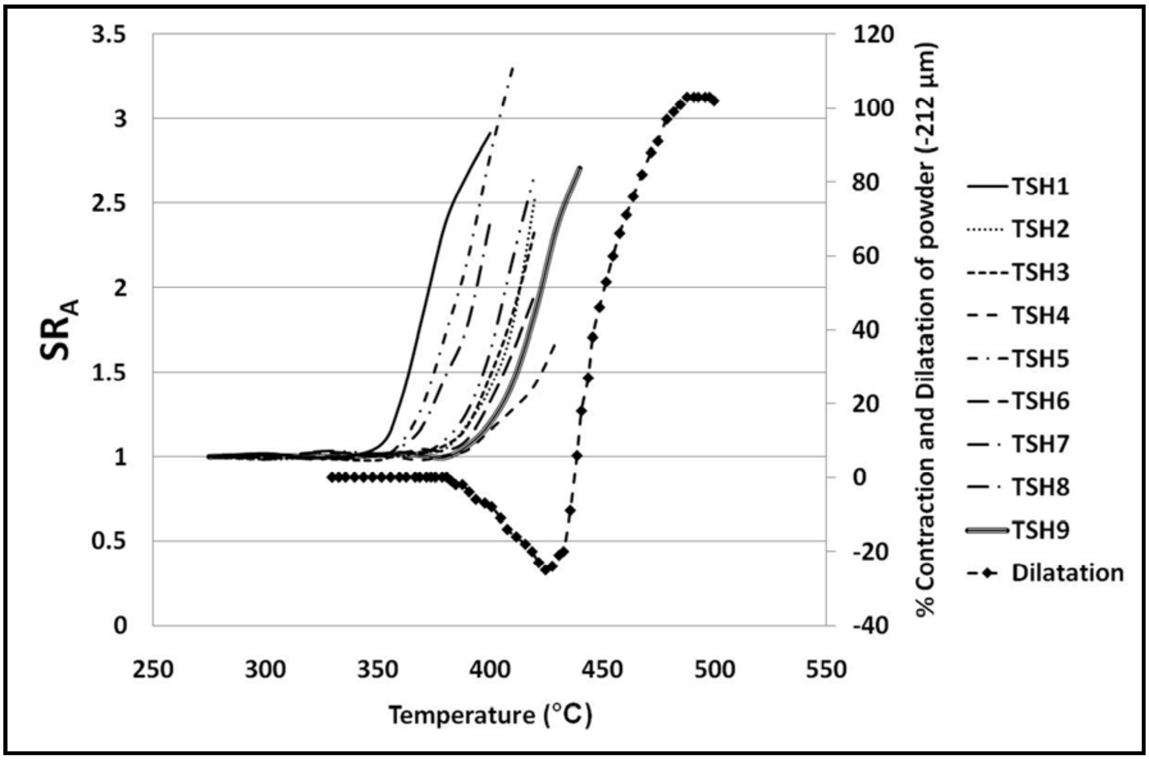


Figure 3.8: Swelling behaviour of individual TSH large coal particles during devolatilisation and contraction/dilatation of pulverised coal

From the results illustrated in Figure 3.8 it can be observed that the initial swelling temperature of TSH is 350 °C, which is lower than the softening temperature of 386 °C as obtained by dilatometry for the -212 µm sample. All the TSH particles follow the same trend for swelling behaviour, as indicated by the results (Figure 3.8). It is also seen that the contraction of the pulverised coal occurs in the same temperature range where the individual particles swell. The SR_{Amax} and T_{max} measurements for TSH particles are given in Table 3.7.

Table 3.7: SR_{Amax}, T_{max}, and mass loss obtained for TSH coal particles during devolatilisation

Sample	SR_{Amax}	T_{max} (°C)	Mass loss (wt.%)*
TSH1	2.9	400	38.1
TSH2	2.5	420	16.1
TSH3	2.3	420	17.0
TSH4	1.7	430	19.0
TSH5	3.3	410	47.9
TSH6	2.0	420	12.5
TSH7	2.4	400	18.4
TSH8	2.7	430	16.2
TSH9	2.7	440	25.5

***- air dry basis**

The results presented in Table 3.7 indicate that the maximum swelling ratio obtained for the selected TSH large particles was from 1.7 - 3.3, at a temperature between 400 and 440 °C. Similar to the TWD and GG results, the mass loss percentage cannot be used as an indication of the degree of swelling obtained for a specific coal particle.

The results from Table 3.5, Table 3.6, and Table 3.7 are summarised in Table 3.8. The averages were obtained by calculating the mean of the experimental values (SR_V, SR_{Amax}, mass loss, temperatures), and an error was determined using a 95% confidence interval.

Table 3.8: Comparison of swelling properties and characteristics of large coal particles and powders

Sample	Method	TWD	GG	TSH
FSI	-	0	6.5	9.0
Average SR_V	Hg-Submersion	1.8 ± 0.4	2.2 ± 1.0	2.5 ± 1.0
Average SR_{Amax}	Image analysis	1.9 ± 0.5	2.1 ± 0.6	2.5 ± 0.9
Average mass loss (wt.%)	Gravimetric	32 ± 8	32 ± 7	22 ± 14
Softening temp. (°C)	Dilatometry	-	371	386
Average initial swelling temp. (°C)	Devolatilisation	381 ± 15	367 ± 16	368 ± 25
Temperature of max. dilatation (°C)	Dilatometry	-	435	496
Re-solidification temperature (°C)	Dilatometry	-	441	488
Average T_{max} (°C)	Devolatilisation	446 ± 14	422 ± 24	418 ± 26

From the results presented in Table 3.8, it can be observed that the swelling ratios obtained for the small and large coal particles follow the same trend, where the swelling ratios increase in the order of TWD <GG <TSH. The most significant observation is the fact that the TWD -212 µm powder did not exhibit any swelling behaviour, whereas the TWD large

coal particles showed significant signs of swelling. It can also be seen that similar results were obtained for the average SR_V from mercury submersion and the average SR_{Amax} during devolatilisation. This shows that the lower devolatilisation temperatures selected for the particles used for mercury submersion and X-ray CT are the temperatures at which the average maximum swelling is obtained. A general correlation between the average mass loss and the average degree of swelling was not obtained. The average mass loss corresponds with the volatile matter (proximate analysis) showing that most of the volatile matter was already released before 700 ^{o}C, as was also observed for some typical South African coals by Hattingh *et al.*[42] The results also indicate that the average initial softening temperatures of the three coals do not differ considerably. The resolidification temperatures for the conventional dilatometry experiments can be determined from Figures 3.6-3.8 as the temperature at which the slope of the curve returns to zero. As can be seen from Figures 3.6-3.8, TWD shows no fluidity, and the resolidification temperatures of GG and TSH are 441 °C and 488 °C, respectively. The average T_{max} values of the GG and TSH large coal particles are similar, while that of the TWD coal is slightly higher.

3.4. Conclusions

X-ray CT and mercury submersion methods were used to study the degree of swelling of large coal particles in terms of swelling ratio. It was found that analysis of the images obtained using the CAF furnace can be used to qualitatively describe the transient swelling behaviour of large coal particles during devolatilisation. The image analysis results also indicated the different phases of plastic behaviour of the coal particles, including swelling and shrinking. From the swelling behaviour results obtained for the powders (FSI 0) and large coal particles (SR_V=1.8 ± 0.4, SR_A=1.9 ± 0.5), it can be concluded that the FSI cannot generally be used to predict the swelling behaviour of large coal particles. The average initial swelling temperature (large particles) was found to be on average 13 °C lower than the softening temperature obtained for dilatation (powders). However, the majority of the swelling behaviour of the large coal particles occurs in the plastic range as indicated by dilatometry. The results give insight into the swelling behaviour of large particles from three South African coals, and will assist in an improved understanding of large coal particle behaviour during coal conversion processes.

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Nomenclature

Notations/Symbols

A/A_i	Ratio of area to initial area (-)
SR_V	Swelling ratio (based on volume) (-)
SR_A	Swelling ratio (based on area) (-)
SR_{Amax}	Maximum swelling ratio obtained during devolatilisation (-)
T_{max}	Temperature at which SR_{Amax} is obtained (°C)
V_f	Final particle volume after devolatilisation (mm^3)
V_i	Initial particle volume before devolatilisation (mm^3)

Abbreviations

a.d.b.	Air dry basis
m.m.f.b.	Mineral matter free basis
ddpm	Dial divisions per minute

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Chapter 4

Influence of potassium carbonate on the swelling propensity of South African large coal particles

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The influence of K_2CO_3-impregnation on the swelling propensity of large coal particles from three different South African coals is investigated in this manuscript. Experimental results obtained from this novel approach indicate the feasibility of additive addition to reduce unwanted particle swelling during coal utilisation processes.

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Abstract

The swelling propensity of some coals may restrict their use in fixed- and fluidised-bed gasification operations, and effective reduction of swelling can widen the applicability of these coals. Extensive research has been published on the influence of additives on the swelling of pulverised coal (<500 µm), while limited knowledge exists on the influence of additives on large coal particle swelling behaviour. This paper presents an investigation on the influence of K_2CO_3 on the extent of swelling of 5, 10 and 20 mm, which are particle sizes suitable for fixed- and fluidised-bed operations. Three South African coals were selected: TSH coal (FSI 9), GG coal (FSI 5.5-6.5), and TWD coal (FSI 0). Large coal particles (5, 10, and 20 mm) were impregnated with a 5.0 M K_2CO_3 solution, and the K-loading increased by a factor 9 - 33, and maximum K-loadings of 3.3, 3.0 and 1.4 wt.% K (coal basis) were obtained for the 5, 10, and 20 mm particles, respectively. The volumetric swelling ratio (SR_V) of the 20 mm GG particles reduced from 3.0 to 1.8, and for the TSH particles from 3.1 to 2.1. The TWD coal particles showed SR_V values up to 1.7, in contrast to the non-swelling behaviour of the pulverised (-212 µm) coal, and was not influenced by K_2CO_3-addition. It was concluded that K_2CO_3 only influences the volumetric transformation of coals which undergo significant plastic deformation, such as GG and TSH. Comparison of the maximum swelling coefficients showed that K_2CO_3 impregnation reduces the k_A value from 0.025 to 0.015 $^{o}C^{-1}$ for GG, and from 0.013 to 0.009 $^{o}C^{-1}$ for TSH. The results show the viability of using an additive for swelling reduction of large coal particles, and together with further development, may be a suitable method for reducing unwanted swelling in relevant coal utilisation processes.

Keywords: Large coal particle swelling, quantification of swelling, reduction of swelling, potassium carbonate.

4.1. Background and Introduction

Coals may undergo physical transformations, such as fragmentation and plastic deformation (softening and swelling), during heating.[1-3] Some coals melt during devolatilisation to produce coke, while other coals do not melt but instead leave a friable char residue.[4] Habermehl *et al.*[1] describes the physical transformation of coal during devolatilisation as a succession of several processes, which may include softening, swelling, resolidifaction, and shrinkage after resolidification. Coal particle swelling during devolatilisation is an important occurrence, since it affects the particle size, density, porosity and reactivity of the char or coke, and consequently the behaviour of the resulting char in coal utilisation processes.[5]

Coal swelling also affects the resulting char or coke structure which may influence combustion, gasification kinetics, and ash formation, while excessive swelling may result in the undesired pressure build-up in ovens.[6,7] Therefore, various pre-treatment methods, such as pre-oxidation and slow heating rates, have been investigated to modify the swelling and caking propensity of coal.[8-11] In addition to these pre-treatment methods, the use of additives such as alkali and alkaline earth metal salts has been investigated extensively in order to determine the influence of these additives on the caking and swelling of coal.[12-26] Thus far, studies investigating the reduction or elimination of coal swelling and caking through the use of an additive have mainly focused on pulverised coal samples (<500 µm); Table 4.1 includes a summary of these studies, and indicates the examined particle size and additive(s) of each study.

Table 4.1: Studies conducted to investigate the transformation of swelling through additive addition

Author	Particle size (μm)	Additive(s)	Main results
Khan and Jenkins[23]	<74	K and Ca species	K_2CO_3 and CaO (individually and combined) were most effective in reducing maximum swelling
Tromp *et al*.[18]	<44, <75, 106-200, 212-400	K_2CO_3	20 wt.% K_2CO_3 reduced dilatation almost completely (atmospheric pressure)
Bexley *et al*.[12]	<212	Li_2CO_3, $NaHCO_3$, Na_2CO_3, $KHCO_3$, K_2CO_3, Na_2O, NaCl, Na_2SO_4, $NaNO_3$, KCl, $CaCO_3$, Fe_2O_3, Al_2O_3 (and others)	-Most sodium and potassium compounds were found to eliminate dilatation when 1-4% w/w was added -These additives also altered the caking and swelling properties of the coals used
Crewe *et al*.[13]	<74	NaOH	Caking and agglomeration were eliminated when 1-2 wt.% (solution impregnation) and 20 wt.% (physical mixing) NaOH was added to the coal
Fernández *et al*.[24,25]	<212	Non-coking coals, coal tar pitch, residue from benzol distillation column, residue from tyre recycling plant	- Coal tar pitch, residue increased maximum fluidity -Tyre residue decreased maximum fluidity
Mulligan and Thomas[16]	<500	Pitch, Na_2CO_3	-Pitch increased plastic range - Na_2CO_3 reduced plastic range
Clemens and Matheson[26]	<425	Chloroform extract, decacyclene	-Chloroform lowered softening point, increased plastic range -Chloroform/decacyclene extracts increased fluidity
McCormick and Jha[15]	<420	Composites of Na and Ca species	Na and Ca reduced Free Swelling Index (FSI) values, depending on the loadings
Strydom *et al.*[30]	<75	KOH, KCl, K_2CO_3, KCH_3CO_2	All oxygen-containing potassium compounds decreased the swelling of the partially demineralised coal

In South Africa, coal sourced from the Highveld coalfield is typically used for gasification processes. The Highveld coalfield has limited coal resources and is reported to have sufficient coal supply until 2050.[27,28] Therefore a need exists to explore alternative coal feedstocks for fixed- and fluidised-bed operations. One such alternative is coal from the Waterberg region, which is relatively uncharted and contains vast amounts of coal.[28,29] However, modification of the swelling and caking characteristics of some of the coals sourced from this area is required to make them more suitable for use in fixed- and fluidised-bed operations. The research in this paper explores the use of additive addition as a possible method to reduce the swelling propensity of the selected coals. None of the cited studies included research on large particles (>1 mm), and the present work was therefore undertaken to address the swelling of large coal particles (5, 10, and 20 mm) through the use of a suitable additive. The particle sizes selected for experimentation falls within the range of typical particle sizes used in fixed- and fluidised-bed gasifiers.

Potassium carbonate was selected as additive, since various authors[12,18,23] have shown this to be an effective additive for decreasing the extent of swelling and fluidity of various pulverised coals. Strydom *et al.*[30] also showed that K_2CO_3 is the most suitable amongst other potassium based additives (KOH, KCl, CH_3COOK), for decreasing the swelling and plasticity of specifically high swelling South African coal (sample size <75 µm). Three coals with various swelling characteristics were selected, and the addition of K_2CO_3 through solution impregnation was investigated. Previously, the quantification of swelling and the transient swelling and shrinkage behaviour of large non-impregnated coal particles (5, 10, and 20 mm) was investigated.[31] This research aims to quantify the reduction of large coal particle swelling due to impregnation with K_2CO_3, and to study the transient swelling and shrinkage behaviour of raw and impregnated 20 mm particles. Comparison of the volumetric swelling and transient swelling of raw and impregnated large particles is novel, since the swelling behaviour of coal is mostly determined using well-known methods such as Free Swelling Index (FSI), Gieseler fluidity and Dilatometry, where pulverised coal is used. Therefore, the use of large coal particles will provide a better understanding of the swelling behaviour of lump coal used in certain industrial coal utilisation operations. This investigation is focused on large coal particle applications and the coal-additive interaction, which has been discussed previously, is not a focus.[12,15,16,18]

4.2. Experimental

4.2.1 Coal and additive

Three South African coals were selected for this study. The coals originate from three different regions in South Africa, and have different swelling characteristics: TSH coal (FSI 9) from the Limpopo province, GG coal (FSI 5.5-6.5) from the Waterberg region, and TWD coal (FSI 0) from the Highveld region. The coals were washed (TWD and GG) and density separated (TSH) to obtain a density of <1500 kg/m^3. The size fractions include -20+16 mm, -11.2+10 mm, and -6+4.75 mm, and will be referred to as 20 mm, 10 mm, and 5 mm particles, respectively. Characterisation of the coal was conducted by Bureau Veritas

Testing and Inspections South Africa, and the proximate analysis and FSI results for the three different particle sizes are presented in Table 4.2. A detailed characterisation of the coals is reported by Coetzee *et al*.[31]

Table 4.2: Characterisation of three South African coals

Characterisation analysis	Standards			
TWD		**5 mm**	**10 mm**	**20 mm**
Proximate analysis** *(a.d.b.)				
Inherent moisture	SANS 5925:2007	5.2	5.0	4.8
Ash yield	ISO 1171:2010	13.9	14.1	14.2
Volatile matter	ISO 562:2010	28.1	28.4	29.7
Fixed carbon	By difference	52.8	52.5	51.3
Ultimate analysis** *(a.d.b.)				
Carbon	ISO 29541:2010	81.0	80.8	80.4
Hydrogen	ISO 29541:2010	4.6	4.7	4.8
Nitrogen	ISO 29541:2010	2.2	2.2	2.1
Oxygen	By difference	11.3	11.3	11.4
Total sulphur	ISO 19579:2006	0.9	1.0	1.2
Free Swelling Index (FSI)	ISO 501:2012	0	0	0
Rank	ISO 11760:2005	Med. Rank C	Med. Rank C	Med. Rank C
GG		**5 mm**	**10 mm**	**20 mm**
Proximate analysis** *(a.d.b.)				
Inherent moisture	SANS 5925:2007	2.7	2.5	2.5
Ash yield	ISO 1171:2010	9.2	13.0	13.9
Volatile matter	ISO 562:2010	36.7	36.6	36.9
Fixed carbon	By difference	51.4	47.9	46.7
Ultimate analysis** *(a.d.b.)				
Carbon	ISO 29541:2010	81.0	81.1	81.1
Hydrogen	ISO 29541:2010	5.6	5.6	5.7
Nitrogen	ISO 29541:2010	1.7	1.8	1.7
Oxygen	By difference	10.4	10.1	9.7
Total sulphur	ISO 19579:2006	1.3	1.5	1.7
Free Swelling Index (FSI)	ISO 501:2012	6.5	5.5	6.5
Rank	ISO 11760:2005	Med. Rank C	Med. Rank C	Med. Rank C
TSH		**5 mm**	**10 mm**	**20 mm**
Proximate analysis** *(a.d.b.)				
Inherent moisture	SANS 5925:2007	0.5	0.6	0.6
Ash yield	ISO 1171:2010	15.7	17.3	18.2
Volatile matter	ISO 562:2010	21.5	20.4	19.7
Fixed carbon	By difference	62.3	61.7	61.5
Ultimate analysis** *(a.d.b.)				
Carbon	ISO 29541:2010	87.7	87.9	87.5
Hydrogen	ISO 29541:2010	4.9	4.8	4.7
Nitrogen	ISO 29541:2010	2.1	2.1	2.1
Oxygen	By difference	4.5	4.5	4.9
Total sulphur	ISO 19579:2006	0.9	0.8	0.8
Free Swelling Index (FSI)	ISO 501:2012	9.0	9.0	9.0
Rank	ISO 11760:2005	Med. Rank B	Med. Rank B	Med. Rank B

a.d.b. **– air dried basis**

The three coals have different swelling characteristics, and the FSI values do not change significantly with particle size variation (Table 4.2). As also evident from Table 4.2, the proximate analysis values do not differ significantly with particle size. Only a marginal variation in volatile matter and fixed carbon exists for the different particle sizes, when calculated on a dry ash-free basis (d.a.f.), which falls within the range of precision for the standard (ISO 562:2010). The change in ash yield can be attributed to size reduction and the associated liberation of mineral matter, since different minerals have different degrees of friability.[32]

The additive used was potassium carbonate (K_2CO_3) with a purity of >99.5%, and was supplied by Merck (Pty) Ltd.

4.2.2 Analyses to study coal swelling, fluidity and caking of pulverised (-212 µm) coal

The Free Swelling Index (FSI) (ISO 501:2003) and Ruhr Dilatometer Test (SANS 6072:2009) were used to study the swelling of the coal, and the effect of K_2CO_3 thereon. Gieseler fluidity (SANS 6072:2009) measurements were conducted to study the influence of K_2CO_3 on the fluidity of the coals. Roga Index tests (SANS 881:2009) were conducted to determine the caking propensity and coke strength of the raw and K_2CO_3-containing samples. These analyses were conducted using the raw coal (-212 µm), as well as mixed coal samples containing 5 and 10 wt.% K_2CO_3, and were carried out by Bureau Veritas Testing and Inspections South Africa.

4.2.3 Quantification of degree of swelling for large coal particles

Mercury submersion was used to determine the volume of the coal samples before and after devolatilisation.[31] With mercury submersion, the volume of coal particles was determined by applying Archimedes' principle, and determining the mass increase while submerging the coal particle in mercury. This was done to obtain the volumetric swelling ratio (SR_V), in order to quantify the degree of swelling.[31] The SR_v value is defined as the final particle volume after devolatilisation, divided by the initial particle volume before devolatilisation.[31] Approximately 5 g of coal (a single 20 mm particle, 6-7 10 mm particles, and 30-35 5 mm particles) was used for each measurement. In order to reduce the variation in composition between different particles or samples, mercury submersion was used to determine particle/sample density. Individual particles (20 mm) and samples (5 and 10 mm) were selected within a density range of 1200-1400 kg/m^3. This selection criteria was used for previous experiments conducted by Coetzee *et al.*,[31] and sufficient repeatability was obtained. The variation for SR_V for 20 mm particles was calculated to be between 20 and 30%, using 90% confidence interval. The 5 particles were hand-selected, and only spherically shaped particles were used for experimentation. Experiments conducted with single 20 mm particles were performed 5 times. Experiments conducted with the 5 and 10 mm particles were repeated once, since each measurement was performed on multiple particles. The variation in the measurements for all particle sizes was calculated using the 90% confidence interval.

4.2.4 Impregnation of large coal particles

Before impregnation, the coal samples were dried in a laboratory oven overnight at 105°C. After drying, the coal samples were submerged in an excess 5.0 M K_2CO_3 solution for 24 hours, at ambient temperature. Containers with tightly sealed lids were used, to prevent evaporation of the impregnation solution. After 24 hours, the coal samples were removed from the impregnation solution and again dried (105°C) overnight. Coal samples were impregnated and X-ray fluorescence (XRF) analysis (UIS Analytical Services) was used to quantify the potassium loading. Table 4.3 shows the potassium loading on a coal basis (a.d.b.), according to the method by Coetzee *et al*.[33]

Table 4.3: Potassium loading (coal basis) of coal samples before and after impregnation with K_2CO_3

	K (wt.%) before impregnation[a]	**K (wt.%) after impregnation[a]**
TWD 5 mm	0.1	3.3
TWD 10 mm	0.1	3.0
TWD 20 mm	0.1	1.4
GG 5 mm	0.1	2.0
GG 10 mm	0.1	2.0
GG 20 mm	0.1	1.2
TSH 5 mm	0.2	2.7
TSH 10 mm	0.2	1.7
TSH 20 mm	0.2	1.4

[a] -coal basis

As evident from the results, the wt.% K (coal basis) significantly increases as a result of impregnation. K-loadings increased by factors of between 14 and 33 and between 9 and 30 for the 5 mm and 10 mm particles, respectively. Coetzee *et al.*[33] obtained significantly lower K-loadings (coal basis) of 0.8 wt.% (for 5 and 10 mm particles), using a 0.5 M concentration K_2CO_3 impregnation solution, indicating that the loading can be increased by using a higher impregnation solution concentration. The results also indicate that the K-loading decreases with an increase in particle size. However, when the average potassium surface loading (mg/cm^2) is calculated for each size fraction, the potassium loading increases with an increase in particle size (Figure 4.1), and does not systematically depend on the type of coal.

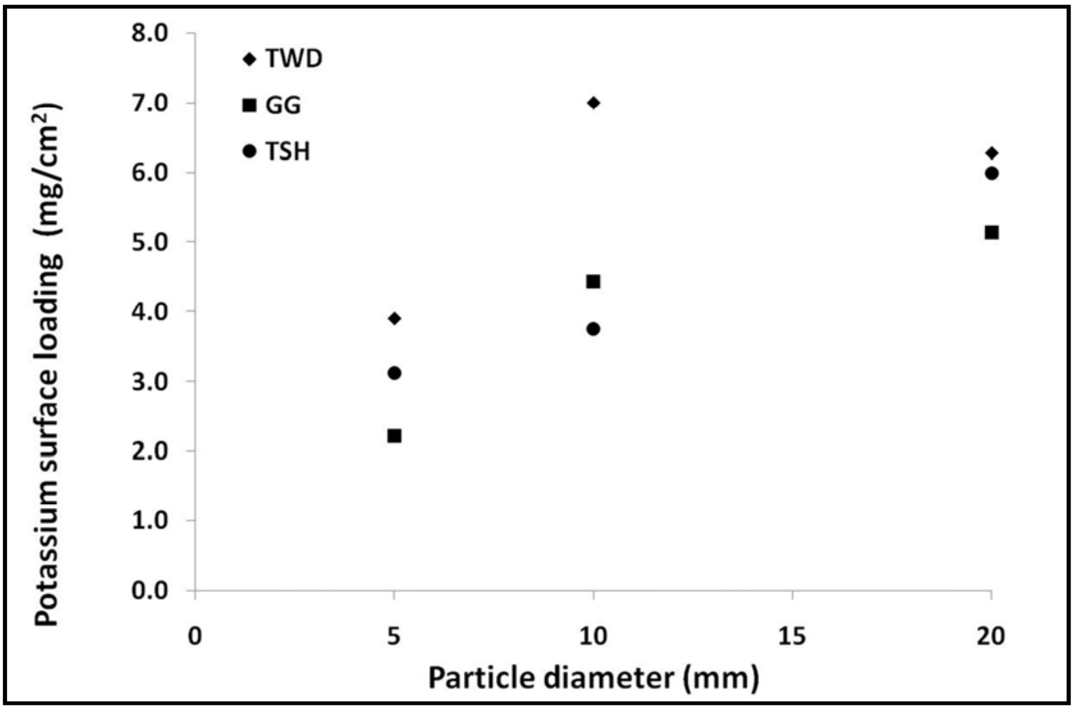


Figure 4.1: Average potassium surface loading (mg/cm^2) for 5, 10 and 20 mm particles

4.2.5 Devolatilisation experiments for large coal particles

Low-temperature devolatilisation experiments were conducted in order to study the effect of K_2CO_3 on the swelling behaviour. A coal ash fusibility (CAF Digital/APC) furnace, supplied by Carbolite, was used for the devolatilisation experiments, and previously described by Coetzee *et al.*[31] The furnace is equipped with a camera, which acquires an image with every 1 °C temperature increase, and makes it possible to study the transient swelling behaviour of the coal particles. A light source illuminates the sample to make image acquisition possible at low operating temperatures (< 700 °C). CAF software is used to log the temperature, time and images concurrently.

Coal samples were placed on a sample holder and inserted into the CAF furnace, approximately 1 cm from a thermocouple. The coal samples were inserted into the furnace at 100 °C, and heated to the specified temperatures at a rate of 7 °C/min. Transient swelling experiments were conducted up to 700 °C, while the volumetric swelling ratio (SR_V) was determined at the average maximum swelling temperatures (445°C for TWD, 422°C for GG, and 425 °C for TSH), as determined from the transient swelling experiments. A flow rate of 6 l/min (STP) nitrogen gas (African Oxygen Limited, UHP grade) was used.

4.3. Results and discussion

The swelling behaviour of the powdered coal (with and without K_2CO_3) is discussed in Section 4.3.1, followed by experimental results obtained for the large coal particles (raw and impregnated), in Section 4.3.2.

4.3.1 Influence of K_2CO_3 on swelling and plastic properties of powdered coal

The results for the FSI, Gieseler fluidity, dilatometry and Roga Index measurements of the raw coal and mixed coal samples containing 5 and 10 wt.% K_2CO_3, are presented in Table 4.4. Since TWD did not exhibit any significant swelling and fluidity for the FSI, dilatometry and Gieseler measurements, no data are presented for this coal.

Table 4.4: Effect of K_2CO_3 on the swelling of GG and TSH powdered coals

Characterisation analysis	**GG**			**TSH**		
	Raw	**5 wt.%***	**10 wt.%***	**Raw**	**5 wt.%***	**10 wt.%***
Free swelling index, FSI[a]	6.5	1.0	0	9.0	7.5	4.0
Gieseler fluidity (°C)[b]						
Initial softening temp.	400	422	-	420	436	452
Maximum fluid temp.	430	431	-	467	475	478
Solidification temp.	457	440	-	508	508	504
Maximum fluidity (DDPM)	50	2	-	1209	605	108
Dilatation (°C)[c]						
Softening temp.	371	415	-	386	389	-
Temp. of maximum contraction	418	500	-	425	500	-
Temp. of maximum dilatation	435	-	-	488	-	-
Maximum contraction (%)	33	10	-	24	16	-
Maximum dilatation (%)	14	-	-	103	-	-
Roga Index[d]	45	21	18	73	69	50

[a]- ISO 501:2003; [b]-SANS 6072:2009; [c]- SANS 6072:2009; [d]- SANS 881:2009; *-K_2CO_3; - not observed

It can be seen that the addition of K_2CO_3 significantly reduces the FSI of both coals, and similar findings were reported by other investigators.[9,12,13,18] It is observed that the different potassium carbonate loadings have a different effect on the swelling behaviour of GG and TSH. This was also observed by Tromp *et al.*[18] for the addition of potassium carbonate and by Crewe *et al*.[13] for various sodium compounds. No significant swelling was observed for the GG coal with 10 wt.% K_2CO_3, while the FSI of the TSH coal is reduced from 9.0 to 4.0 with the same amount of additive.

The results of the Gieseler fluidity measurements indicate that the addition of K_2CO_3 decreases the fluidity of GG and TSH. A 5 wt.% addition of K_2CO_3 to GG coal reduces the fluidity considerably, whereas no significant fluidity can be observed with the addition of 10 wt.% K_2CO_3. With a 5 wt.% addition of K_2CO_3, the initial softening temperature is increased, while the solidification temperature is decreased, indicating that the addition of potassium carbonate reduces the plastic range of the coal. Similar results were obtained by Fernández *et al*.,[24,25] for a high-volatile and low-volatile coal of similar rank to TSH,[31] and Clemens and Matheson,[26] for three New Zealand coals (no petrographic results reported), with the use of various additives. For the TSH coal it can be seen that an increase in K_2CO_3 loading also decreases the fluidity of the coal. In contrast to the GG sample, the TSH sample containing 10 wt.% K_2CO_3 still exhibits fluidity. This can be attributed to the higher maximum fluidity of the raw TSH sample (1209 ddpm) compared to the raw GG sample (50 ddpm). The plastic range of TSH is also reduced by the addition of K_2CO_3.

From the dilatation results it can be observed that the addition of K_2CO_3 increases the softening temperature of coals GG and TSH. It can also be seen that the addition of 5 wt.% K_2CO_3 to GG and TSH reduces the extent of dilatation, and only contraction is observed for these samples. This was also observed by Bexley *et al*.,[12] for 3% sodium carbonate addition to Manvers Wath coal, which is of similar rank to TWD and GG.[24] The results also show that the addition of 10 wt.% K_2CO_3 reduces dilatation characteristics of both coals. It has been reported that potassium carbonate reacts with the phenolate and carboxylate groups in the coal, to form corresponding alkali metal salts.[12,15,16] The corresponding alkali metal salts promote cross-linking which in turn reduces the mobility of the coal matrix and reduces swelling.[12,15,16,18]

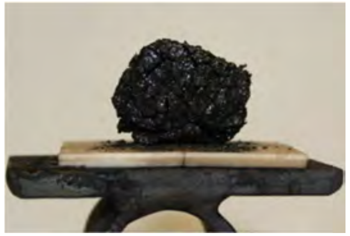
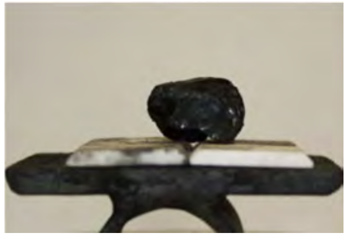
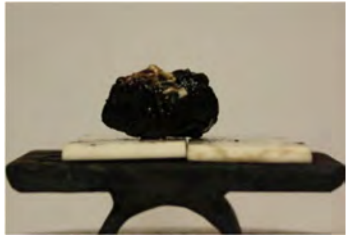
The Roga Index (R.I.) values indicate that the caking propensity of the GG and TSH coals decreases with an increase in K_2CO_3, whereas the raw and K_2CO_3-containing TWD samples had a Roga Index < 5. According to Speight[34] and Chang *et al.*,[35] the Roga Index can also be used to measure coke strength. Chang and co-workers[35] reported improvements in coke strength with the addition of different coal extracts, with an increase in Roga Index from 20 up to 38. Results in Table 4.4 indicate a decrease in GG and TSH coke strength with the addition of K_2CO_3. A 5wt.% K_2CO_3-addition does not change the caking characteristics of the two coals, with GG remaining a medium caking coal (R.I. 20-50) and TSH remaining a strongly caking coal (R.I. >50).[34] With the addition of 10wt.% K_2CO_3, GG becomes a weakly caking coal (R.I. 5-20) while TSH becomes a medium caking coal (R.I. 20-50).[34]

4.3.2 Influence of K_2CO_3 on swelling of large coal particles

Visual observations

Table 4.5 shows photos of the raw and impregnated 20 mm coal particles before and after devolatilisation.

Table 4.5: Comparison between raw and impregnated coal particles before and after devolatilisation

	Raw before devolatilisation	Raw after devolatilisation	Impregnated before devolatilisation	Impregnated after devolatilisation
TWD				
GG				
TSH				

The images show that the addition of K_2CO_3 decreases the swelling of the GG and TSH large coal particles. Similar results were also observed for the 5 and 10 mm particles. The images of the impregnated particles before devolatilisation show a white residue on the surface of the particles, which is caused by the K_2CO_3 adhering to the surface, and is a result of the samples being dried in the oven after impregnation. The white residue is still visible on some of the impregnated coal particles after devolatilisation.

Influence of K_2CO_3 on the swelling of large coal particles

The volumetric swelling ratios (SR_V) obtained from mercury submersion[28] for raw and impregnated coal samples, are presented in Table 4.6.

Table 4.6: SR_V ratios of raw and K_2CO_3-impregnated coal samples

Coal samples	Raw coal		K_2CO_3-impregnated coal		Reduction in swelling
	SR_V	Variation	SR_V	Variation	
TWD					
5 mm	1.2	0.4	1.1	0.4	not significant
10 mm	1.2	0.0	1.3	0.1	not significant
20 mm	1.6	0.8	1.7	0.3	not significant
GG					
5 mm	2.0	0.4	1.5	0.4	moderate
10 mm	3.5	0.4	2.2	0.0	significant
20 mm	3.0	0.9	1.8	0.3	significant
TSH					
5 mm	3.6	1.0	3.2	0.1	moderate
10 mm	4.6	1.7	2.4	0.1	significant
20 mm	3.1	1.8	2.1	0.5	significant

moderate – less than 30% reduction in swelling
significant – more than 30% reduction in swelling

The results show that the swelling of the GG and TSH large coal particles is reduced due to impregnation with K_2CO_3. It can be seen that the reduction in swelling for TSH decreases with increasing particle size, and relative smaller amounts of K_2CO_3 were impregnated (Table 4.3). The K-loading was not constant and generally decreased with an increase in particle size, and the reduction of the degree of swelling followed the same trend. It was also observed that TWD coal particles did exhibit swelling even with a reported FSI of 0, as was also found by Coetzee *et al.*[31] Lower SR_V values are reported by Coetzee *et al.*[31] for raw GG and TSH 20 mm particles, since the softening temperatures from Gieseler results were initially used, which is lower than the average T_{max} used for experiments in Table 4.6. Results also indicate that the K_2CO_3 does not reduce the degree of swelling of the TWD coal significantly, as was observed for GG and TSH. In order to rule out any influence of oxidation during impregnation, additional TSH samples were impregnated with deionised water (following the same impregnation procedure as given in Section 4.2.4). It was determined that the SR_V of 20 mm water-impregnated TSH particles were 3.2 ± 1.3, which does not differ significantly from the SR_V obtained for the raw particles. Therefore it can be concluded that any oxidation which may occur during impregnation does not influence the degree of swelling of large particles. Oxidation was not expected under the low-temperature impregnation conditions; Havens *et al.*[37] investigated low-temperature oxidation at 140 °C and only detected oxidation after 16 days using magic-angle ^{13}C n.m.r. spectroscopy. From the results presented in Table 4.6 it can also be proposed that the K_2CO_3 only influences the volumetric transformation of coals such as GG and TSH which exhibit significant softening and swelling (plastic deformation), as seen from the FSI and Gieseler fluidity results in Table 4.4.[31]

Image analysis was used to obtain a swelling ratio (SR_A), as defined by Coetzee *et al.*,[31] to study the transient swelling and shrinkage behaviour of the coal particles during devolatilisation. ImageJ 1.46r[36] was used for image analysis, and the coal particle was manually selected to exclude the background and sample holder as previously illustrated by Coetzee *et al.*[31] Experiments were conducted up to 700 °C with raw and impregnated coal particles for the 20 mm particle size. Figure 4.2 represents the average transient swelling and shrinkage behaviour (reported as SR_A, and based on area) of 20 mm particles of each coal, up to 600 °C. It was previously found[31] that individual TSH coal particles reach a maximum swelling ratio between 400 and 440 °C, after which the particles become completely fluid and deformed. Therefore, Figure 4.2 only shows the observed average transient swelling behaviour for TSH up to maximum swelling. The temperature at which maximum swelling is obtained may deviate from 435 °C for individual particles.

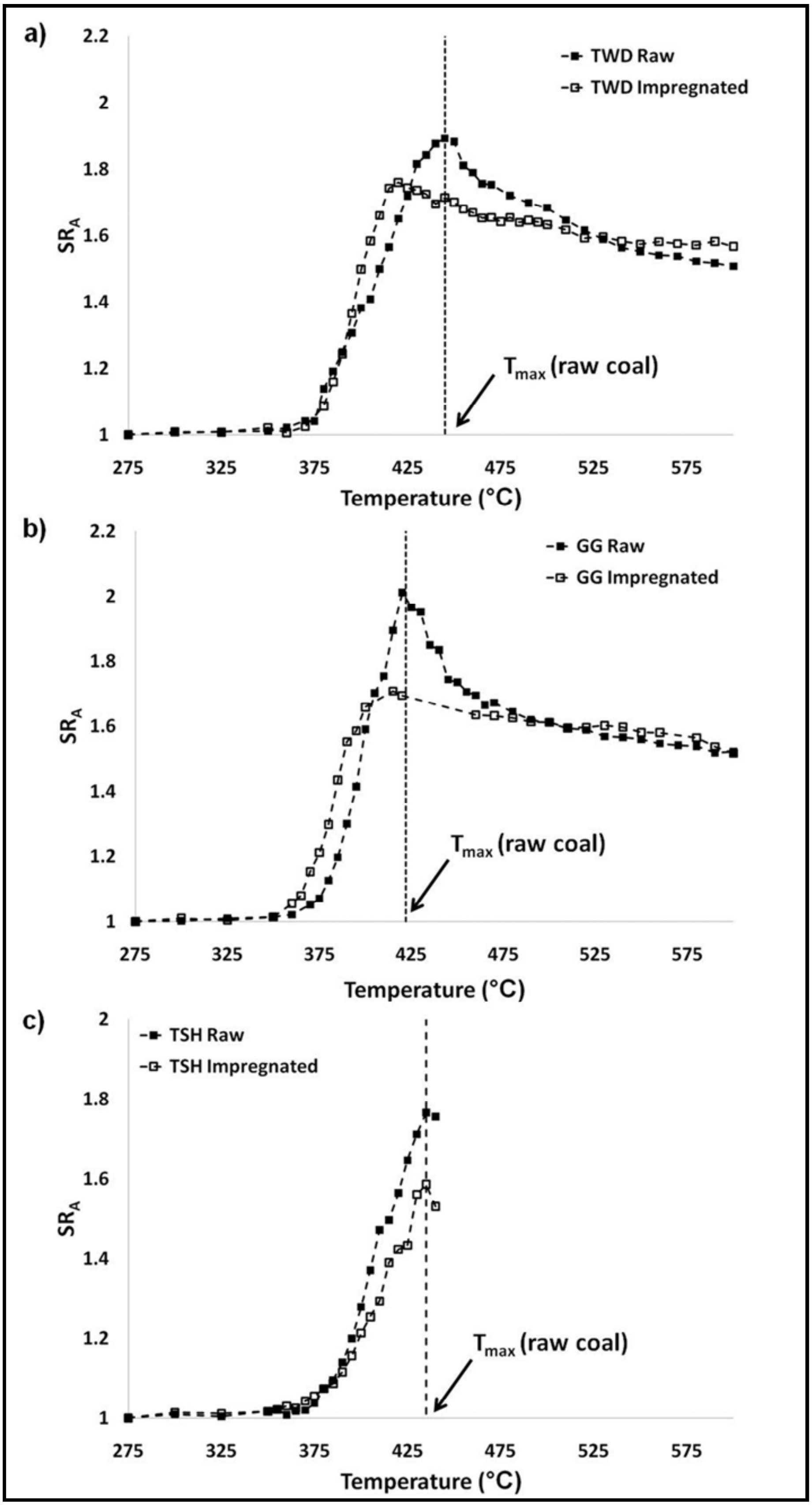


Figure 4.2: Average transient swelling and shrinkage behaviour of 20 mm particles for a) TWD, b) GG, c) TSH

Evident from Figure 4.2 is that the impregnated coal particles on average have lower SR_A values throughout, compared to the raw particles. The reduction in swelling due to the addition of K_2CO_3 is more pronounced for the GG and TSH samples, which was also observed from the mercury submersion data in Table 4.6. The impregnated TWD particles appear to swell slightly less than the raw TWD particles, which is in contrast to the results presented in Table 4.6. However, the SR_V values are volume-based, and are therefore more accurate than the semi-quantitative SR_A, which is based on a 2D projection. For both the TWD and GG coals, the final SR_A after shrinkage is similar for the raw and impregnated particles. The T_{max} for the impregnated TWD and GG particles is between 10 and 20 °C lower than for the raw coal particles. For the TSH coal, the observed T_{max} was not influenced by impregnation with K_2CO_3. Table 4.7 includes the average experimental variation of SR_A at T_{max}, for each coal sample, as determined using an 80% confidence interval.

Table 4.7. Comparison of FSI and k_A (raw and impregnated)

Coal samples	T_{max} (°C)	$SR_{A,max}$	Variation
TWD Raw	445	1.9	0.3
TWD Impregnated	420	1.8	0.7
GG Raw	420	2.0	0.4
GG Impregnated	415	1.7	0.6
TSH Raw	435	1.8	0.6
TSH Impregnated	435	1.6	0.2

The transient swelling and shrinkage behaviour of the coals was further compared by defining an average swelling and shrinkage coefficient, k_A (based on area), for the raw and impregnated coals. The equation used by Fu *et al.*[7] for volumetric swelling of coal blocks was adapted in order to incorporate the relative area (used to obtain the average SR_A presented in Figure 4.2) obtained from image analysis:

$$k_A = \frac{1}{A_0}\frac{dA_T}{dT} = \frac{dSR_A}{dT} \qquad \text{Eq. (4.1)}$$

where A_T is the relative area at a specific temperature, A_0 the initial relative area as also used in Coetzee *et al.*[31] The curves for k_A (raw and impregnated) are shown in Figure 4.3, from the average temperature of initial swelling up to 600 °C for TWD and GG, and to 440 °C for TSH.

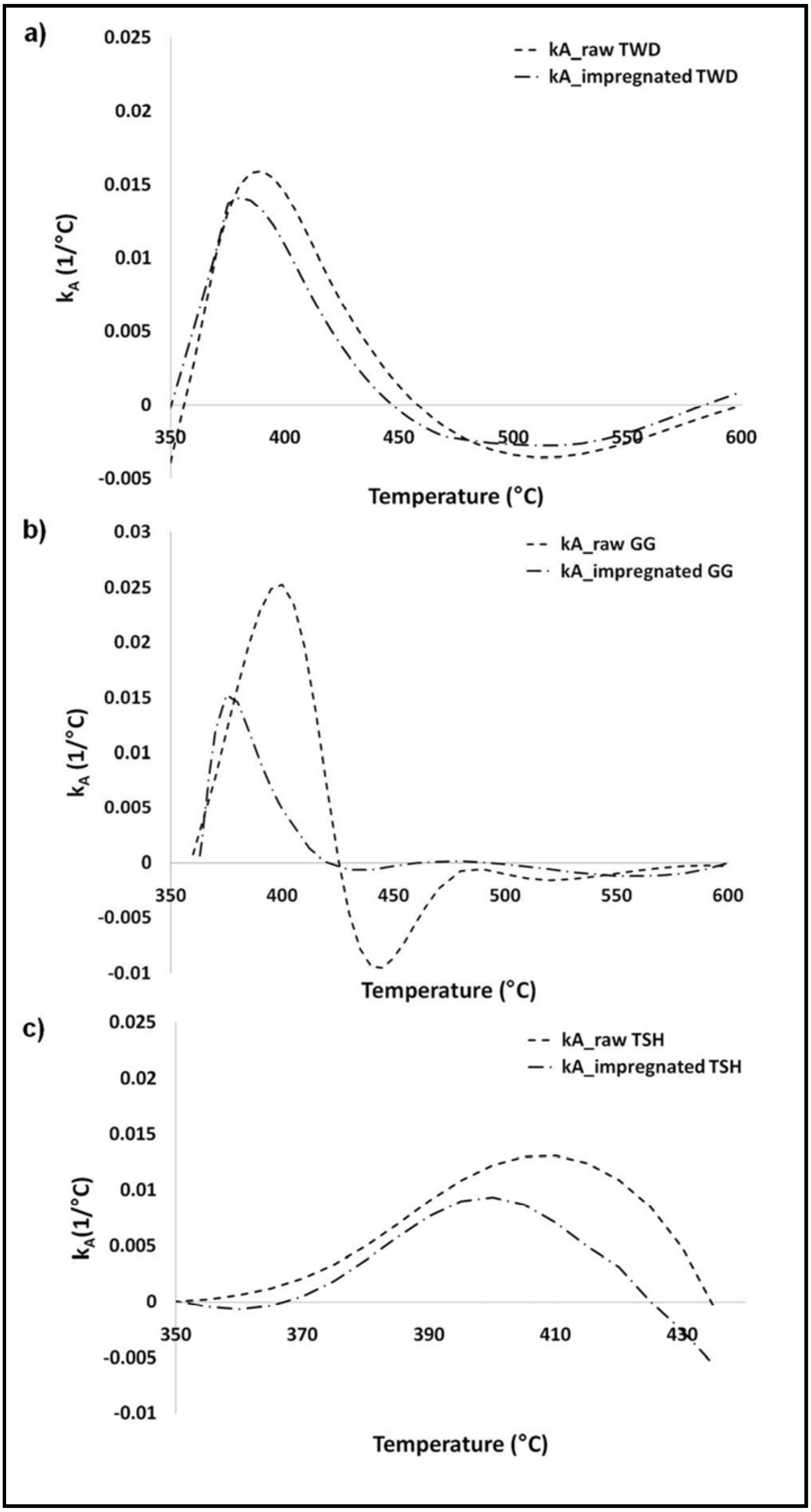


Figure 4.3: Swelling and shrinkage coefficient curves for a) TWD, b) GG and c) TSH

From Figure 4.3, swelling peaks are observed for all the coals, with visible shrinkage peaks shown for the TWD and GG coals. For the TWD raw particles, a maximum k_A is observed at 390 °C, followed by a minimum at 520 °C. For the TWD impregnated particles, a maximum k_A is observed at around 380 °C, with a minimum at 520 °C. The maximum k_A for the GG raw particles is evident at 400 °C, while the impregnated particles have a maximum at 375 °C. Minimum k_A values for the raw and impregnated particles (GG) are observed at around 440 °C and 430 °C, respectively. For the swelling peaks (maximum values), k_A is reduced from 0.025 to 0.015 $°C^{-1}$ for GG, and from 0.013 to 0.009 $°C^{-1}$ for TSH. No significant reduction is perceived for the TWD coal. It is also observed that the maximum k_A value for swelling increases with an increase in SR_V (Table 4.6), and does not correlates with the FSI values of the raw coal (Table 4.4), as shown in Table 4.8.

Table 4.8: Comparison of FSI and k_A (raw and impregnated)

Coal samples	FSI	k_A (raw) ($°C^{-1}$)	k_A (Impregnated) ($°C^{-1}$)
TWD	0	0.015 ± 0.007	0.014 ± 0.003
GG	6	0.025 ± 0.006	0.015 ± 0.002
TSH	9	0.013 ± 0.004	0.009 ± 0.001

The following relationship between k_A (based on area) and k_V (based on volume) was used to compare the swelling and shrinkage coefficient values of this study with the values obtained by Fu *et al.*:[7]

$$k_V = \frac{3}{2} k_A \qquad \text{Eq. (4.2)}$$

Using equation (4.2), the k_V values for the raw coal particles corresponding to the k_A values presented in Figure 4.3 result in maximum swelling coefficients ranging between 0.020 and 0.038 $°C^{-1}$, and maximum shrinkage coefficient ranging between -0.008 and -0.014 $°C^{-1}$. These values are larger than the maximum swelling (0.005-0.018 $°C^{-1}$) and shrinkage (-0.005 $°C^{-1}$) coefficient values obtained by Fu *et al.*[7] This may be attributed to the difference in nature of the Chinese coals used by Fu and co-workers,[7] but are difficult to compare, since no detailed coal characteristics were given.

4.4. Conclusions

From the experimental results it can be concluded that the addition of K_2CO_3 significantly reduces the swelling and fluidity of not only pulevrised coal, but also large coal particles. Results showed that large coal particle impregnation with a 5.0 M K_2CO_3 solution increased the potassium content (coal basis) by factors of between 9 and 33, while the K-loading decreased with increasing particle size. From the SR_V results it was found that the addition of K_2CO_3 through solution impregnation significantly reduces the extent of swelling of GG and TSH coal particles, by between 25 and 75%. It was also observed that the reduction of swelling increased with particle size. Results showed that the TWD coal particles exhibited SR_V values of up to 1.7, even with an FSI of 0, and that the addition of K_2CO_3 did not influence the swelling behaviour. Therefore, it was proposed that K_2CO_3 only influences the volumetric transformation of coals which undergo significant plastic deformation, as observed for GG (medium-swelling coal) and TSH (high-swelling coal). Comparison of the swelling coefficients showed that impregnation with K_2CO_3 reduces k_A from 0.025 to 0.015 $^oC^{-1}$ for GG, and from 0.013 to 0.009 $^oC^{-1}$ for TSH. It was also concluded that K_2CO_3 impregnation reduced the degree of shrinkage of the more fluid GG coal, while no significant influence was observed for the TWD coal. Overall, it can be concluded that K_2CO_3 impregnation might be a feasible method for reducing large coal particle swelling, and together with further development, may be applied for reducing unwanted swelling in large-scale coal utilisation processes. Further investigation, including a detailed techno-economical study and pilot-scale experiments, is recommended in order to determine the economical feasibility and industrial practicality of using an additive such as K_2CO_3 in industrial coal operations.

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Nomenclature

Notations/Symbols

A_T	Relative area (a.u.)
A_0	Initial relative area (a.u.)
k_A	swelling coefficient based on area (°C^{-1})
k_V	swelling coefficient based on volume (°C^{-1})
SR_V	Swelling ratio (based on volume) (-)
SR_A	Swelling ratio from image analysis (based on area) (-)
T_{max}	Temperature at which maximum swelling is obtained (°C)

Abbreviations

a.d.b.	Air dried basis
ddpm	Dial divisions per minute

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Chapter 5

Reduction of caking propensity in large (mm sized) South African coal particles with potassium carbonate impregnation to expand fixed and fluidised bed gasification feedstock suitability

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The influence of K_2CO_3-impregnation on the caking propensity of large South African coal particles (5, 10, and 20 mm) during devolatilisation up to 700 °C, is evaluated in this Chapter. Results show that the addition of K_2CO_3 is an effective method to reduce, and in some cases eliminate, the caking tendency of a coal which exhibits moderate fluidity during heating.

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Abstract

The caking propensity of coal causes challenges in combustion, gasification and fluidised-bed applications where this property limits coal selection. Certain gasifiers are fitted with mitigation technologies such as stirrers to overcome operational problems associated with caking. However, additive addition is a possible alternative method with benefits such as reduction of caking and swelling and increased reaction rates. It is known that select additives alter the coal's thermoplastic behaviour, where studies have predominantly focused on powdered coal. Here, large coal particles (5, 10, and 20 mm) suitable for select fluidised-bed and gasification applications, from three South African coal fields were examined. The coals have different thermal swelling characteristics: TWD (FSI 0), GG (FSI 5.5-6.5), and TSH (FSI 9). Digital photography, SEM, and X-ray computed tomography were used to evaluate the caking propensity during devolatilisation, and its reduction with K_2CO_3 addition. Particles were impregnated with an excess 5.0 M K_2CO_3 solution, and devolatilised in batch samples to 700 °C. The K_2CO_3-impregnation resulted in brittle and fragmented TWD char, while it decreased the caking tendency of GG coke particles, and decreased the apparent surface fluidity of the TSH coke. Impregnation before devolatilisation decreased the fluid-like appearance of the GG coke, and decreased the amount and size of the blow-holes of the TSH coke. The pore structure of the devolatilised GG particles were mostly influenced by impregnation, showing little to no signs of fusion/caking with smaller internal voids in comparison to the raw sample. The TWD char was classified as group III char, while GG and TSH were classified as group II and I coke, respectively. Bridging neck size measurements quantitatively indicated that K_2CO_3-impregnation reduced the bridging neck size of GG coal by up to 50%. The K_2CO_3 can be used to alter the caking propensity of a moderately fluid coal such as GG, and make it suitable for use in fixed- and fluidised-bed gasifiers. Using an additive such as K_2CO_3 has utility in expanding gasification feedstock suitability, but reactivity and ash behaviour should further be investigated to progress this approach.

Keywords: Caking, large coal particles, low-temperature devolatilisation, char classification, image analysis, fluidity.

5.1. Background and Introduction

The caking or agglomeration of coal is generally defined as the fusion of materials to form agglomerates or cakes,[1] and is described as the softening of coal during heating, which causes the particles to form a coalesced solid.[2-5] The term “softening” is often replaced by terms such as “agglomeration” and “caking”, while coals which generally exhibit little or no fluidity are deemed as “non-plastic” or “non-caking” and “non-agglomerating” coals.[2] The degree of fluidity influences thermal coal swelling, as well as the tendency of coal particles to coalesce and form agglomerates during devolatilisation.[4]

The occurrence of coal caking during heating is complex, and prediction and potentially manipulation of caking propensity is required for safe operation.[6] Coal caking or agglomeration has been recognised as a serious technical complication during the development of industrial devolatilisation processes,[2,5,7-9] and can cause operational problems in processes where fixed-bed or fluidised-bed gasification units are used. During heating, coals may become viscous and plastic, forming agglomerates which can adhere to the gasifier or coking oven walls, and/or reduce gas permeability through the coal bed resulting in channelling.[5,9] The use of additives such as alkali and alkaline earth metals has been identified as an effective method to manipulate the caking behaviour of various coals.[10] Various investigators have reported a reduction in caking propensity of powdered coals (<212 µm), using a variety of additives.[8,10-12] However, examining larger particles (>1 mm) suitable for fluidised-bed and fixed-bed operations will benefit large scale operations. In South Africa, the coal typically used for gasification operations is sourced from the Highveld coalfield. However, the coal resources in this coalfield are expected to be depleted by 2050.[13,14] Therefore, the use of alternative coal feedstocks is being investigated. The Waterberg coalfield is still relatively unexplored, and contains vast amounts of coal which can possibly be used for gasification purposes.[14,15] However, certain coals from this region have characteristic caking tendencies which make them less suitable for use in fixed- and fluidised-bed gasifiers. The research in this paper explores the use of additive addition as a possible method to manipulate the caking propensity of a coal, and make it suitable for use in specific coal utilisation operations. The manipulation of caking properties of larger particles will also be beneficial to the coal selection process, particularly in those locations where coals are in close proximity to combustion and gasification sites.

An important characteristic of the formed agglomerates is the char structure, which strongly depends on the temperature, heating rate and pressure.[2,16,17] The type of char structure depends on the maceral constituents in the parent coal, and results in the formation of a complex, heterogeneous structure.[16,17] Quantifying the influence of an additive such as potassium carbonate on the caking propensity and resulting char structure will aid in the potential manipulation of caking behaviour. While most work has investigated the caking behaviour of small particles or powders, here larger particles with a slower heating rate are considered. The pore structure of the char or coke influences internal mass and heat transfer,[19] and also has a significant impact on char combustion, gasification kinetics, and ash formation.[16,20] Bailey[21] and Lightman[22] proposed a three-group char classification system based on geometric parameters and porosity determined from image analysis. In Table 5.1, the char classification system proposed for a high-volatile bituminous C coal, devolatilised at 1 atm and temperatures between 900 and 1500 °C, is illustrated.

Table 5.1: Three-group char classification system (Adapted from Yu *et al.*[16]and Benfell *et al.*[23])

	Group I	**Group II**	**Group III**
			
Char subtypes[a]	Tenuispheres, tenuinetwork	Crassispheres, crassinetwork, mesospheres, mixed porous (mixed dense)	Inertoid, solid, fusinoid (mixed dense)
Dominant maceral component	Vitrinite	Vitrinite and Inertinite	Inertinite
Pore shape	Spheroidal	Spheroidal to irregular	Spheroidal, rectangular or irregular
Porosity (%)	>70	40-70	<40
Wall thickness (µm)	<5	>5	>5
Shape	Spherical-subspherical	Subspherical	Rectangular to irregular
Typical swelling ratio	>1.3	<1.0	<0.9
Typical residual mass ratio	0.1~0.5	0.1~0.5	1.0

[a] – 'tenui' refers to walls of carbon <5 µm thick, 'crassi' refers to walls >5 µm thick.

The parameters of the classification system include sphericity, porosity, and wall thickness, which can be determined using image analysis.[16] The char classification system has previously demonstrated its viability in evaluating char characteristics[19,21] and has been applied by various researchers[18,23-25] for classifying chars derived from coal particles in the range of 63 to 90 µm (between 230 and 170 mesh).

Klose and Lent[6] examined agglomeration, specifically the agglomeration kinetics of softened coal using the principle of bonding neck growth. A similar approach to bonding neck growth, defined as bridging neck size, will be applied in this investigation. The theory of bonding neck growth has also previously been applied to describe the sintering mechanisms of ceramics and base metal conductors.[26] It was found that bonding neck growth can be used to describe coal agglomeration, and it was also concluded that the following factors influenced the growth of the bonding neck between particles:[6] volume change (swelling), particle size, viscosity, and surface tension.

Recently, devolatilisation of lump coal has received increasing attention,[27-29] while research investigating the use of additives to manipulate the caking of coal has mainly focused on pulverised coal samples.[8,10-12] Therefore, the need exists to investigate the caking behaviour of large coal particles and the influence of additive addition on the caking propensity of such large particles. The aim of this paper is to investigate the influence of potassium carbonate (K_2CO_3) on the reduction of caking propensity of large coal particles (5, 10, and 20 mm) derived from three South African coals (TWD, GG, and TSH) with varying swelling and caking characteristics. Results are expected to indicate the viability of using additive addition as a method of reducing the caking propensity of certain coals to make them more suitable for use in fixed- and fluidised-bed gasifiers. The various batch chars/cokes formed during devolatilisation (up to 700 °C, 7 °C/min heating rate, nitrogen atmosphere) are also investigated using digital photography, scanning electron microscopy (SEM) and X-ray computed tomography (CT).

5.2. Experimental

5.2.1 Coal

Coals obtained from three different South African coalfields were selected based on differences in FSI: washed TWD coal (FSI 0) from the Highveld region, washed GG coal (FSI 5.5-6.5) from the Waterberg region, and TSH coal (FSI 9) from the Limpopo province. The TSH coal was density-separated (Bureau Veritas Testing and Inspections South Africa) to a particle density <1500 kg/m^3 (as-received cleaned coal). Three different size fractions were used for screening of the coal particles, 6 to 4.75 mm, 11.2 to 10 mm, and 20 to 16 mm, and will be referred to as 5, 10, and 20 mm particles, respectively. Additionally, the 20 mm particles used for experimentation were hand-selected to ensure near-spherical particles, for the X-ray CT observations performed. Coal characterisation was conducted by

Bureau Veritas Testing and Inspections South Africa, while the petrographic analysis was conducted by Petrographics SA.

5.2.2 Potassium carbonate impregnation

The coal samples were dried overnight at 105 °C, prior to being submerged in an excess 5.0 M K_2CO_3 solution for 24 hours, at ambient temperature. The potassium carbonate (K_2CO_3) used for large coal particle impregnation, was supplied by Merck (Pty) Ltd (purity >99.5%). Impregnation was conducted in sealed containers, to prevent evaporation. The coal samples were removed and dried (105 °C) overnight. X-ray fluorescence (XRF) analysis (UIS Analytical services) indicated that K_2CO_3-impregnation increases the K-loading by factors up to 33 for 5 mm particles, 30 for 10 mm particles, and 14 for 20 mm particles. It was found that the K-loading decreased with increasing particle size, while the calculated average surface loading (mg/cm^2) increased with increasing particle size. The K-loading obtained through solution impregnation did not depend on the coal types used in this investigation.

5.2.3 Thermal caking/agglomerating behaviour

Low-temperature devolatilisation experiments were conducted to evaluate the effect of K_2CO_3 on the caking propensity of the large coal particles. The extent of caking of the coals was evaluated using a coal ash fusibility (CAF Digital/APC) furnace, supplied by Carbolite.[30] Batch coal samples were used for devolatilisation experiments, and the sample mass varied between 10 to 30 g, depending on the fluidity of the specific coal during heating. Coal samples (raw and impregnated) were placed in a ceramic sample holder and inserted into the furnace, approximately 1 cm from a thermocouple. These were inserted into the furnace at 100 °C, and heated to 700 °C. A devolatilisation temperature of 700 °C was selected to study caking, since the plastic behaviour of these coals occur in the range of 350 to 500 °C, as reported by Coetzee *et al.*[30] The selected temperature of 700 °C is high enough to cause caking, and is within the range of fluidised bed operations. A heating rate of 7 °C/min was used, with a 6 l/min (STP) nitrogen gas flow rate (African Oxygen Limited, UHP grade) was used. During devolatilisation, TWD behaved as a char, while GG and TSH behaved as cokes, and the samples will be referred to accordingly throughout the paper.

Visual observations

Digital photographs were taken (with a Canon 1000D digital camera), before and after devolatilisation, to examine the coal's caking tendency. The outer surface of the devolatilised material from raw and impregnated coal was investigated using scanning electron microscopy (SEM). The SEM micrographs were acquired using an FEI QUANTA 250 FEG ESEM analyser integrated with an OXFORD X-MAX 20 EDS system.

X-ray computed tomography (CT) was used to study the internal structure of the devolatilised material. X-ray CT scans were obtained at the MIXRAD facility at the South African Nuclear Energy Corporation (Necsa), using a Nikon XTH 225 ST micro-focus X-ray tomography system. Further details are given elsewhere.[30] The scanning parameters which were used for each scan were 100 kV tube voltage and 100 µA tube current. X-ray CT scanning was conducted on devolatilised material from 5 and 20 mm particles, while raw and impregnated 10 mm particles of each coal were scanned before and after devolatilisation to evaluate the change in pore structure during devolatilisation.

Wall Thickness

ImageJ 1.46r[31] was used to quantify the wall thickness and porosity using X-ray CT slices of the 10 mm char/coke, to classify char/coke types. An average wall thickness was obtained from a total of 100 measurements, where 50 measurements were conducted on the horizontal, middle cross-sectional slice and 50 on the vertical, middle cross-sectional slice, from the same 3-dimensional tomogram.

Porosity

The same slices used for wall thickness measurements were used for the porosity determination, and a method similar to that of Yu *et al*.[18] was applied, as illustrated in Figure 5.1. Single char/coke particles (in grayscale) were isolated from the whole X-ray CT slice (Figure 5.1a), while agglomerates which form one particle were used as is, to determine an average porosity.

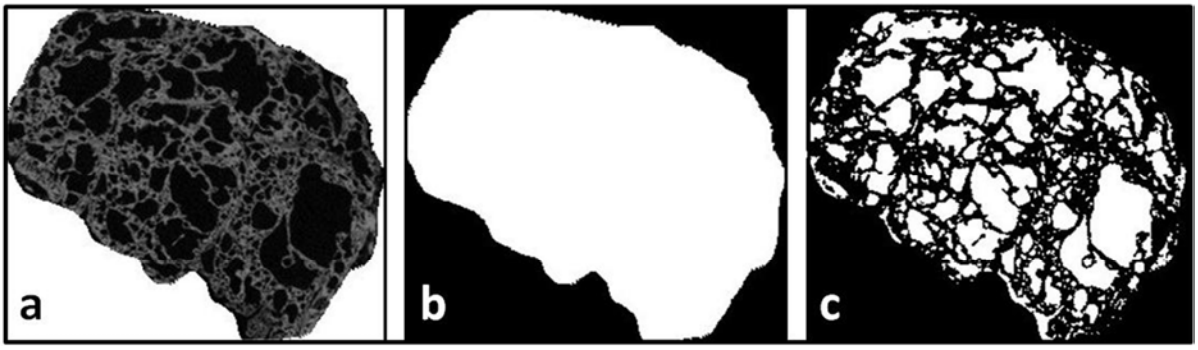


Figure 5.1: Image analysis for porosity measurements using ImageJ: (a) grayscale char particle separated from the entire X-ray CT slice, (b) Black/white threshold set to include entire area of particle, (c) Black/white threshold set to include the total area of the voids.

The threshold of the image is adjusted (using black/white colour) to include the total area of the entire particle/agglomerate (white in Figure 5.1b). The porosity is determined by dividing the area fraction of the voids, a_V (white voids in Figure 5.1c), by the area fraction of the entire particle, a_P (white area in Figure 5.1b):

$$Porosity\ (\%) = \frac{a_V}{a_P} \times 100 \qquad \text{Eq. (5.1)}$$

Bridging neck size

The bridging neck size, similar to the approach of bonding neck growth used by Klose and Lent,[6] was applied to X-ray CT slices to quantify the extent of caking of the GG particles. For the purpose of this study, the bridging neck size is defined as the cross-section length of the bond between two particles, as illustrated in Figure 5.2.

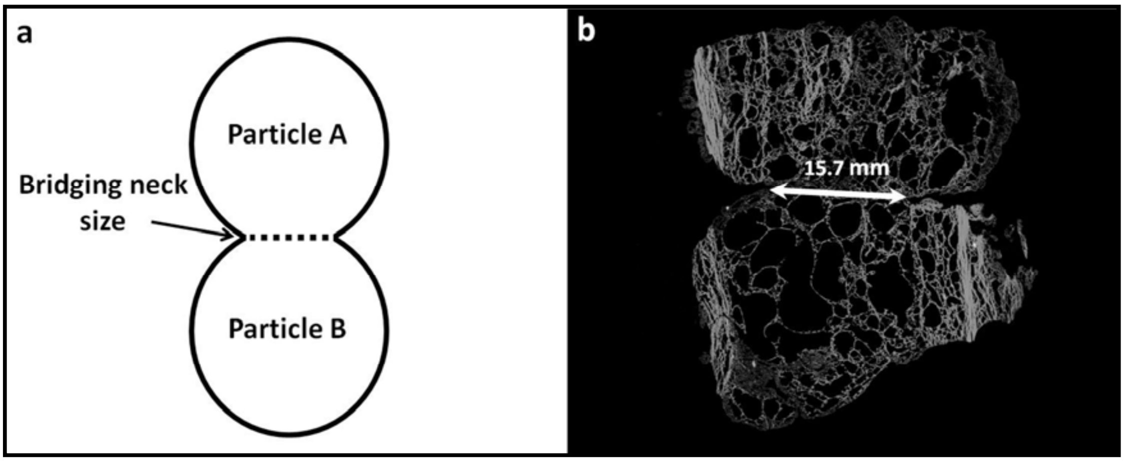


Figure 5.2: Bridging neck size a) schematic, b) X-ray CT slice view of the interior of GG 20 mm raw char sample after devolatilisation

An average of 30 measurements was performed for the GG coke from the 5 and 10 mm raw particles, and 10 for the coke from 20 mm raw particles. An average of 10 measurements was taken for the coke samples from impregnated coal, for all particle sizes.

5.3. Results and discussion

5.3.1 Coal characterisation

The coal properties are presented in Table 5.2.

Table 5.2: Properties and rank of three South African coals

Analysis	**Standards**			
TWD coal		**5 mm**	**10 mm**	**20 mm**[24]
Proximate analysis (wt.%, a.d.b.)				
Inherent moisture	SANS 5925:2007	5.2	5.0	4.8
Ash yield	ISO 1171:2010	13.9	14.1	14.2
Volatile Matter	ISO 562:2010	28.1	28.4	29.7
Fixed Carbon	By difference	52.8	52.5	51.3
Free Swelling Index (FSI)	ISO 501:2003	not observed	not observed	not observed
Petrographic analysis (vol.%, mmfb)	ISO 7404-3:1994			
Vitrinite		52	46	59
Liptinite		4	3	4
Inertinite		44	51	37
Mean vitrinite random reflectance (Rr)	ISO 7404-5:1994	0.64	0.63	0.63
GG coal		**5 mm**	**10 mm**	**20 mm**[24]
Proximate analysis (wt.%, a.d.b.)				
Inherent moisture	SANS 5925:2007	2.7	2.5	2.5
Ash yield	ISO 1171:2010	9.2	13.0	13.9
Volatile Matter	ISO 562:2010	36.7	36.6	36.9
Fixed Carbon	By difference	51.4	47.9	46.7
Free Swelling Index (FSI)	ISO 501:2003	6.5	5.5	6.5
Petrographic analysis (vol.%, mmfb)	ISO 7404-3:1994			
Vitrinite		87	86	86
Liptinite		5	6	6
Inertinite		8	8	8
Mean vitrinite random reflectance (Rr)	ISO 7404-5:1994	0.70	0.69	0.68
TSH coal		**5 mm**	**10 mm**	**20 mm**[24]
Proximate analysis (wt.%, a.d.b.)				
Inherent moisture	SANS 5925:2007	0.5	0.6	0.6
Ash yield	ISO 1171:2010	15.7	17.3	18.2
Volatile Matter	ISO 562:2010	21.5	20.4	19.7
Fixed Carbon	By difference	62.3	61.7	61.5
Free Swelling Index (FSI)	ISO 501:2003	9.0	9.0	9.0
Petrographic analysis (vol.%, mmfb)	ISO 7404-3:1994			
Vitrinite		84	84	82
Liptinite		0	0	0
Inertinite		16	16	18
Mean vitrinite random reflectance (Rr)	ISO 7404-5:1994	1.33	1.34	1.35

***a.d.b.* – air dried basis; mmfb – mineral matter free basis**

As is evident from Table 5.2, the proximate analysis values do not vary significantly with particle size, with only a minor increase in ash yield with increasing particle diameter. The three coals have different swelling characteristics, as indicated by the FSI, which also remain relatively unchanged with particle size variation. Coals TWD and GG were classified as medium-rank C coals, while TSH was found to be a medium-rank B coal.

5.3.2 Caking propensity and physical appearance of chars

The caking propensity of the three different coals was established by inspecting coal samples (raw and impregnated) before and after devolatilisation. Figure 5.3-5.5 show digital images of 10 mm particles of TWD, GG, and TSH coals (raw and impregnated), before and after devolatilisation; the same observations were made for the 5 and 20 mm particles (appendix A.1). Before devolatilisation, individual particles (top left) are loaded as a batch into the sample holder (bottom left). After devolatilisation, the devolatilised material is allowed to cool in the sample holder (bottom right), after which the sample holder was emptied to evaluate the content (top right).

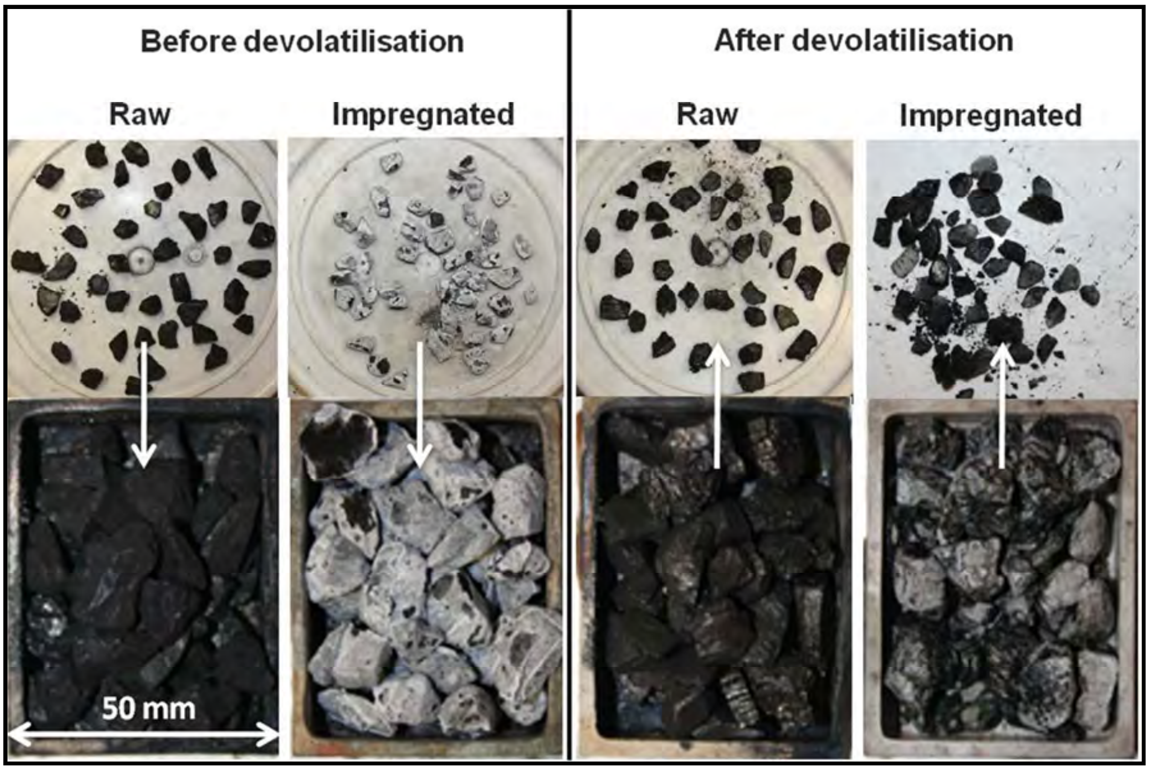


Figure 5.3: Raw and K_2CO_3-impregnated TWD coals and char, upper images show the individual particles before and after devolatilisation, the lower images show the same particles in the sample holder

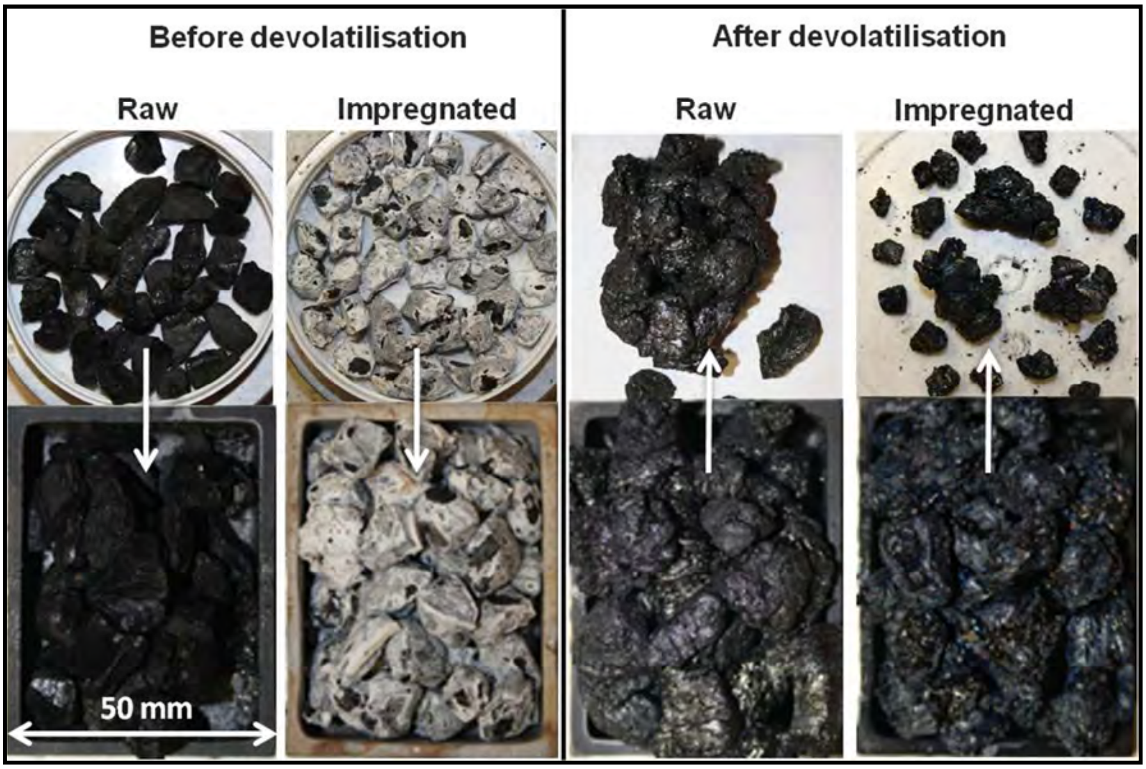


Figure 5.4: Raw and K_2CO_3-impregnated GG coals and char, upper images show the individual particles before and after devolatilisation, the lower images show the same particles in the sample holder

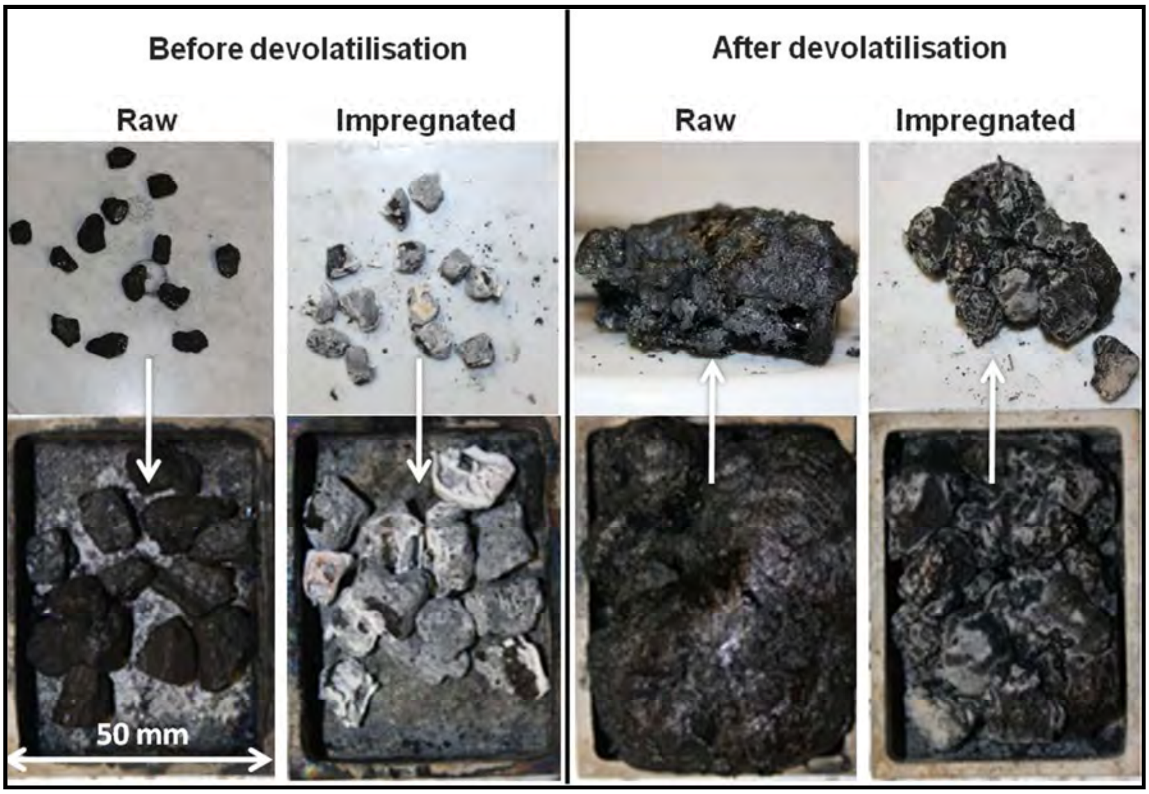


Figure 5.5: Raw and K_2CO_3-impregnated TSH coals and char, upper images show the individual particles before and after devolatilisation, the lower images show the same particles in the sample holder

Evident from Figure 5.3 is that the raw TWD coal does not cake during devolatilisation, even though swelling was reported for this coal (-20+16 mm particle size) by Coetzee *et al.*[30] It can also be seen that impregnation results in apparent brittleness of the char, where part of the 10 mm char particles fragmented (Figure 5.3). Figure 5.4 shows significant caking of the raw 10 mm GG particles, where the majority of the particles adhered together to form a solid mass. A reduction in caking propensity of the GG coal is observed as a result of impregnation with a K_2CO_3-solution. The appearance of the impregnated GG coke surface is also not as smooth when compared to the raw coke, which indicates that the additive reduced the fluidity of the coal during devolatilisation, and resulted in a decrease in caking tendency. It was also visually observed that K_2CO_3-impregnation resulted in a decrease in particle swelling. The TSH raw coke shows severe signs of caking (Figure 5.5); with no individual particles identifiable as is seen for the GG raw coke. This can be attributed to the high fluidity of the TSH coal (Table 5.2). In contrast with the TSH raw coke, the individual particles can be identified in the TSH impregnated agglomerate. The results indicate that the K_2CO_3-impregnation was most effective in reducing the caking tendency of GG coal. Standard caking tests (Roga Index, SANS 881:2009) were also conducted on raw powdered coal sample, and samples containing 10 wt.% K_2CO_3. The addition of K_2CO_3 reduced the Roga Index of GG and TSH from 45 to 18 and from 73 to 50, respectively. The K_2CO_3 did not influence the noncaking properties of TWD, and the Roga Index remained < 5 irrespective of additive addition.

Table 5.3 gives a detailed description of the characteristics of the devolatilised material of the 10 mm particles of each coal (which were also observed for the 5 and 20 mm particle sizes), after the samples have been carefully removed from the sample holder; to minimise particle segregation from the mass.

Table 5.3: Char/coke characteristics of 10 mm particles after devolatilisation at 700 °C

	Raw samples, following devolatilisation	**Impregnated samples, following devolatilisation**
TWD	• Crack formation visible on particle surface • Shiny sections visible (indicating fluidity) • Mostly strong, solid structure with occasional brittleness 	• Crack formation visible on particle surface • Severe fragmentation • Particles show signs of brittleness 
GG	• Molten, shiny exterior • Fusion of particles clearly visible • Extremely hard char • Strong particle fusion 	• Ragged, uneven appearance • Additive visible on surface • Caking is significantly reduced (5 mm) and/or eliminated (10, 20 mm) • Brittleness of char observed sporadically 
TSH	• Molten, shiny exterior • Individual particles indistinguishable • Hard, unbreakable solid • Strong caking propensity 	• Molten, slightly dull exterior • Additive visible on surface • Individual particles indistinguishable only for 20 mm particle size • Hard, unbreakable solid • Strong caking propensity 

5.3.3 SEM micrographs

Figure 5.6 shows micrographs obtained from SEM, to compare the surface characteristics of the devolatilised samples on a microscopic level. The micrographs are presented for 10 mm particles of all coals. Similar observations were made for the 5 and 20 mm particles (Appendix A.2).

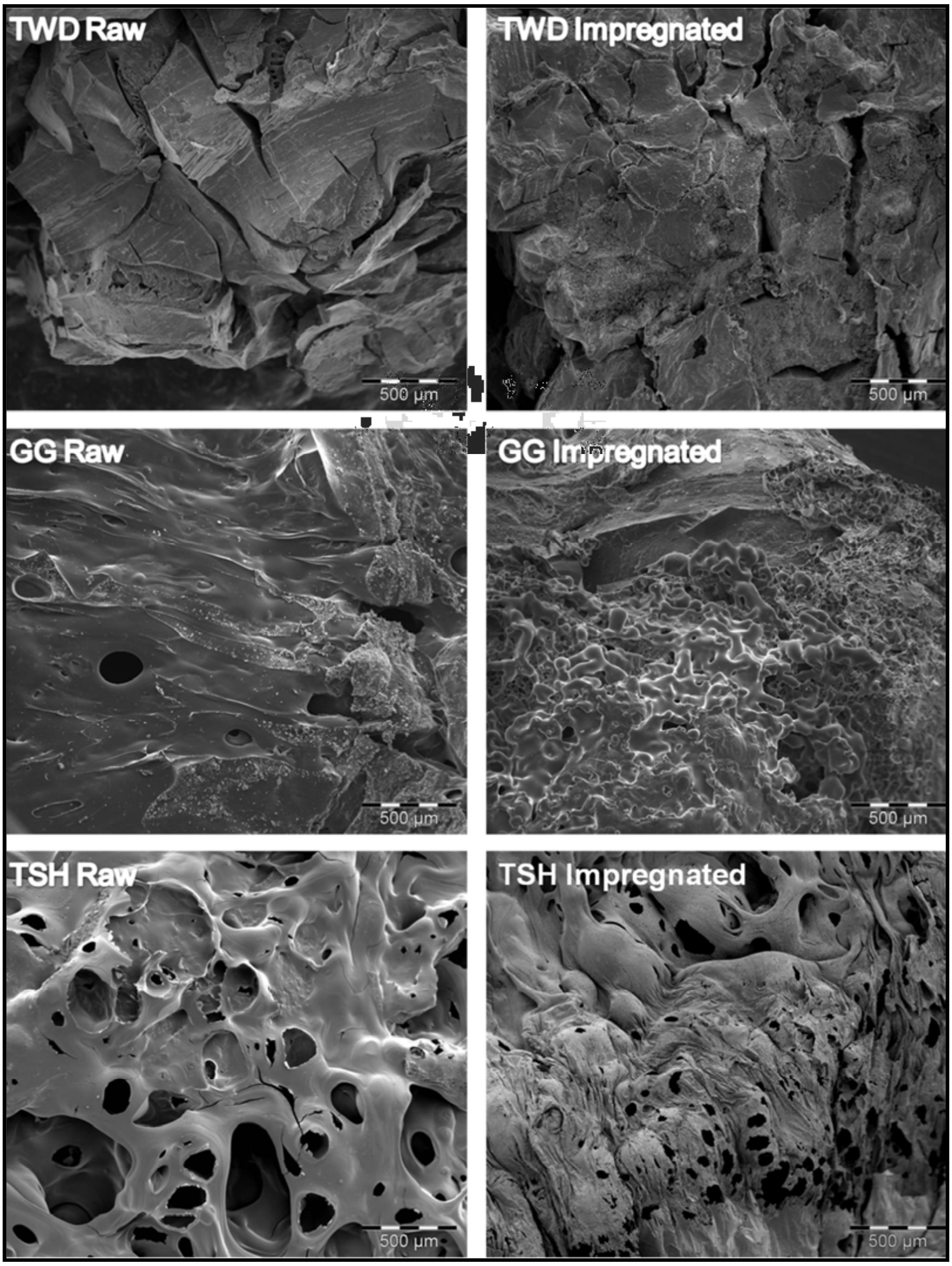


Figure 5.6: SEM micrographs of raw and impregnated 10 mm particles, after devolatilisation at 700 °C

Figure 5.6 shows the surface texture of the devolatilised material from raw and impregnated samples of the different coals. No significant difference can be observed between the TWD char from the raw and impregnated coal. Both the samples show signs of crack formation, while some sections of both samples indicate that the particle contracted (where possible softening occurred) as opposed to cracking. As reported by Gray,[32] non-caking coals may relieve pressure build-up through crack formation if release channels are sealed off by softened coal. The slightly rougher texture of the impregnated TWD sample can be attributed to some form of the additive still being present on the surface. Comparison of the GG samples shows a distinct difference between coke of the raw and impregnated coal samples. The surface of the raw GG coke has a fluid-like appearance indicative of the high fluidity exhibited during devolatilisation. Blow holes which were formed during the release of volatiles are also present on the surface. In contrast, the impregnated GG sample does not display blow holes, and shows a more coarse texture indicating a reduction of surface fluidity. A distinct difference in appearance can be observed between the raw and impregnated TSH samples. Both samples have an uneven fluid-like appearance due to softening and melting. The raw and impregnated samples have multiple holes on the surface, which can be attributed to explosive bursts from gas bubbles at the already slightly hardened outer layer of the coal.[32] However, the size of holes and opened pores (likely formed during volatile release) on the surface of the impregnated sample are reduced compared to the raw sample, due to the addition of K_2CO_3. This is also an indication that the additive influences the plasticity of the coal's surface.

5.3.4 X-ray CT

Figure 5.7 shows an X-ray CT slice (single, cross-sectional middle slice taken from the 3-D tomogram) of the internal structure of raw 10 mm GG particles before devolatilisation, and an X-ray CT slice (middle slice) of the same 10 mm particles taken after devolatilisation. This shows how the internal structure of coal can change during devolatilisation.

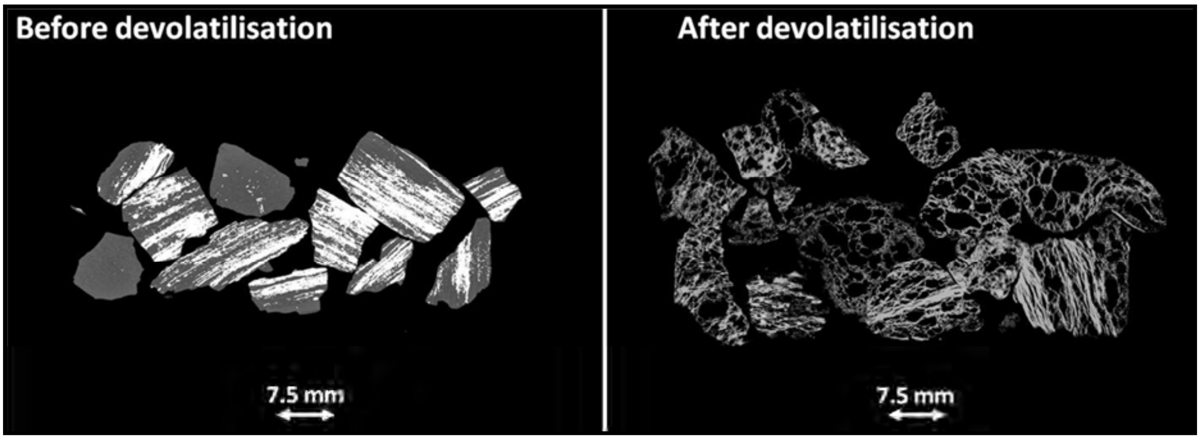
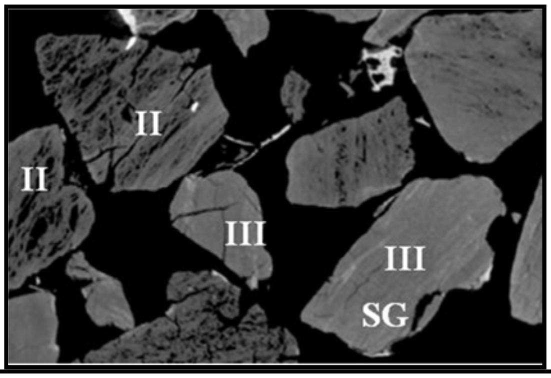
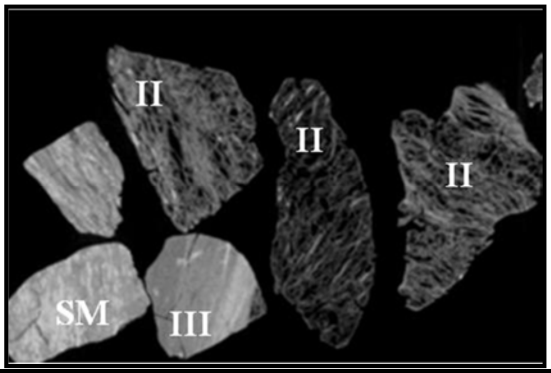
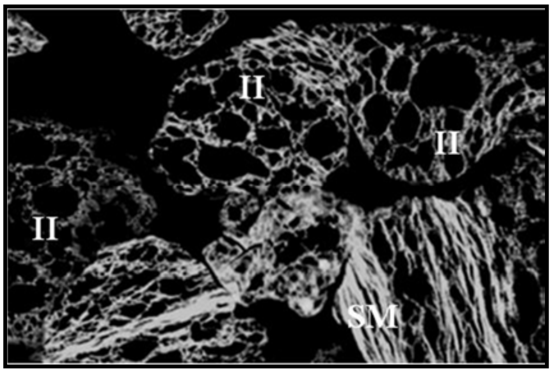
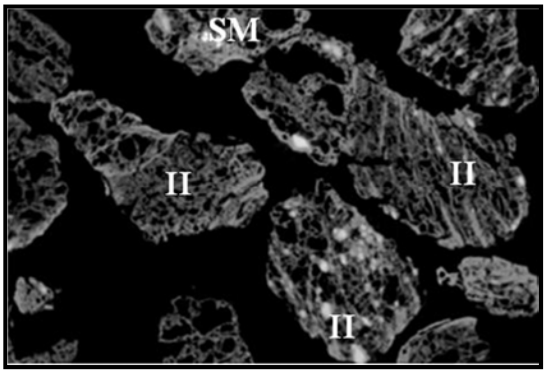
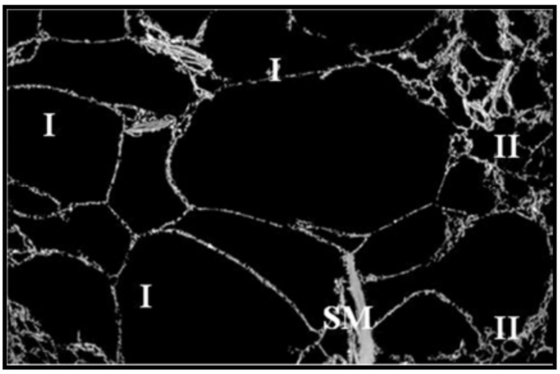
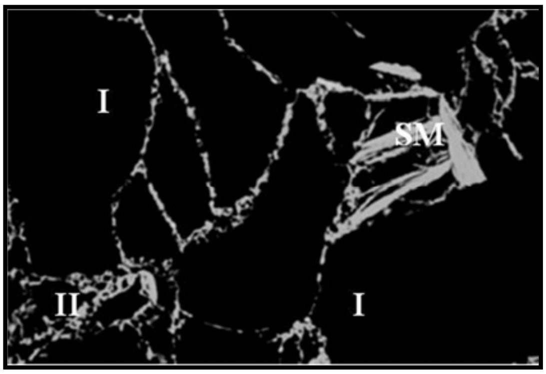


Figure 5.7: Internal structure of 10 mm raw GG coal particles before and after devolatilisation

The change in internal pore structure of the GG coal particles during devolatilisation is clearly evident from Figure 5.7. The mineral inclusions are clearly observed in the raw coal particles (lighter areas), and the resultant ash can be observed in the devolatilised samples, specifically in areas where little to no bubble formation occurred. In contrast to the dense, solid structure of the particles before devolatilisation, the coke has a honeycomb or foam structure.[16] The cokes' internal structure consists of an arrangement of many voids or bubbles distributed inside the particle.[16,18]

Table 5.4 provides comparisons between the internal structures of raw and impregnated 10 mm particles after devolatilisation, as acquired from X-ray CT. The images presented are single cross-sectional slices obtained from the tomograms. The char classification system presented in Table 5.1,[21-24,33] as well as classifications used by Yu *et al*.,[16,18] were used to characterise the devolatilised samples. Results for the 5 and 20 mm particles are presented in Appendix A.3.

Table 5.4: X-ray CT slices of 10 mm TWD particles (from raw and impregnated coal) after devolatilisation

	Raw	Impregnated
TWD After devolatilisation		
GG After devolatilisation		
TSH After devolatilisation		

The X-ray CT slices of the TWD particles (Table 5.4) acquired after devolatilisation show the different types of char formed during devolatilisation. Particles of the same size fraction may exhibit different behaviour during devolatilisation, and may form different types of char/coke, depending on the maceral composition of each individual particle.[32,34-37] X-ray CT observations of multiple sections, as labelled in Table 5.4, show that TWD char particles (from raw and impregnated coal) are comprised of both group II and III chars. The raw sample consisted of 45% group II and 55% group III char, based on a single slice. The impregnated sample did not show significant changes, with 40% group II char, and 60% group III char. Some of the solid char particles are relatively pure carbon (SG), while others are comprised of carbon as well as some mineral inclusion (SM), as labelled in Table 5.4.

Impregnation with K_2CO_3 does not influence the char formation of the TWD coal during devolatilisation (Table 5.4).

Both the raw and impregnated cokes of the GG coal (Table 5.4) were classified as group II char, with highly porous internal bubble formation clearly visible. Mineral fractions (SM) labelled in Table 5.4 can also be observed in lighter coloured areas where bubble formation was not as significant due to reduced fluidity. Significant differences can be observed between the coke from raw and impregnated coal, in terms of particle fusion and bubble formation. Fusion/caking of the coke particles from raw coal is evident, whereas little to no particle fusion is observed for the coke from impregnated samples. The size of the internal voids of the coke from impregnated coal is visibly reduced compared to the coke from raw coal, which indicates that the reduction of surface fluidity (due to impregnation) may suppress volatile evolution which consequently results in a reduction in gas bubble size.

The internal structures of the TSH coke from raw and impregnated coal (Table 5.4) indicate significant bubble formation, and as a result noticeably higher porosity compared to the GG coke. The internal structure of the TSH coke comprises of large voids with very thin walls, and areas where the absence of bubble formation (voids) can be attributed to higher density minerals. The TSH coke can mostly be classified as group I char, while small parts of the coke can be classified as group II. In contrast to the classification of pulverised coal particles, the agglomerated samples formed by larger millimetre sized particles can comprise of up to two different char group classifications. The occurrence of mixed mode types is more likely given the larger size of particles in comparison to pulverised coal. Although previous results (Figure 5.5) indicate that impregnation with K_2CO_3 reduces the surface fluidity of the TSH 10 mm particles, the slices of the samples presented in Table 5.4 do not indicate a noticeable difference between the internal structure of the raw and impregnated samples, as seen for the GG samples.

Quantification of the average wall thickness and porosity, as measured using image analysis, is presented in Table 5.5. Since the classification system (Table 5.1) was based on pulverised coal particles (63-90 µm), the quantification of specifically wall thickness was adapted to compare the characteristic wall thickness of the pulverised particles with that of the large particles. For comparative purposes, the ratio of wall thickness to initial particle size was determined. The wall thickness was not determined for the TWD chars, since these chars did not present clearly distinguishable walls.

Table 5.5: Comparison of wall thickness and porosity between pulverised coal (63 to 90 μm) and large coal particles (10 mm)

	Wall thickness (μm)	Wall thickness ratio	Porosity (%)
Group I char*	<5	<0.08	>70
Group II char*	>5	>0.08	40-70
Group III char*	>5	>0.08	<40
TWD 10 mm Raw	-	-	15
TWD 10 mm Impregnated	-	-	17
GG 10 mm Raw	210	0.021	52
GG 10 mm Impregnated	190	0.019	37
TSH 10 mm Raw	240	0.024	77
TSH 10 mm Impregnated	150	0.015	76

*** based on particle size of 63 to 90 μm[20-23,32]**

The average thickness of walls between voids is much larger for the 10 mm particles than for the pulverised coal (Table 5.5). When comparing the average wall thickness of the GG and TSH cokes from raw and impregnated coal, it appears that K_2CO_3 impregnation has a larger influence on the wall thickness of the TSH sample. According to the wall thickness ratios of the different coal sizes, both GG and TSH coke samples (raw and impregnated) are classified as group I chars. This is, however, not accurate when the other characteristics of the char classification system (Table 5.1) are considered, and is therefore not a suitable method to characterise devolatilised samples from large coal particles. As is evident from the porosity values, the TWD chars can generally be classified as group III chars, while the porosity of both the raw and impregnated TSH coke is in accordance with the porosity proposed for group I char. GG coke from raw coal can be classified as a group II char. Even though the porosity of the GG coke from impregnated coal is slightly less than indicated by the char classification system for group II char, it can generally still be classified as a group II char when the other geometric characteristics are taken into account. The porosities of the raw and impregnated GG samples quantitatively indicate that the coke from raw coal is more porous compared to the impregnated sample, which was also observed from the X-ray CT slices presented in Table 5.4. A correlation exists between the coke porosity and the Roga Index caking property of coals GG and TSH. The GG coke, with a Roga index of 45, has lower porosity compared to the TSH coke, which has a Roga Index of 73.

5.3.5 Quantification of caking/agglomeration

Impregnation with K_2CO_3 was most effective in reducing the caking propensity of the GG large coal particles (with additional results shown in Appendix A.4). Therefore, the caking behaviour and influence of the additive, was quantified for this coal. The values obtained from the measurements of bridging neck size are presented in Table 5.6 (with an example of the measurements given in Appendix A.5).

Table 5.6: Bridging neck sizes (mm) for GG char (5, 10, and 20 mm)

	Raw		Impregnated	
	Average	**SD***	**Average**	**SD***
5 mm	5.3	1.4	2.6	0.9
10 mm	8.0	2.3	4.5	2.0
20 mm	13.5	3.7	10.2	4.0

*** - Standard deviation**

From the table it can be seen that the average bridging neck size decreases as a result of impregnation of the coal. Since swelling and surface fluidity is reduced due to additive addition, it can be expected that the extent of particle fusion or adhesion will reduce. It is also evident from the measurements that the bridging neck size lengths increase with increasing particle size. These results quantitatively show that the addition of K_2CO_3 reduces the degree of particle bonding, and consequently the caking propensity of the GG coal.

5.3.6 Summary of influence of K_2CO_3-impregnation on caking properties

Table 5.7 provides a summary of the influence of K_2CO_3-impregnation on the extent of caking, surface texture, porosity, wall thickness, and bridging neck size of the three coals.

Table 5.7: Influence of K_2CO_3 on caking properties

	TWD	GG	TSH
Extent of caking	-	Y ↓↓	N
Surface texture	N	Y	Y
Wall thickness	-	Y ↓↓	Y ↓
Porosity	N	Y ↓↓	N
Bridging neck size	-	Y ↓↓	-

Y: Significant influence, N: No significant influence, ↓: Decrease in property,
↓↓: Strong decrease in property, –: Property not observed

Table 5.7 shows that K_2CO_3-impregnation influenced all the listed characteristics of the GG coal. Impregnation only influenced the measured average wall thickness and surface texture of the TSH coke, and had no influence on the extent of caking and porosity. No bridging necks were observed for TSH coke. The surface texture and porosity of the TWD char was not influenced by impregnation, while no caking, visible walls, or bridging necks were observed. The results in Table 5.7 show that impregnation with K_2CO_3 has the largest influence on the behaviour and resulting characteristics of GG coal during devolatilisation. In addition to influencing the caking propensity of GG coal, it has also previously been reported that K_2CO_3 solution impregnation with a concentration as low as 0.5 M can increase the steam gasification rate of large coal particles by up to 40%, for a South African coal similar to TWD.[38] The influence of K_2CO_3 on the ash properties of these three coals, as well as the amount of additive present in the ash after heating, are currently being investigated. An in-depth techno-economical study is recommended, along with pilot-scale experiments, to determine the industrial practicality and economical viability of using K_2CO_3 in industrial coal utilisation processes.

5.4. Conclusions

The extent of caking, surface texture of devolatilised material, porosity, wall thickness, and bridging neck size were evaluated for batches of char or coke generated in an inert atmosphere, at a low heating rate (7 °C/min, up to 700 °C). Impregnation with K_2CO_3 did not influence the surface texture of the TWD char, but increased the overall brittleness and extent of fragmentation of the devolatilised samples. The char obtained from TWD coal was generally classified as a group III char. The caking propensity of GG coal was significantly reduced due to impregnation with K_2CO_3, and the coke from the impregnated coal had a less fluid-like appearance compared to the samples from the raw coal. The porosity of the GG coke was also reduced as a result of impregnation. Devolatilised GG samples were classified as a group II char. The impregnated samples showed little to no signs of fusion/caking with smaller internal voids in comparison to the raw sample. The bridging neck size measurements quantitatively indicated that K_2CO_3-impregnation reduced the caking propensity of the GG large coal particles. The TSH coke from impregnated coal had significantly less and smaller holes and opened pores on the surface when compared to the coke from the raw coal. Coke from TSH coal was classified as a group I char. Impregnation with K_2CO_3 did not influence the extent of caking and porosity of the TSH coke. From the results it can be concluded that the devolatilised material from large particles/agglomerates can be classified according to a char classification system proposed for pulverised coal, using porosity, pore shape, and particle shape. However, the type of void and pore network (usually defined by wall-thickness) of samples obtained during this investigation is much larger than that of pulverised samples, and can therefore not be directly compared or classified according to existing char classification systems.

The overall conclusion made from this investigation is that an additive such as K_2CO_3 (using solution impregnation) can be used to significantly reduce the caking tendency of a coal which exhibits a moderate degree of fluidity, such as GG. Using an additive such as K_2CO_3 has utility in expanding gasification feedstock suitability, but reactivity and ash behaviour should further be investigated to progress this approach.

Acknowledgements

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Chapter 6

Concluding summary

The conclusions drawn throughout this investigation are summarised in this Chapter. Implications for practical application are discussed, and recommendations are provided to assist future research.

6.1. Concluding Remarks

The swelling and caking behaviour of large coal particles from three South African coals from different origin have been the focus of this investigation. The main objectives have been to qualitatively and quantitatively evaluate the swelling and caking behaviour of large coal particles, as well as the influence of K_2CO_3 on the degree of swelling and caking. The main conclusions made during this investigation, implications for practical application, and recommendations for future research, will be discussed.

A novel approach was used to quantify the swelling of single large coal particles, whereby a volumetric swelling ratio (SR_V) was defined to determine the degree of swelling using measurements obtained from mercury submersion. It was found that this method can be used to quantify the swelling of 5, 10 and 20 mm coal particles. The average SR_V values for GG and TSH 20 mm particles, obtained at the Gieseler softening temperatures, was found to be 2.1 and 2.5 respectively. An average SR_V value of 1.8 was determined for TWD 20 mm particles, whereas standard methods for characterising swelling, such as FSI, did not show swelling for the powdered coals. These results consequently show the swelling behaviour of large coal particles does not directly correlate with results obtained by conventional analyses for pulverised coal.

Impregnation with a 5.0 M K_2CO_3-solution was effective in increasing the K-loading by a factor between 9 and 33, with maximum K-loadings of 3.3, 3.0 and 1.4 wt.% K (coal basis) for the 5, 10, and 20 mm particles, respectively. The overall K-loading decreased with an increase in particle size. It was, however, determined that the average surface loading of K (mg/cm^2) increased with an increase in particle size. Based on the comparison of SR_V values obtained for raw and K_2CO_3-impregnated coal particles, obtained at the average maximum temperature (T_{max}), the degree of swelling of GG and TSH coal particles was reduced by between 25 and 75% due to K_2CO_3 impregnation. In particular, the SR_V of the 20 mm GG particles was reduced from 3.0 to 1.8, while the SR_V for the 20 mm TSH particles was reduced from 5.7 to 1.4. The degree of large particle swelling of TWD was not influenced by impregnation. Consequently, the use of an effective additive such as K_2CO_3 is proven to be a novel approach to reduce unwanted coal swelling of large coal particles which exhibit moderate to high degrees of fluidity. The K_2CO_3 not only influenced the large particle swelling of GG and TSH coals, but also the swelling and fluidity of the powdered coal as measured by FSI, Gieseler, and dilatometry. The transient swelling and shrinkage behaviour of the large particles was described by a defined swelling coefficient, k_A. The maximum k_A was reduced from 0.025 to 0.015 $^oC^{-1}$ for GG, and from 0.045 to 0.027 $^oC^{-1}$ for TSH, as a results of impregnation.

Coal caking, and the effect of K_2CO_3 thereon, was evaluated based on extent of caking, surface texture, bridging neck size, wall thickness, porosity. The K_2CO_3 was most effective in reducing the caking propensity of the GG coal particles, which was quantified using a parameter defined as bridging neck size. The average bridging neck size of the various particle sizes was reduced by between 25 and 50%. The internal structure of the char and coke was examined using X-ray CT, and image analysis of the tomograms showed a decrease in the wall thickness and porosity of the GG and TSH agglomerates, as a result of impregnation. By applying a char classification system generally used for powders, TWD was classified as group III char, GG as group II char, and TSH as group I char. In addition to reducing the extent of caking of the GG coal, K_2CO_3-impregnation increased the brittleness of the TWD char, while having no significant influence on the TSH coke. Comparison of the char characteristics showed a similarity between the porosity of the pulverised coal and large coal particles, while the wall thickness of the large particle char was up to 50 times larger than the wall thickness of the powders.

The results obtained from the swelling and caking behaviour of the large coal particles can be used to explain the relationship between coal swelling and caking. For GG and TSH coal, there is a correlation between the swelling behaviour and caking behaviour of the large coal particles. TSH coal particles exhibited higher degrees of swelling and a higher degree of caking, while the GG coal exhibited less swelling and caking. For the GG and TSH coals, the behaviour of the large coal particles also correlate with the fluidity and swelling behaviour of the pulverised coal. In the case of TWD coal, the large coal particles exhibited swelling, but no caking was observed. Therefore it can be concluded that the swelling and caking are not interdependent, whereby a coal particle may soften enough to swell but does not reach the fluid state where caking occurs.

6.2. Contribution to science

The following attainments made throughout this investigation are considered valuable additions to the current knowledge in coal science:

- Development of a method which can be used to quantify the volumetric swelling of unaltered large coal particles.[1]

- A semi-quantitative evaluation of the transient swelling behaviour of large coal particle swelling using image analysis.[1]
- Comparison of the swelling behaviour of powders and large coal particles of three South African coals indicate that coal selection cannot solely be based on the characteristics of the powdered coal.[1]
- Reduction of the degree of swelling of large coal particles of various sizes, in particular for coals which exhibit moderate to high degrees of swelling.[2]
- Evaluation of maximum swelling coefficient, k_A, obtained from transient swelling behaviour of unaltered raw and impregnated particles.[2]
- Reduction of extent of caking of GG coal, and the quantification of large coal particle caking using bridging neck size measurements.[3]
- Evaluation of the influence of K_2CO_3-impregnation on the internal structure of char and coke, using X-ray CT.[3]

6.3. Implications for practical application

Previous research has focused on the swelling and caking behaviour of powdered coal, and the modification thereof with additives, whereas the research conducted in this investigation shows the viability and benefits of using an additive to modify large coal particle swelling and caking. The installation of stirrers in the gasifiers is recommended when caking coals are used.[4] This method is efficient, however, gasifiers are operated under high pressure, and maintenance and wear rate cost may be high. The use of a method such as additive addition may be considered as alternative method for reduction of cake formation, and provides many alternative benefits.

The results obtained from this investigation ultimately show that the swelling and caking tendency of large particles from a moderately swelling coal such as GG (Waterberg), can be modified using K_2CO_3 as additive. Thus, a coal which is generally less suitable for fixed- and fluidised-bed applications due to its swelling and caking characteristics, can be made suitable for such applications by means of K_2CO_3, or a similar additive. Various benefits are associated with the use of an additive, such as K_2CO_3, in industrial coal utilisation processes. The means to modify the swelling and caking characteristics of coal will broaden the selection criteria for prospective coals which can be selected for utilisation, and will also allow the selection of alternative feedstocks when certain coal resources are limited or depleted. Specifically in South Africa, coal used for the countries’ fixed-bed gasification operations are mainly supplied by the Highveld region, which does not have unlimited coal resources. The findings of this investigation show that the swelling and caking characteristics of coal from the Waterberg region, which contain vast amounts of coal, can be suitably modified for existing gasification technologies. In addition to decreasing the degree of swelling and caking, the use of K_2CO_3 will also increase the reaction rate in gasification processes, which will consequently increase the throughput of coal per reactor unit.[4] Potentially recycling the selected additive will also provide an additional benefit. Considering alternative additives, the use of $CaCO_3$ will provide the additional benefit of promoting sulphur capture from the gas, and may be more cost effective to use than potassium carbonate. Therefore, the use of an additive in existing coal utilisation processes such as gasification will result in a more efficient process with increased coal throughput, which is not limited by the type of coal available as feedstock.

6.4. Future prospects

In order to expand existing knowledge regarding large coal particles, future research and prospects are proposed to close the gap between laboratory-scale testing and large-scale industrial operations. Previous research investigating the reactivity of large coal particles,[5] reported a significant increase in reactivity when using K_2CO_3 as additive. Advantages associated with the use of this additive in large-scale operations include increased coal throughput and lower operating temperatures. A further study should be focused on integrating the combined findings of large coal particle devolatilisation[1] and gasification[4] using K_2CO_3, together with a systematic influence of process conditions including temperature, pressure, and heating rate. Since laboratory scale experiments were conducted in this investigation, it is proposed that future work investigate the effectiveness of additive addition in a pilot-scale operation. Ideally, the effectiveness of various additives should be evaluated under process conditions typically used in industrial processes, such as high temperature and high pressure, to identify the most suitable compound. The efficiency of K_2CO_3 or other additives should also be investigated in different gas atmospheres such as H_2, CO, CH_4, and air. The shortcomings of using potassium carbonate for specifically dry bottom operated fixed bed gasification, such as the influence of the additive on process equipment and recovery of the potassium compound should be evaluated. The change in chemical state and distribution of the selected additive should also be investigated as a function of temperature, as well as the influence of the additive on the surface functional groups of the coal. Furthermore, a detailed techno-economic evaluation should be conducted to determine the technical and economic feasibility for industrial application. From an environmental perspective, the effectiveness of an additive such as calcium carbonate ($CaCO_3$) should also be evaluated, as this additive may increase reactivity and decrease coal swelling and caking, while also promoting the capture of sulphur in the gas phase.

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Appendix A

Additional results and experimental procedures

This Appendix provides additional experimental results which have not been included in preceding chapters, as well as detailed discussions regarding certain experimental procedures.

A.1 Caking/agglomeration results

In addition to the results presented in Section 5.3.2, Figure A.1-A.6 shows the influence of K_2CO_3-impregnation on the 5 mm and 20 mm particles of each coal.

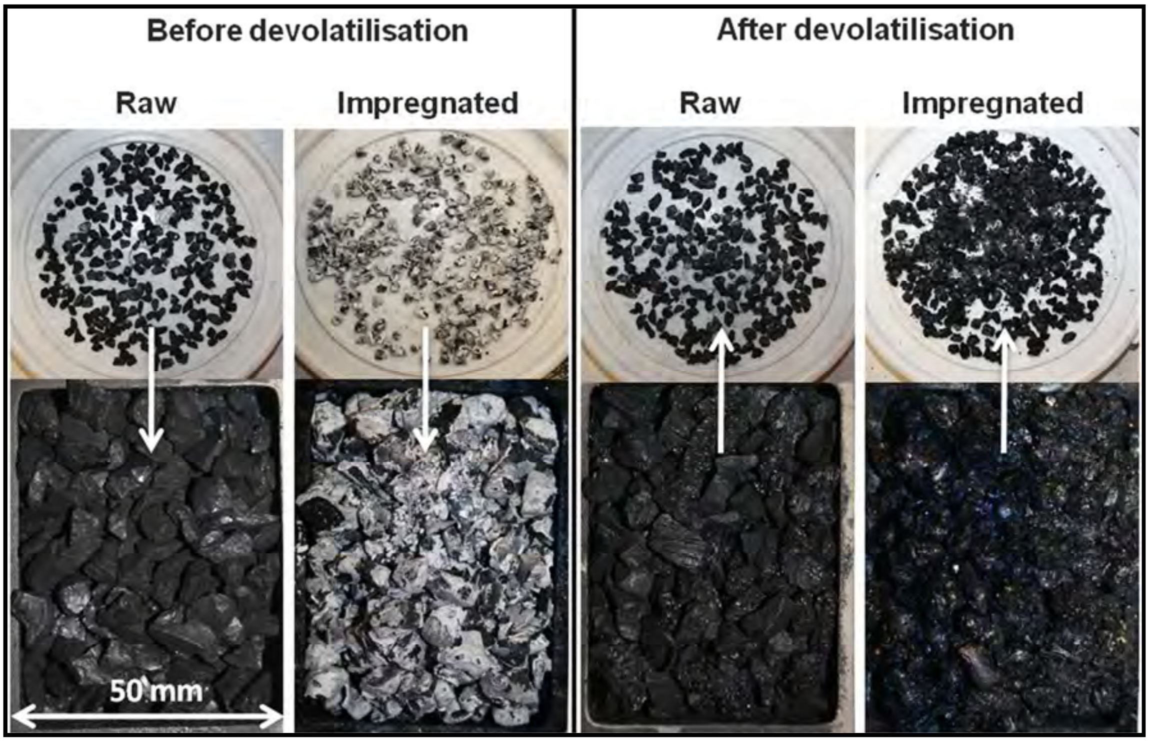


Figure A.1: Raw and K_2CO_3-impregnated 5 mm TWD coals and char, upper images show the individual particles before and after devolatilisation, the lower images show the same particles in the sample holder

Figure A.2: Raw and K_2CO_3-impregnated 5 mm GG coals and char, upper images show the individual particles before and after devolatilisation, the lower images show the same particles in the sample holder

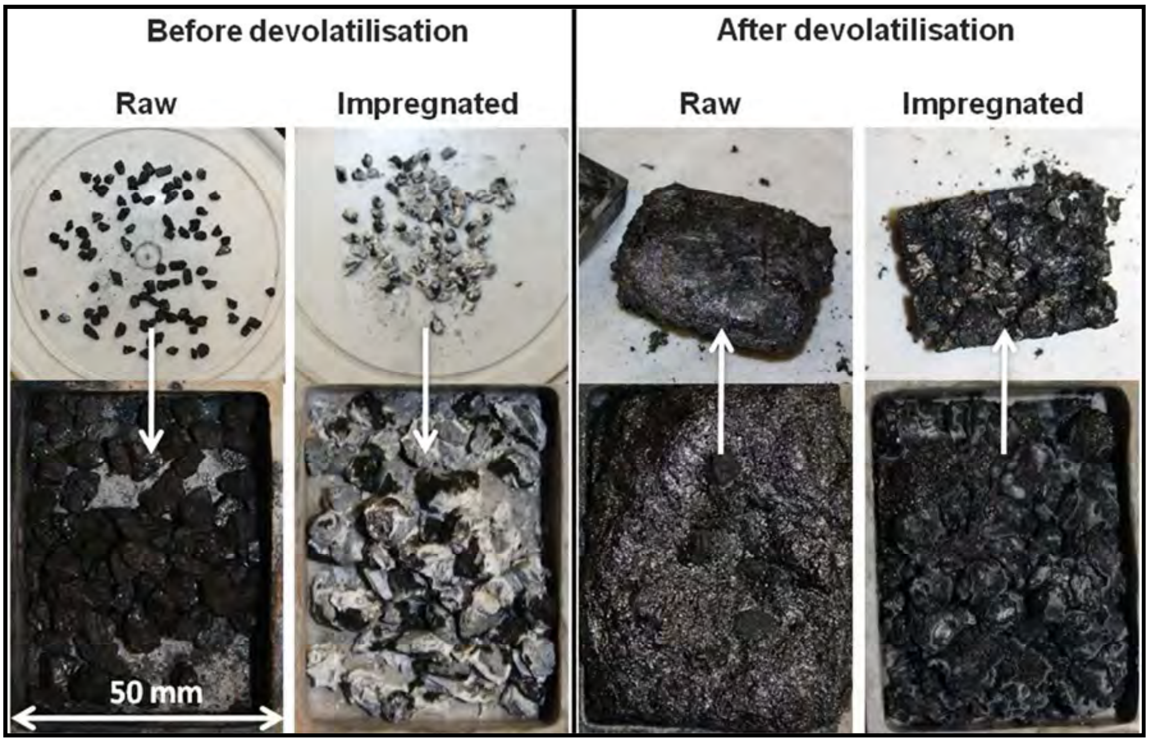


Figure A.3: Raw and K_2CO_3-impregnated 5 mm TSH coals and char, upper images show the individual particles before and after devolatilisation, the lower images show the same particles in the sample holder

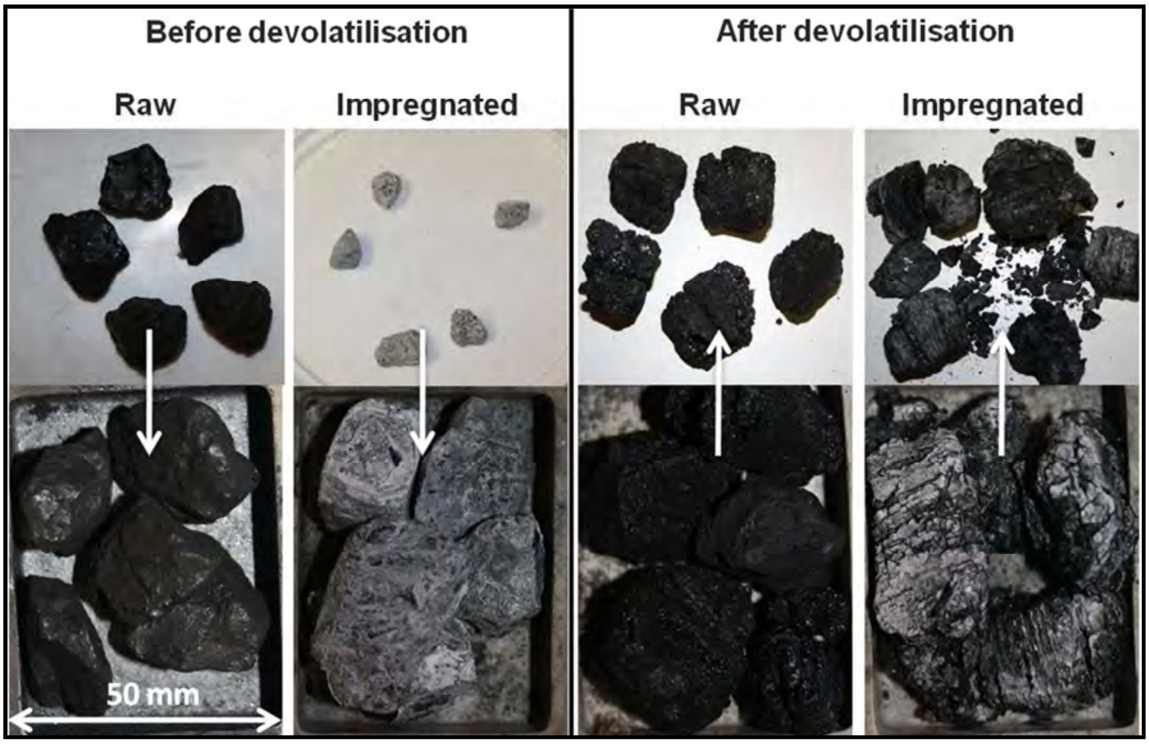


Figure A.4: Raw and K_2CO_3-impregnated 20 mm TWD coals and char, upper images show the individual particles before and after devolatilisation, the lower images show the same particles in the sample holder

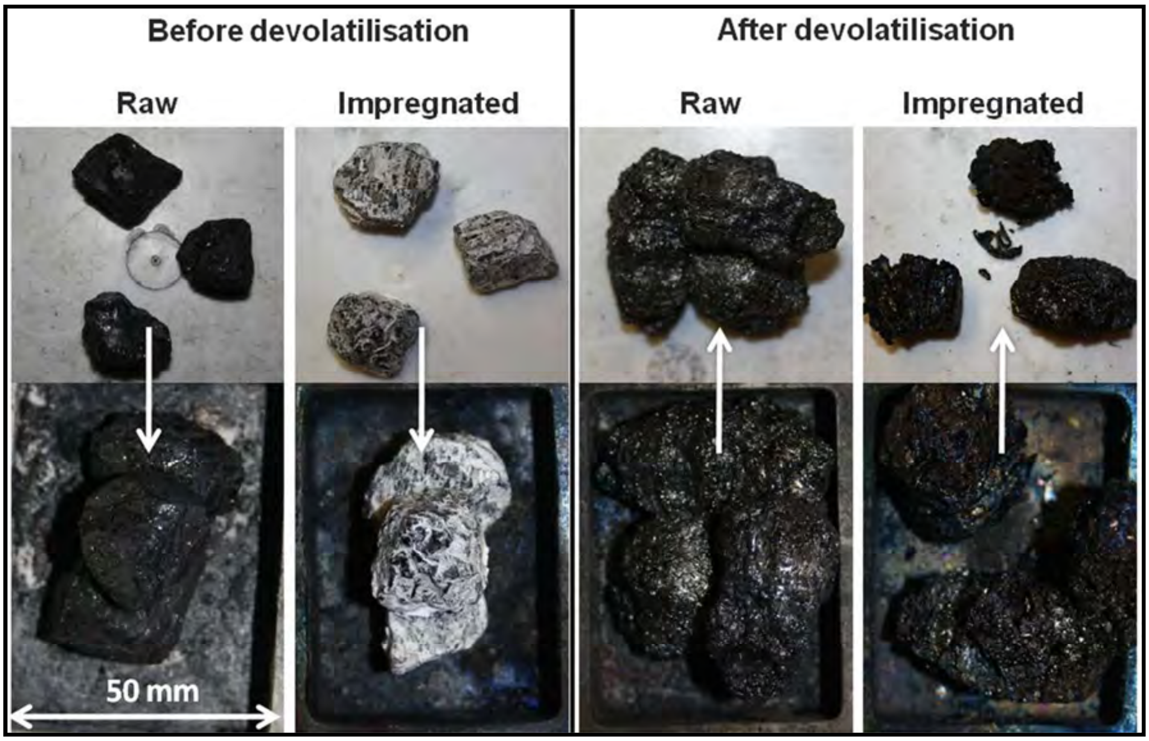


Figure A.5: Raw and K_2CO_3-impregnated 20 mm GG coals and char, upper images show the individual particles before and after devolatilisation, the lower images show the same particles in the sample holder

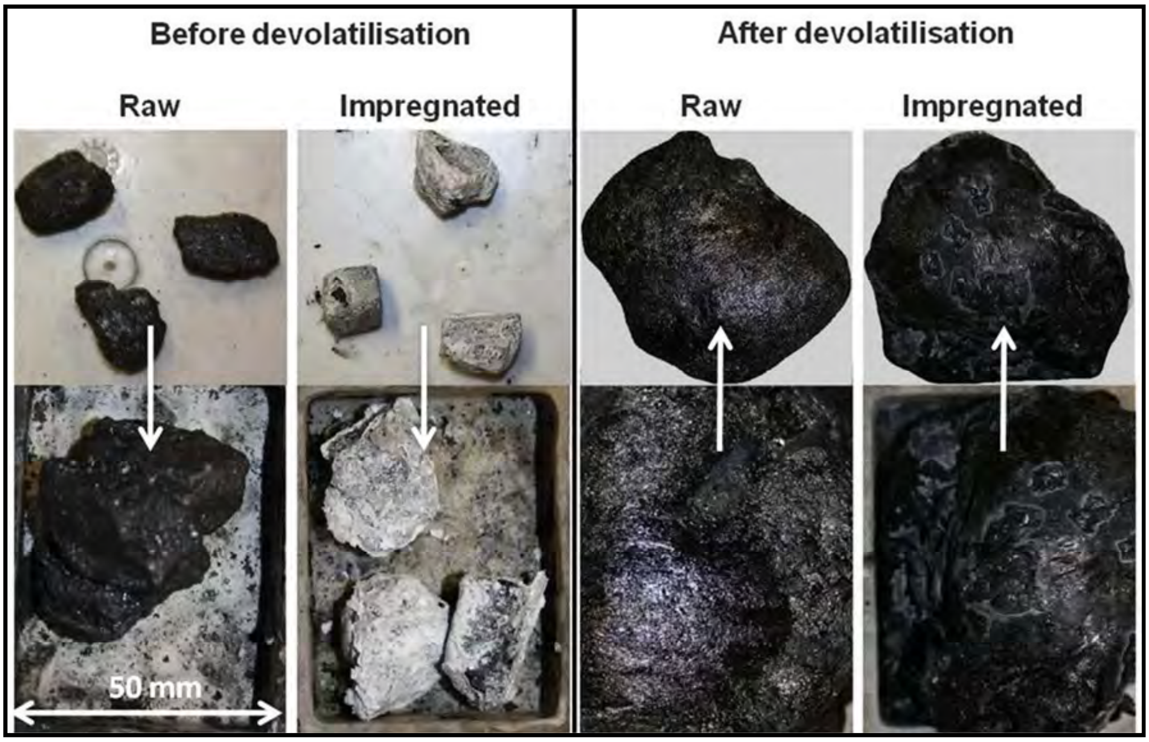


Figure A.6: Raw and K_2CO_3-impregnated 20 mm TSH coals and char, upper images show the individual particles before and after devolatilisation, the lower images show the same particles in the sample holder

A.2 SEM micrographs

In addition to the results presented in Section 5.3.3, Figures A.7 and A.8 show the SEM micrographs for the 5 mm and 20 mm particles of each coal.

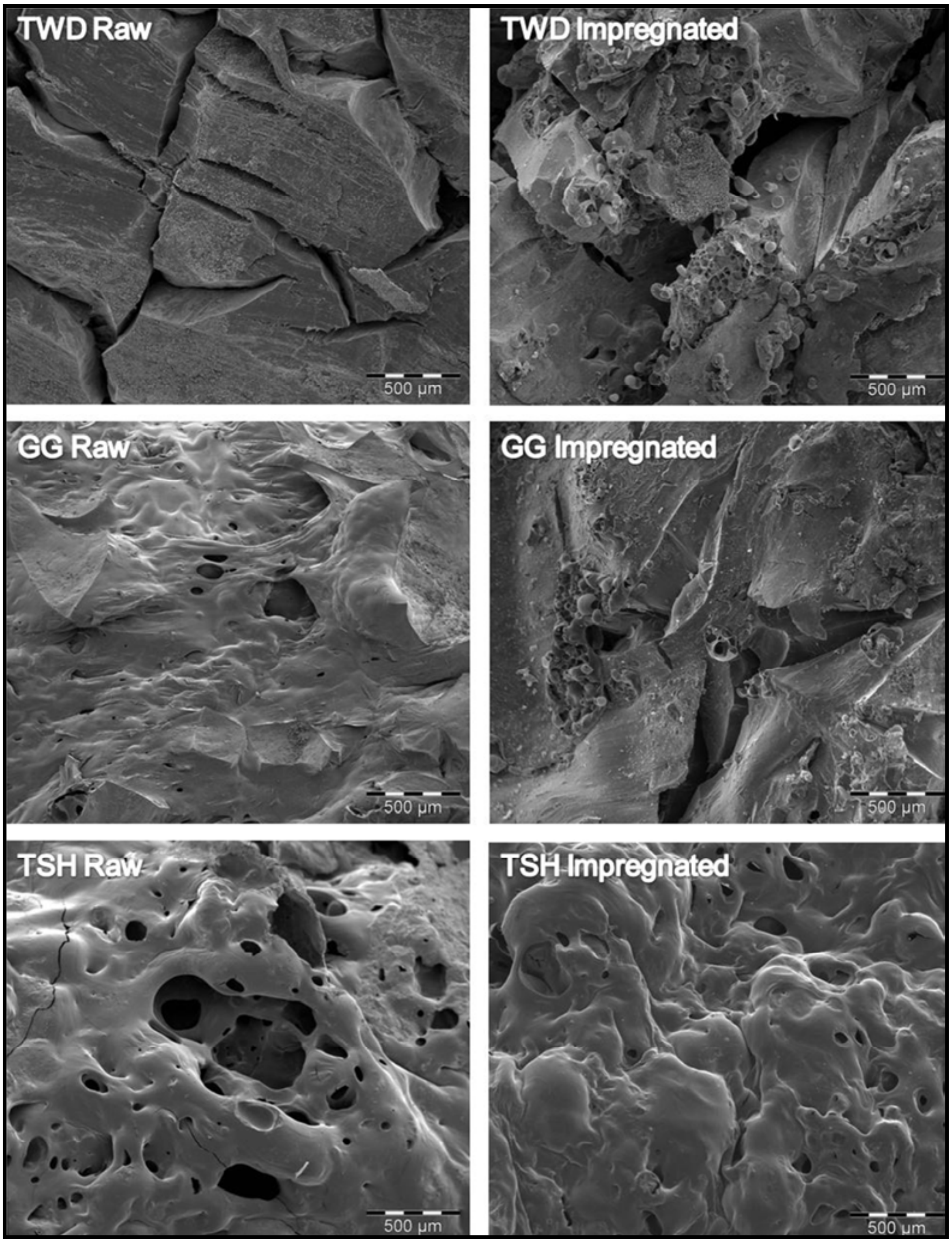


Figure A.7: SEM micrographs for 5 mm particles

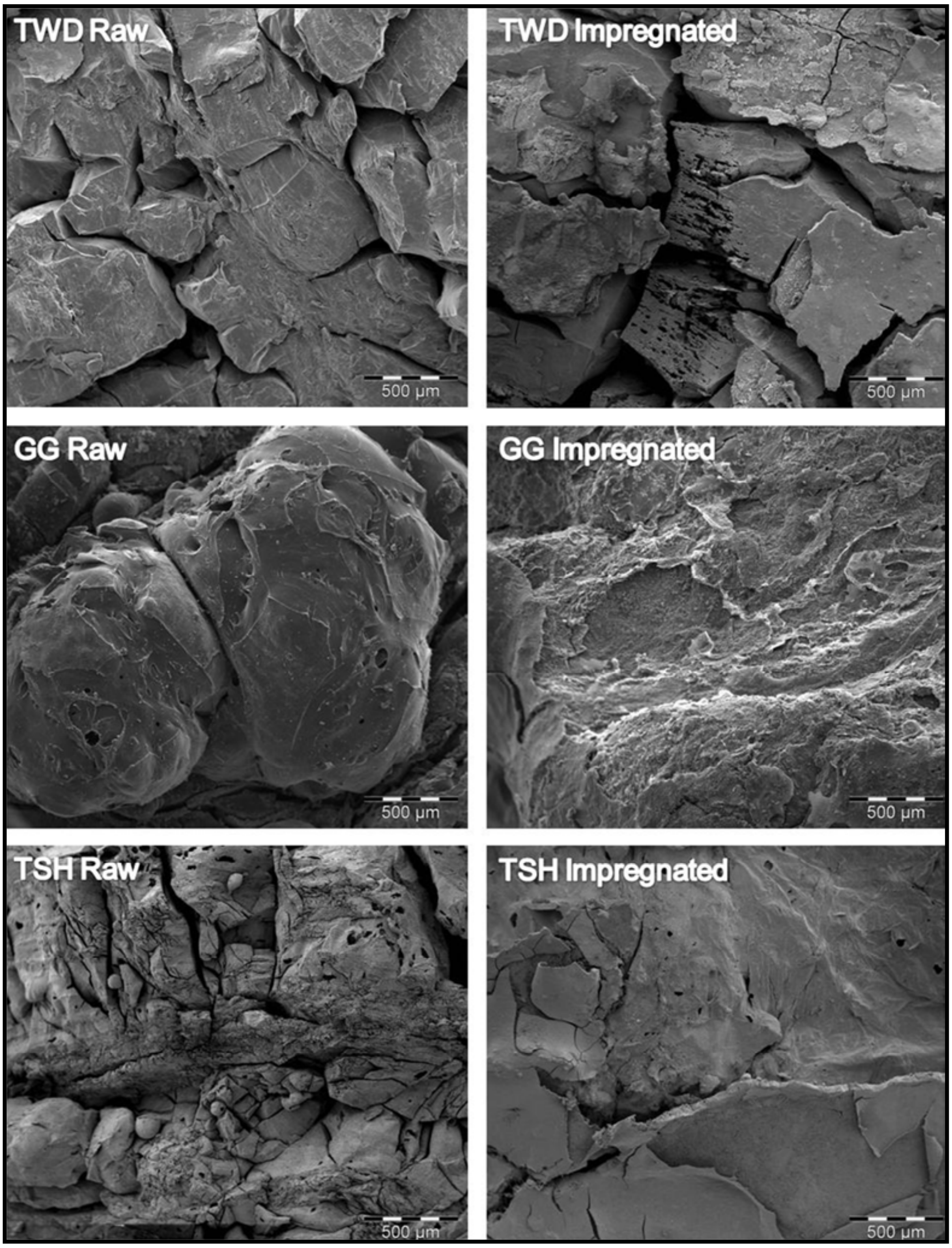


Figure A.8: SEM micrographs for 20 mm particles

A.3 X-ray CT slices

Tables A.1 to A.3 present selected comparisons between the internal structures of 5 and 20 mm raw and impregnated particles after devolatilisation, as acquired from X-ray CT.

Table A.1: X-ray CT slices of 5 and 20 mm TWD particles (from raw and impregnated coal) after devolatilisation

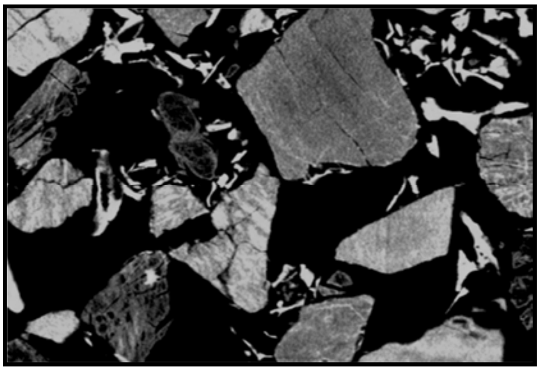
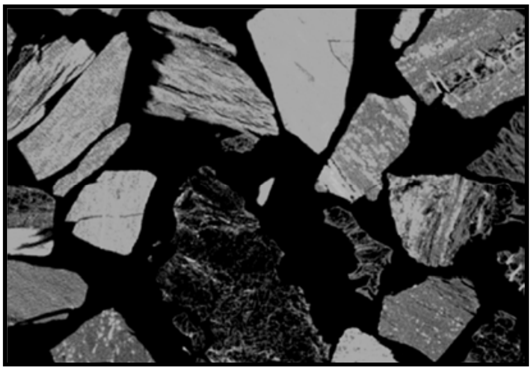
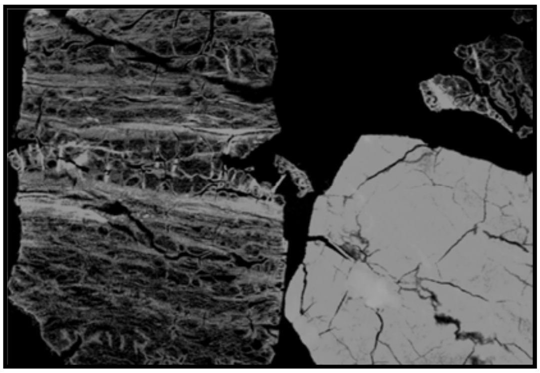
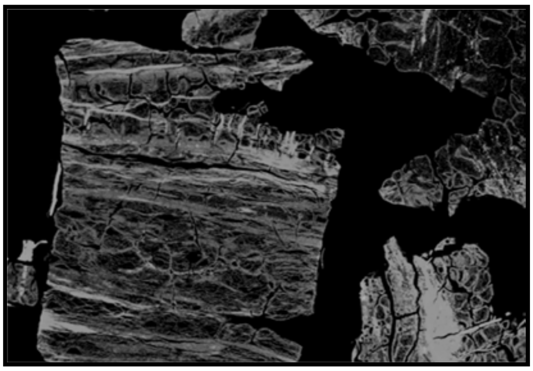
	TWD Raw	TWD Impregnated
5 mm particles		
20 mm particles		

Table A.2: X-ray CT slices of 5 and 20 mm GG particles (from raw and impregnated coal) after devolatilisation

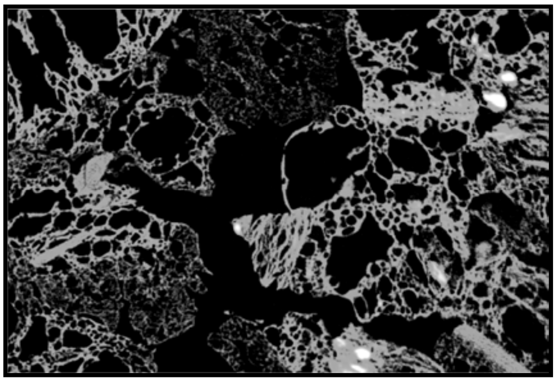
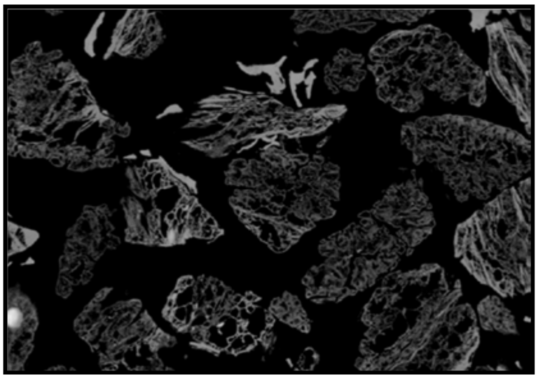
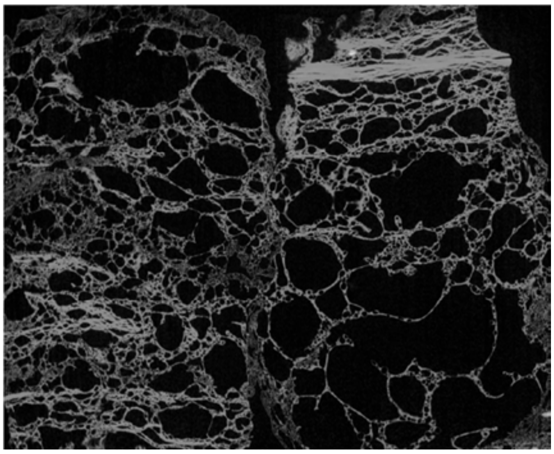
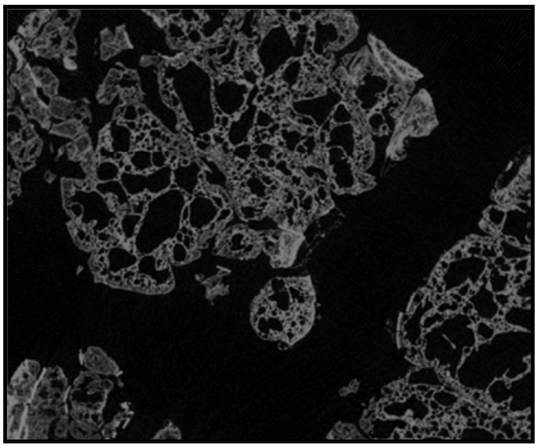
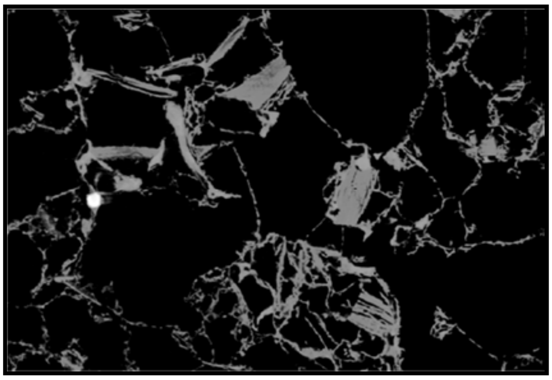
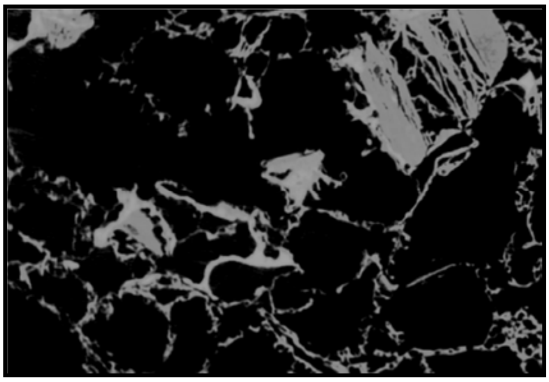
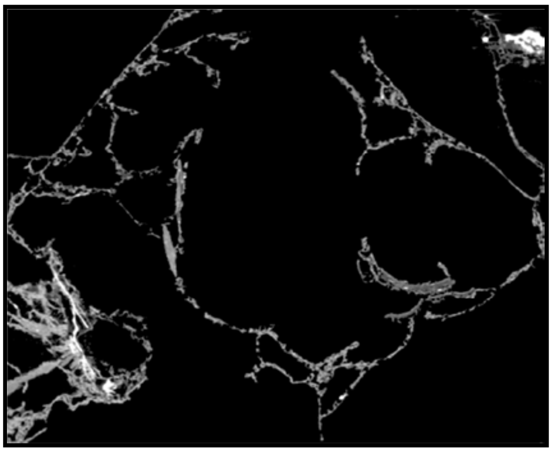
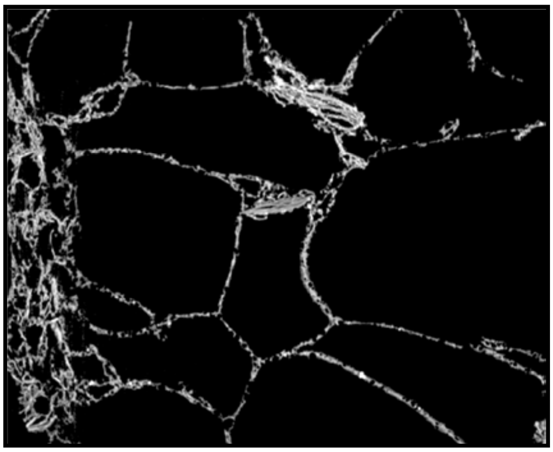
	GG Raw	GG Impregnated
5 mm particles		
20 mm particles		

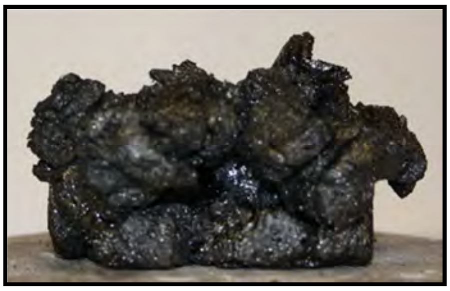
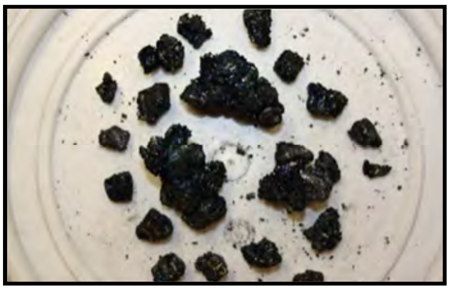
Table A.3: X-ray CT slices of 5 and 20 mm TSH particles (from raw and impregnated coal) after devolatilisation

	TSH Raw	TSH Impregnated
5 mm particles		
20 mm particles		

A.4 Effectiveness of K_2CO_3 to reduce caking of GG coal

The images presented in Table A.4 further emphasise the effectiveness of K_2CO_3-impregnation as a suitable method to reduce the caking tendency of various particle sizes of the GG coal.

Table A.4: Raw and impregnated GG char after devolatilisation at 700 °C

	Raw	Impregnated
5 mm		
10 mm		
20 mm		

A.5 Bridging neck size measurements

Figure A.9 is an example of the bridging neck size measurements of a single X-ray CT slice of the coke from 10 mm raw GG coal particles.

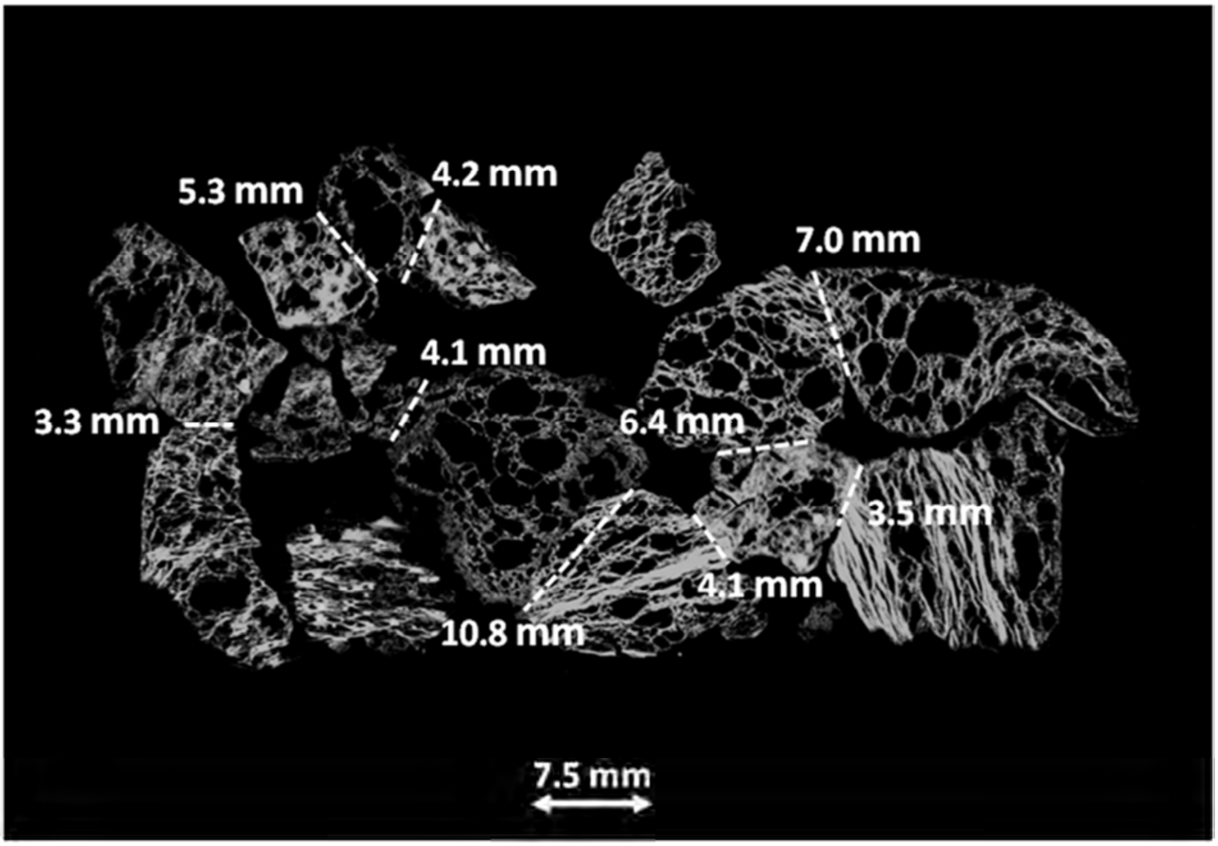


Figure A.9: Bridging neck size measurements for coke from 10 mm raw GG particles