

The influence of particle size on the pore development of coal chars during gasification

GH Coetzee



orcid.org 0000-0001-9935-376X

Thesis accepted in fulfilment of the requirements for the degree
Doctor of Philosophy in Chemical Engineering at the North-
West University

Promoter:	Prof HWJP Neomagus
Co-promoter:	Prof RC Everson
Co-promoter:	Prof JR Bunt

Graduation: October 2019
Student number: 20253362



In memory of G.H. Coetzee

Declaration

I, Gert Hendrik Coetzee, hereby declare that this thesis entitled: “The influence of particle size on the pore development of coal chars during gasification”, submitted in fulfilment 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.

Signed at Swellendam



Gert Hendrik Coetzee

30/05/2019

Date

Preface

Format of thesis

The format of this thesis is in accordance with the academic rules of the North-West University, where rule **A.5.4.2.7** states: *“Where a candidate is permitted to submit a thesis in the form of a published research article or articles, or as an unpublished manuscript or manuscripts in article format and more than one such article or manuscript is used, the thesis must still be presented as a unit, supplemented with an inclusive problem statement, a focused literature analysis and integration and with a synoptic conclusion, and the guidelines of the journal concerned must also be included.”*

Rule **A.5.4.2.8** states: *“Where any research article or manuscript and/or internationally examined patent is used for the purpose of a thesis in article format to which other authors and/or inventors than the candidate contributed, the candidate must obtain a written statement from each co-author and/or co-inventor in which it is stated that such co-author and/or co-inventor grants permission that the research article or manuscript and/or patent may be used for the stated purpose and in which it is further indicated what each co-author's and/or co-inventor's share in the relevant research article or manuscript and/or patent was.”*

Rule **A.5.4.2.9** states: *“Where co-authors or co-inventors as referred to in A 5.4.2.8 above were involved, the candidate must mention that fact in the preface and must include the statement of each co-author or co-inventor in the thesis immediately following the preface.”*

Format of numbering and referencing

The manuscripts published in the Carbon Journal adhere to rules prescribed in the author guidelines of Carbon. The technical content of the published manuscripts was not modified for this thesis. However, the referencing styles, numbering of tables and figures, and general outline of the manuscripts may have been adapted to ensure uniformity throughout the thesis.

Statement from co-authors

To whom it may concern,

The co-authors hereby give consent that **Gert Hendrik Coetzee** may submit the following published manuscripts as part of his thesis entitled: Modelling pore development of single large coal particles, for the degree *Philosophiae Doctor in Chemical Engineering*, at the North-West University:

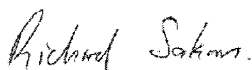
Coetzee, G. H.; Sakurovs, R., Neomagus, H. W. J. P.; Morpeth, L., Everson, R. C.; Mathews, J. P., Bunt, J. R. Pore development during gasification of South African inertinite-rich chars evaluated using small angle X-ray scattering. *Carbon* **2015**, 95, 250-260.

DOI: 10.1016/j.carbon.2015.08.030

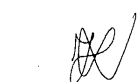
Coetzee, G. H.; Sakurovs, R., Neomagus, H. W. J. P., Everson, R. C.; Mathews, J. P., Bunt, J. R. Particle size influence on the pore development of nanopores in coal gasification chars: From micron to millimeter particles. *Carbon* **2017**, 112, 37-46.

DOI: 10.1016/j.carbon.2016.10.088.

(This letter of consent complies with rules **A5.4.2.8 and A.5.4.2.9** of the academic rules, as stipulated by the North-West University)



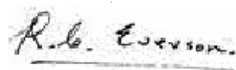
Richard Sakurovs



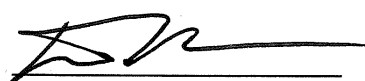
Hein. W. J. P. Neomagus



Leigh Morpeth



Raymond C. Everson



Jonathan P. Mathews



John R. Bunt

1/06/2019

Date

11/09/2019

Date

10/09/2019

Date

12/09/2019

Date

11/09/2019

Date

12/09/2019

Date

List of publications

Journal articles

Coetzee, G.H., Sakurovs, R., Neomagus, H.W.J.P., Morpeth, L., Everson, R.C., Mathews, J.P., Bunt, J.R. Pore development during gasification of South African inertinite-rich chars evaluated using small angle X-ray scattering. *Carbon* **2015**, 95, 250-60.

Coetzee, G. H., Sakurovs, R., Neomagus, H.W.J.P., Everson, R.C., Mathews, J.P., Bunt, J.R. Particle size influence on the pore development of nanopores in coal gasification chars: From micron to millimeter particles. *Carbon* **2017**, 112, 37-46.

Conference proceedings

Coetzee G.H. (presenter), Sakurovs R., Neomagus H.W.J.P., Bunt J.R., Morpeth L. SAXS measurements of pore development during steam and CO₂ gasification. Presented at 31st Annual International Pittsburgh Coal Conference, Pittsburgh, USA, October 6-9, 2014. (**Oral presentation**)

Coetzee G.H. (presenter), Neomagus H.W.J.P., Bunt J.R., Everson, R.C. The effect of particle size on CO₂ reactivity. Presented at 6th International Freiberg Conference on IGCC & XtL Technologie, Radebeul, Dresden, Germany, May 19-22, 2014. (**Oral presentation**)

Coetzee G.H. (presenter); Neomagus H.W.J.P.; Bunt J.R.; Everson R.C. Modeling the gasification of single large coal particles: CO₂ gasification reactivity. Presented at 18th Southern African Coal Science & Technology Indaba, Parys, South Africa, November 13-14, 2013. (**Oral presentation**)

Coetzee G.H. (presenter), Neomagus H.W.J.P., Bunt J.R., Everson, R.C. The influence of particle size on the steam gasification of coal. Presented at the International Conference on Coal Science and Technology, Oviedo, Spain, October 9-13, 2011. (**Oral presentation**)

Acknowledgements

The author would like to acknowledge and thank the following people/institutions for their involvement throughout the course of this study:

- Above all, praise and thanks to our Heavenly Father for His unabiding love and guidance, and for giving me the strength, encouragement, and insight when I needed it the most.
- My supervisors Professors Neomagus, Professor Everson and Professor Bunt, for their guidance, encouragement, and valuable insight throughout this investigation.
- Dr. Sakurovs and Dr. Morpeth for their valuable input regarding SAS and application thereof.
- Mrs. Botes and Mrs. Bekker for their assistance in anything related to administration. A special mention must be made to Mrs. De Koker, who passed away.
- Jan Kroeze, Adrian Brock, Ted Paarlberg, and Johan Broodryk for their technical assistance with experimental equipment.
- Koos Carstens and Gavin Hefer from Bureau Veritas Testing and Inspections South Africa for their assistance with all the characterisation analyses.
- Colleagues from the Coal Research Group for their insight and suggestions.
- My parents and sisters for their love and motivation.
- And lastly, my wife, Sansha, for her love, patience and encouragement, and for always believing in me.

The work presented in this thesis is based on research financially supported by the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation (NRF) of South Africa (Coal Research Chair Grant number 86880). Any opinion, finding, or conclusion or recommendation expressed in this material is that of the authors and the NRF does not accept any liability in this regard.

Abstract

In recent times, there is a strong drive towards the reduction and dependency of coal for the production of energy globally, and specifically in Europe and Japan. However, coal utilisation, includes gasification technology, will remain an important energy source in countries like China, India and South Africa for the coming decades. Environmental impact of coal utilisation is seen as the greatest driving force to reduce coal dependency and consumption, with optimisation of coal conversion technologies aimed at increasing technology efficiency and thereby minimising the environmental impact of the operation. The fundamental knowledge of the heterogeneous coal conversion processes is hereby pivotal in the retrofitting and design of clean coal technologies.

One aspect in the basic description of coal reaction processes is the change in the solid structure of coal as the carbonaceous material reacts. The changing solid structure is known to influence the carbon reactivity and also impacts internal mass transfer limitations, mostly studied in detail for powdered coal chars. Studies have predominantly focused on single reaction gases, where pore structure development is studied by both gas adsorption and mercury porosimetry techniques. It is hereby useful to combine results from different measuring techniques in order to evaluate a wider pore size range. However, the influence of time-temperature histories on the char behaviour and the dissimilarities between various techniques complicate the application of combining these methods. Small angle scattering techniques have been used to probe the pore structure of coal and char, with the main advantage of small angle scattering measurements probing a wide pore size range (from Ångström to millimetres) with a single experiment, mitigating the difficulties encountered when combining multiple measuring techniques required to evaluate a similar pore size range. A comprehensive study was therefore proposed to evaluate the pore development arising from CO₂ and steam gasification using SAXS measurements, focusing on evaluating the effect of reagent gas, particle size and temperature.

A typical inertinite rich South African coal with low ash values from the Witbank coalfield was selected, with the parent coal sample being a single source coal (Witbank seam 4) that was density separated at $< 1500 \text{ kg/m}^3$, with particle size $> 30 \text{ mm}$. A low ash coal was selected in order to reduce the influence of mineral matter on experimental results. A detailed coal sampling procedure was developed to prepare representative samples for parent coal characterisation, smaller particle samples and 20 mm particles from the 300 kg bulk sample. Parent coal characterisation results showed typical values for Witbank seam 4 washed coal,

specifically resulting in a low ash coal with high calorific value and petrographic classification as an inertinite-rich, medium rank C bituminous coal. A detailed char preparation procedure was developed to reduce the influence of charring parameters on experimental results. Char preparation was conducted at 1000°C and further processed using a detailed sampling procedure which resulted in a three particle size classification (75 µm, 2 and 20 mm). The resulting chars were characterised and generally, it is concluded that the chemical composition of the three particle sizes does not differ significantly. However, pore structure parameters obtained for different sized chars using low pressure CO₂ gas adsorption measurements show particle size dependent pore structure with an increase in micropore volume and surface area as char particle size increases.

Partially gasified chars were prepared in a thermogravimetric analyser for the three sized samples using steam and CO₂. The lowest gasification temperature (800°C for steam and 850°C for CO₂) was experimentally proven to be in the chemical reaction controlled regime for the smallest particle size. The highest gasification temperatures were chosen as 950 and 1000°C for steam and CO₂ gasification, to illustrate the effect of mass transfer limitations. Chars were partially converted to prepare samples with specific conversions of 10, 25, 35 and 50%, with a precise time required for each specified conversion.

The partially converted samples were scanned at the Australian Synchrotron in Melbourne using two detector positions, which resulted in a Q-range probed from $1.698 \cdot 10^{-3}$ to 0.8333 Å^{-1} and an assumed pore diameter between 0.25 and 147 nm. A novel ratio analysis technique was developed to study the pore development of individually sized pores from SAXS experimental data without requiring non-fractal pore modelling. Three separate ratios were specified from the SAXS data to compare results of different scans: scaled intensity (SI), intensity conversion ratio (ICR) and scaled conversion intensity ratio (SCIR). The scaled intensity allows direct comparison of changes in pore size distributions between samples. The ICR was calculated by dividing the scattering intensity of the gasified char at each Q by that of the unreacted char. The SCIR was calculated by dividing the scaled intensity of the gasified char with the scaled intensity of the char (at each Q). The proposed ratio analysis technique was used to qualitatively compare the relative extent to which the number of pores at different sizes grow, allowing multiple samples comparison, without requiring non-fractal modelling to determine pore volume and/or surface area..

The influence of reagent gas on the pore development was evaluated using partially gasified 75 μm chars. Comparing the trends observed using large lumped pore ranges (IUPAC) from SAXS results compares well to literature, with broadening of meso- and macropores from onset of CO_2 gasification being the only exception, likely to be maceral related. Further, steam shows greater development of pore structure for all conversions of 75 μm chars, with increased pore volume and surface area, compared to CO_2 . The ratio analysis results showed that, for both CO_2 and steam, size dependent pore growth rate. In particular, the intermediate pore sizes (between 1 and 40 nm) showed increased pore growth when compared to other pore sizes. Compared to CO_2 , steam gasification resulted in an increased pore growth of pore sizes between 1 and 40 nm. The ratio analysis technique further resulted in classification of critical cross over pore size, where the critical cross over pore size indicates at what size the pore generation rate is observed to be below the largest pore size. Comparison of the critical cross over pore size results for steam and CO_2 gasification showed that a smaller cross over pore size (0.6 nm for steam, compared to 1 nm for CO_2) and a smaller critical cross over value is observed for steam, which may be a direct consequence of the smaller kinetic diameter of water molecules.

It was also observed that particle size influenced the pore development of CO_2 gasified chars over the entire pore scale studied, specifically the development of micro- and macropores, which prevailed over the intermediate sized pores. For steam gasification, particle size only influenced the growth rate in the macropore range. For both the steam and the CO_2 gasified chars, larger particle sizes resulted in a decrease in growth rate for < 0.6 nm pores as well as an increase in critical cross over pore size. A novel application to evaluate the radial pore development of a 20 mm particle was developed, with the sampling spanning from the surface to the interior of the particle. The surface sample showed the greatest pore development over the entire pore range evaluated, followed by interior and centre. For both CO_2 and steam chars, the radial changes in growth rate for individual pore sizes confirmed intra-particle mass transfer limitations for 20 mm particles.

The results obtained during this study further demonstrates the advantages of using small angle scattering techniques over other techniques, due to increased pore size range and pore size resolution probed using a single measurement. Further, this study developed a novel ratio analysis technique to elucidate pore structure development of gasified char, with results showing different sized pores grow at different rates. The techniques developed here gave greater insight into dependence of reagent gas, with steam and CO_2 studied here, on pore

development of gasified chars. On a pore scale, the results for micropore surface area development suggest that reported trends (increased surface area development for steam compared to CO₂) are mainly due to differences in pore growth of pores smaller than 7 nm and could be a direct implication of the smaller kinetic diameter of water, compared to CO₂. The detailed evaluation also highlights the additional complexities that needs to be addressed in advanced dynamic single particle reaction modelling.

Keywords: SAXS, pore development, lump char, CO₂ and steam gasification, ratio analysis

Table of Contents

DECLARATION	II
PREFACE	III
STATEMENT FROM CO-AUTHORS	IV
LIST OF PUBLICATIONS	V
ACKNOWLEDGEMENTS	VI
ABSTRACT	VII
TABLE OF CONTENTS	XI
CHAPTER 1.	1
INTRODUCTION	1
1.1. INTRODUCTION AND MOTIVATION	2
1.2. AIM AND OBJECTIVES	7
1.3. SCOPE AND LIMITATIONS	7
1.4. OUTLINE OF THESIS	8
1.5. NOMENCLATURE	10
1.6. CHAPTER REFERENCES	11
CHAPTER 2.	14
COAL PROCUREMENT, AND COAL AND CHAR SAMPLE PREPARATION	14
2.1. COAL ORIGIN	15
2.2. COAL PROCUREMENT AND SAMPLE PREPARATION	17
2.3. PARENT COAL CHARACTERISATION	18
2.4. CHAR SAMPLE PREPARATION	21
2.5. CHAR CHARACTERISATION	23
2.6. NOMENCLATURE	26
2.7. CHAPTER REFERENCES	27
CHAPTER 3.	29
PARTIALLY CONVERTED CHAR SAMPLE PREPARATION AND GAS ADSORPTION MEASUREMENTS	29
3.1. INTRODUCTION	30
3.2. THERMOGRAVIMETRIC ANALYSER SETUP	30
3.3. EXPERIMENTAL PROCEDURE	31
3.4. DETERMINATION OF GASIFICATION DURATIONS	33
3.5. LOW PRESSURE CO ₂ GAS ADSORPTION OF PARTIALLY CONVERTED CHARS	35
3.6. NOMENCLATURE	39
3.7. CHAPTER REFERENCES	40

CHAPTER 4.	42
PORE DEVELOPMENT DURING GASIFICATION OF SOUTH AFRICAN INERTINITE-RICH CHARS EVALUATED USING SMALL ANGLE X-RAY SCATTERING	42
4.1. INTRODUCTION AND BACKGROUND	44
4.2. EXPERIMENTAL SECTION	45
4.3. RESULTS AND DISCUSSIONS	49
4.4. CONCLUSIONS	61
4.5. NOMENCLATURE	63
4.6. CHAPTER REFERENCES	64
CHAPTER 5.	71
PARTICLE SIZE INFLUENCE ON THE PORE DEVELOPMENT OF NANOPORES IN COAL GASIFICATION CHARS: FROM MICRON TO MILLIMETER PARTICLES	71
5.1. BACKGROUND AND INTRODUCTION	73
5.2. EXPERIMENTAL	74
5.3. RESULTS AND DISCUSSION	78
5.4. CONCLUSIONS	94
5.5. NOMENCLATURE	95
5.6. CHAPTER REFERENCES	96
CHAPTER 6.	101
CONCLUDING SUMMARY	101
6.1. CONCLUDING REMARKS	102
6.2. CONTRIBUTION TO SCIENCE	103
6.3. FUTURE PROSPECTS AND RECOMMENDATIONS	104
APPENDIX A	106
ADDITIONAL RESULTS	106
A.1 TEMPERATURE PROFILE OF FURNACE	107
A.2 TOTAL GAS FLOW INFLUENCE	107
A.3 SAMPLE SIZE INFLUENCE	108
A.4 OBSERVED REACTION REGIME FOR 75 μM	109

Chapter 1.

Introduction

A general introduction on the topic of pore development during coal conversion as well as the aims, objectives, and scope for this evaluation is discussed here.

1.1. Introduction and Motivation

Coal uses nowadays include power generation, steel production, cement manufacturing and utilisation in petro-chemical industries, with worldwide consumption of coal approximated at 5357 million tonnes for 2016. In 2016, for the first time since 1992, coal consumption showed a reduction in year-to-year use for two consecutive years [1]. The reduction in coal consumption is driven by lower natural gas prices, increase in renewable energy supply, increase in energy efficiency enhancements, and a drive towards improved air quality [1].

Coal utilisation technologies are based on fundamental principles of combustion, gasification, liquefaction, and carbonisation, where carbonisation is mainly applied in coke production for the metallurgical industry through thermal decomposition of coal [2-4]. Coal combustion, gasification, and liquefaction are mostly utilised in the power generation and petrochemical industries. The exothermic nature of the combustion of coal is used to generate heat, with the heat converted into high value energy sources such as electricity. In contrast, coal gasification is overall an endothermic process, and the main purpose of this conversion is the generation of synthesis gas, a precursor for a variety of fine and bulk chemicals. Due to the complex formation and structure of coal, utilisation of this fossil fuel is associated with atmospheric emissions such as CO_2 , SO_x , NO_x , H_2S , and Hg [3]. Although there is a global desire to reduce the use of coal, specifically in Europe and Japan, coal will remain an important energy source in the coming decades, with expected growth in countries like China and India [1]. In an attempt to reduce the environmental impact of coal, the optimisation strategies for coal conversion technologies, with emphasis on the reduction of the emissions of green-house gases and particulate matter, are studied intensively [3]. This is conducted in order to allow current coal dependent industries to continue operating even with the enforcement of stricter emission limits as described by COP24 laws [5]. Optimisation of coal conversion technologies is mainly aimed at increasing the efficiency of specific gas-solid reactions in order to maximise the production of heat and/or chemical species, as well as to reduce undesirable by-products, and thereby minimise the environmental impact of the operation. The fundamental knowledge of these heterogeneous coal conversion processes is hereby pivotal in the retrofitting and design of clean coal technologies [3,6].

As one of the pioneers in the theory of gas-solid heterogeneous reactions, Yagi and Kunii [7] proposed a multi-step fundamental reaction model to account for chemical species transfer between gas and solid phases. Yagi and Kunii [7] defined three layers for gas-solid reactions, with the first layer defined as the bulk gas phase where gas species characteristics do not

deviate. The second boundary layer is defined as a hypothetical gas film, which is defined as a thin film around the solid particle where the gas specie characteristics deviate from the bulk gas. The third and final layer for this gas-solid reaction model is defined as the porous solid. The steps, as developed by Yagi and Kunni [7], are:

- Mass transfer of the reaction gas from the bulk phase through the gas film, to the surface of the solid particle.
- Diffusion of the reaction gas through the pores of the particle.
- Chemical reaction between the gas and solid at the surface of the particle.
- Diffusion of the product gas through the pores to the exterior of the porous particle.
- Mass transfer of the product gas from the surface of the particle, through the gas film, to the bulk phase.

This multi-step reaction model for gas-solid reactivity has evolved into a traditional reactor theory classification, with the overall reaction rate dependent on all three regimes. Generally, one elemental step will limit the rate of the other steps, which is recognised as the rate-controlling or rate-limiting step [8,9]. Where chemical reaction for gas-solid is known to be the rate-limiting step, the process is in Regime I [8,9]. Regime II is associated with conversions where intra-particle mass transfer determines the observed reaction rate, whereas Regime III represents reactions where external mass transfer through the gas film has the largest influence on the observed conversion rate [8,9]. For gas-solid coal reactions, it has been found that variables such as parent coal characteristics, char preparation conditions, char characteristics, particle size, and process conditions influence the rate-limiting step [10-16].

The reaction rate for coal char reactions in Regime I has been studied extensively for coals from different regions globally, using a variety of process conditions [17-33]. The results for Regime I reaction rates have been used to develop numerous reaction models, either kinetic or structural, aimed at predicting conversion trends. Kinetic models apply fundamental reactor theory principles to gas-solid systems to mathematically predict conversion trends, which includes shrinking core, volumetric, Wen, and Langmuir Hinshelwood models [34-36]. Structural models were developed to generate mathematical approximations to describe solid structures by including porosity, surface area and pore size. The structural parameters are incorporated with fundamental reactor theory principles to predict solid structure change as conversion progresses, and includes models such as capillary and random pore models [37-41]. Extensive research has also been conducted on Regime II gas-solid reactivity, with the

majority of research focusing on catalytic systems. Observed reaction rates, which are characterised by Regime II and consequently influenced by intra-particle mass transfer, can be described by Regime I reactivity and the Thiele modulus [34-36]. In the Thiele modules concept, fundamental mass and reactivity principles are used to obtain an effectiveness factor. This factor is used to determine the influence of internal mass transfer limitations on the overall observed reaction rate using intrinsic kinetics for gas-solid reactions. One of the assumptions of the original Thiele modules concept is that the solid structure remains unchanged as conversion progresses, which is valid for catalytic gas-solid reactions [34-36]. However, for coal char conversions, this assumption does not hold, since the structure changes when carbonaceous material is reducing as the conversion progresses [31,42,43].

A significant amount of studies have recognised that there is a correlation between reactivity and the char's structural changes during conversion [31,44-48]. The solid structural changes are generally ascribed to changes in pore structure and therefore often evaluated using porosity, surface area, and pore size distribution measurements. It has been shown that surface area increases to a maximum as conversion progresses, where after a steady decrease in surface area is observed until conversion is complete [31,44-48]. The influence of char solid structure on reactivity has resulted in the development of numerous different measurement techniques to determine solid structure parameters. Due to the complex nature of the coal solid structure, multiple measurement techniques are combined to fully characterise the structure, including gas adsorption, mercury intrusion porosimetry, optical surface and small angle scattering [49-51]. Gas adsorption, using CO₂, N₂ and Ar, is mostly used to determine coal char structures, and is based on adsorption of the gas onto the solid structure, with the relative pressure varied and the adsorbed volume measured. A wide pore size distribution can be determined when combining the results for different adsorbed gases. Mercury intrusion porosimetry involves the intrusion of mercury (non-wetting liquid for coal) into the pores using force, where the pore size penetrated is inversely proportional to the amount of force applied to the non-wetting liquid. Combining the results from gas adsorption and mercury intrusion has extensively been used to obtain pore size distributions ranging from Ångström to millimetres [49,52,53]. While useful, the influence of time-temperature histories on the char behaviour, as well as the dissimilarities between different techniques, complicate the application of combining different methods to determine pore size variations due to gasification. Small angle scattering techniques have been proven to mitigate these difficulties, which further also include accessibility of ultrafine pores of molecular sizes and enclosed pores, by probing a wide pores size range using a single measurement [52,53].

Small angle scattering (SAS) involves the measurement of scattering strength and deflection trajectory of an energy beam from the probed sample. The energy beam is focused and aimed at the sample and deflected from the straight trajectory as it passes through the sample. The beam energy is measured at set increments of trajectory deflection angles and converted to intensity and scattering vector [54,55]. The energy beam can consist of neutrons (Small angle neutron scattering, SANS) or fixed wavelength electrons (Small angle X-ray scattering, SAXS), with neutron scattering probing the nuclei scattering cross section and X-ray scattering probing fluctuations in electron density. Small angle scattering has been used to study the size, shape and orientation of structures ranging from nano-particles to larger protein structures, where coal pore structure is studied over a wide pore size range, from Angstrom to millimetre in size [49,54-56]. A summary of the research conducted on pore development during gasification, using Small Angle Scattering, is shown in Table 1.1.

Table 1.1: Summary of research on the pore development during carbon conversion using SAS.

Reference	Source	Reagent	Temperature (°C)	Analysis
Bale <i>et al.</i> [57]	Lignite	O ₂	240	SAXS
Calo <i>et al.</i> [58]	Subbituminous coal & Phenolic resin char	O ₂	400, 470	SANS with contrast matching
Calo <i>et al.</i> [59]	Saran char, raw and calcium-loaded cellulose	O ₂	340, 425, 560	SAXS
Antxustegi <i>et al.</i> [60]	Argonne Premium Pittsburgh No. 8	O ₂	400	SANS with contrast matching
Diduszko <i>et al.</i> [61]	Activated carbon (hard coal)	Steam	-	SAXS, benzene adsorption
Foster and Jensen [62]	Anthracite	CO ₂	825	SAXS
Foster and Jensen [63]	Carbosieve-S	CO ₂	825	SAXS
Pfeifer <i>et al.</i> [64]	Olive stone	Steam	750	SAXS
Luo <i>et al.</i> [65]	5 types of coal	CO ₂	400 - 1000	SAXS

Relating to pore development, Diduszko *et al.* [61] and Pfeifer *et al.* [64] reported that steam gasification yields an increase in all pore sizes from the onset of gasification, whereas CO₂ gasification produces a narrow micropore structure with broadening of microporosity only observed after long activation periods. Calo *et al.* [58] used a modified thermogravimetric analyser (TGA), allowing a SAXS beam to pass through the sample inside the TGA resulting in transient measurements. The pore development of Saran char, cellulose and calcium-loaded cellulose was determined during oxygen activation, with a change in mesoporosity only

observed at extended conversions. The opposite trend was observed for microporosity development with an initial large development at low conversions.

Calo *et al.* [59], and Foster and Jensen [62,63] studied the pore development during combustion and gasification of char, respectively. Calo *et al.* [59] used SANS and a contrast matching technique to evaluate the development of open, accessible to reagent gas, and closed (inaccessible to reagent gas) pores during oxygen activation. Small angle scattering, unlike gas adsorption and mercury porosimeter, probes both open and closed pores, with closed pores not kinetically participating at initial conversions. Calo *et al.* [59] determined mesoporosity to be mostly accessible pores, with small changes in distribution as conversion proceeded. Compared to mesoporosity, the microporosity was found to be mostly closed pores which opened during conversion [59]. Foster and Jensen [62] studied the pore development of Primrose anthracite and Carbosieve-S for chemical reaction controlled CO₂ gasification at 825°C. As conversion progressed, an increase in macro-, meso- and micropores was observed, however, it was found that micropore development was greater than that of macro- and mesopores. The difference in pore development reported above [57-65] could be due to variation in char preparation, gasification temperature (ranging from 240 to 1000 °C) and initial char structure of different carbonaceous material used.

The results for these studies demonstrated the advantages of using SAS to evaluate pore development in char and gasified char, with a single measurement probing a wide range of pore sizes (from Ångström to millimetres). The authors noted only a few studies have used SAS to evaluate pore growth during gasification, with no systematic approach to evaluate the influence of particle size on pore development during gasification.

1.2. Aim and objectives

The aim of this study is to evaluate the influence of particle size on char pore structure development during CO₂ and steam gasification of a typical South African coal. The specific objectives for this evaluation were to:

- Prepare partially converted chars using either CO₂ or steam as gasification reagent and determine the micropore volume and surface area.
- Evaluate the influence of gasification reagent and temperature on pore development of partially converted powder char, using SAXS measurements.
- Evaluate the influence of particle size on pore development of partially converted char, using SAXS measurements.
- Investigate radial pore development of lump char particles using SAXS measurements.

The evaluation here further intends to contribute to the understanding of fundamental pore structure development during char gasification, over a wide pore size range. The findings observed could additionally be used to advance previously developed pore structure models, *i.e.* capillary and random pore models, which could consequently be applied to optimise clean coal technology.

1.3. Scope and limitations

The scope of this study was developed to ensure that the objectives are met and to guide the research process. Firstly, a low ash South African coal is identified, and a bulk sample procured. A structured sampling procedure is executed to obtain representative coal samples for parent coal characterisation, small particle sizes and lump coal particles. The representative samples are charred at 1000°C, with charred particles further processed to obtain 3 fractions in the size range of powders (75 µm), medium sized char (2 mm) and lump particles (20 mm). Representative samples for parent coal, and the various sized char fractions are then characterised using chemical, mineralogy, and petrographic analysis respectively.

Partially converted chars for the three selected particle sizes are prepared using a thermogravimetric analyser, with required time for specific conversion experimentally determined. The micropore volume and surface area is determined using low pressure CO₂ gas adsorption measurements, with results used to calibrate SAXS measurements due to complex, non-fractal structure observed for chars and partially converted chars.

Prepared char and partially converted char samples are mounted for SAXS measurements, with measurements done at the Australian Synchrotron in Melbourne. Data is then processed using Scatterbrain 2.3, Irena 2.56 and Matlab software, and novel ratio analysis methods (SI, ICR and SCIR) are developed to allow interpretation of SAXS measurements using scatter intensity data only, without requiring non-fractal modelling.

The influence of CO₂ and steam as gasification reagent on pore development of powder coal chars is firstly evaluated, with the influence of temperature and particle size to follow. A novel application of radial SAXS measurement will be implemented to allow the evaluation of radial pore development for large char particles. The limitations listed are aimed to keep the scope focused on the fundamental evaluation of pore development during gasification, where limitations could be explored in future studies. The following factors were excluded for consideration:

- Influence of mineral matter on pore development and SAXS measurements.
- Lowest gasification temperature samples for 20 mm particles due to sample preparation reaction times being too long for practical purposes.
- Influence of inert gas on pore development during charring and gasification.
- Conversion above 50%.
- Detailed reactivity evaluation and modelling thereof.

1.4. Outline of thesis

This thesis consists of 6 chapters, where a concise and detailed literature overview is given in Chapter 1, which also forms the motivation of the study. Further, comprehensive, subject-relevant literature summaries are presented in the introductory sections of Chapter 4 and 5.

Coal procurement, and coal and char preparation are detailed in Chapter 2, with characterisation results for coal and different sized chars also discussed. The preparation of partially converted chars is given in Chapter 3, specifically describing experimental equipment, experimental procedures and determination of time required for partially converted chars. A pore structure parameter characterisation for the partially converted chars using low pressure CO₂ gas adsorption measurements is also given.

The evaluation of pore development during gasification of a typical South African char is presented in Chapter 4, using SAXS measurements. Emphasis is placed on comparing the

influence of gasification reagent on pore structure development on a pore scale, for a wide pore size range. Moreover, the results in Chapter 3 are incorporated with the SAXS results to quantitatively study pore development of powder chars. The novel developed techniques are presented in Chapter 4 and are used to evaluate the influence of a wide particle size range on the pore development during gasification, which is reported in Chapter 5. In Chapter 5, details of the radial pore development of lump partially converted char particles using SAXS measurements are discussed.

The conclusions, contributions to science, and prospects are presented in Chapter 6.

1.5. Nomenclature

Abbreviations

ICR– Intensity conversion ratio

NO_x- Nitrogen oxides

SAS- Small Angle Scattering

SANS- Small Angle Neutron Scattering

SAXS- Small Angle X-ray Scattering

SCIR- Scaled conversion intensity ratio

SI- Scaled intensity ratio

SO_x- Sulphur oxides

TGA-Thermogravimetric analyser

1.6. Chapter References

- [1] Sadamori K. Coal 2017: Analysis and Forecasts to 2022- executive summary. New Delhi India. 2017.
- [2] Grainger L, Gibson J. Coal Utilisation: Technology, Economics and Policy. Berlin: Springer Science & Business Media, 2012.
- [3] Miller BG. Clean Coal Engineering Technology. Burlington, MA : Elsevier Science, 2016.
- [4] Suarez-Ruiz I, Rubiera F, Diez MA. New Trends in Coal Conversion: Combustion, Gasification, Emissions, and Coking. Cambridge, MA: Elsevier Science, 2018.
- [5] www.worldcoa.org. WCA's engagement at COP24 in Katowice. Date visited: 15 Decemeber 2018. <https://www.worldcoal.org/wca%E2%80%99s-engagement-cop24-katowice>.
- [6] Higman C, Van Den Bergt M. Gasifiation. 2nd Ed. Berlington: MA, Gulf professional publishinh, 2011.
- [7] Yagi S, Kunii D. Studies on combustion of carbon particles in flames and fluidized beds. Symp Int Combust 1955;5:231-44, [https://doi.org/10.1016/S0082-0784\(55\)80033-1](https://doi.org/10.1016/S0082-0784(55)80033-1).
- [8] Wicke E, Fetting F. Wärmeübertragung in Gaswirbelschichten. Chemie Ingenieur Technik 1954;26(5):301-10. <https://doi.org/10.1002/cite.330310502>.
- [9] Walker PL, Rusinko F, Austin LG. Gas reactions of carbon. Advan Catal 1959;11:133-221, [https://doi.org/10.1016/S0360-0564\(08\)60418-6](https://doi.org/10.1016/S0360-0564(08)60418-6).
- [10] Tamhankar SS, Hasatani M, Wen CY. Kinetic studies on the reactions involved in the hot gas desulfurization using a regenerable iron oxide sorbent—I: Reduction and sulfidation of iron oxide. Chem Eng Sci 1981;36:1181-91, [https://doi.org/10.1016/0009-2509\(81\)85066-X](https://doi.org/10.1016/0009-2509(81)85066-X).
- [11] Tyler RJ, Schafer HNS. Flash pyrolysis of coals: influence of cations on the devolatilization behaviour of brown coals. Fuel 1980;59:487-94, [https://doi.org/10.1016/0016-2361\(80\)90175-1](https://doi.org/10.1016/0016-2361(80)90175-1).
- [12] Scaroni AW, Walker PL, Essenhigh RH. Kinetics of lignite pyrolysis in an entrained-flow, isothermal furnace. Fuel 1981;60:71-6, [https://doi.org/10.1016/0016-2361\(81\)90035-1](https://doi.org/10.1016/0016-2361(81)90035-1).
- [13] Yeasmin H, Mathews JF, Ouyang S. Rapid devolatilisation of Yallourn brown coal at high pressures and temperatures. Fuel 1999;78:11-24, [https://doi.org/10.1016/S0016-2361\(98\)00119-7](https://doi.org/10.1016/S0016-2361(98)00119-7).

-
- [14] Alonso MJG, Borrego AG, Alvarez D, Menéndez R. Pyrolysis behaviour of pulverised coals at different temperatures. *Fuel* 1999;78:1501-13, [https://doi.org/10.1016/S0016-2361\(99\)00081-2](https://doi.org/10.1016/S0016-2361(99)00081-2).
- [15] Cai H-Y, Megaritis A, Messenböck R, Dix M, Dugwell DR, Kandiyoti R. Pyrolysis of coal maceral concentrates under pf-combustion conditions (I): changes in volatile release and char combustibility as a function of rank. *Fuel* 1998;77:1273-82, [https://doi.org/10.1016/S0016-2361\(98\)00039-8](https://doi.org/10.1016/S0016-2361(98)00039-8).
- [16] Cetin E, Moghtaderi B, Gupta R, Wall TF. Influence of pyrolysis conditions on the structure and gasification reactivity of biomass chars. *Fuel* 2004;83:2139-50, <https://doi.org/10.1016/j.fuel.2004.05.008>.
- [17] Yang Y, Watkinson AP. Gasification reactivity of some Western Canadian coals. *Fuel* 1994;73:1786-91. [https://doi.org/10.1016/0016-2361\(94\)90169-4](https://doi.org/10.1016/0016-2361(94)90169-4).
- [18] Lee WJ, Kim SD. Catalytic activity of alkali and transition metal salt mixtures for steam-char gasification. *Fuel* 1995;74:1387-93. [https://doi.org/10.1016/0016-2361\(95\)00081-F](https://doi.org/10.1016/0016-2361(95)00081-F).
- [19] Feng B, Bhatia SK. Variation of the pore structure of coal chars during gasification. *Carbon* 2003;41:507-23, [https://doi.org/10.1016/S0008-6223\(02\)00357-3](https://doi.org/10.1016/S0008-6223(02)00357-3).
- [20] Everson RC, Neomagus HWJP, Kasaini H, Njapha D. Reaction kinetics of pulverized coal-chars derived from inertinite-rich coal discards: Gasification with carbon dioxide and steam. *Fuel* 2006;85:1076-82, <https://doi.org/10.1016/j.fuel.2005.10.016>.
- [21] Wu S, Gu J, Li L, Wu Y, Gao J. The reactivity and kinetics of Yanzhou coal chars from elevated pyrolysis temperatures during gasification in steam at 900–1200 °C. *Process Saf Environ Prot* 2006;84:420-8, <https://doi.org/10.1205/psep06031>.
- [22] JAFFRI G, ZHANG J. Catalytic gasification of Pakistani Lakhra and Thar lignite chars in steam gasification. *J Fuel Chem and Technol* 2009;37:11-9, [https://doi.org/10.1016/S1872-5813\(09\)60009-8](https://doi.org/10.1016/S1872-5813(09)60009-8).
- [23] Matsuoka K, Kajiwarra D, Kuramoto K, Sharma A, Suzuki Y. Factors affecting steam gasification rate of low rank coal char in a pressurized fluidized bed. *Fuel Process Technol* 2009;90:895-900, <https://doi.org/10.1016/j.fuproc.2009.04.001>.
- [24] Hanson S, Patrick JW, Walker A. The effect of coal particle size on pyrolysis and steam gasification. *Fuel* 2002;81:531-7, [https://doi.org/10.1016/S0016-2361\(01\)00153-3](https://doi.org/10.1016/S0016-2361(01)00153-3).

-
- [25] Ye DP, Agnew JB, Zhang DK. Gasification of a South Australian low-rank coal with carbon dioxide and steam: kinetics and reactivity studies. *Fuel* 1998;77:1209-19, [https://doi.org/10.1016/S0016-2361\(98\)00014-3](https://doi.org/10.1016/S0016-2361(98)00014-3).
- [26] Zhu W, Song W, Lin W. Effect of the coal particle size on pyrolysis and char reactivity for two types of coal and demineralized coal. *Energy Fuels* 2008;22:2482-7, <https://doi.org/10.1021/ef800143h>.
- [27] Huang J, Watkinson AP. Coal gasification in a stirred bed reactor. *Fuel* 1996;75:1617-24, [https://doi.org/10.1016/S0016-2361\(96\)00133-0](https://doi.org/10.1016/S0016-2361(96)00133-0).
- [28] Liu G, Benyon P, Benfell KE, Bryant GW, Tate AG, Boyd RK *et al.* The porous structure of bituminous coal chars and its influence on combustion and gasification under chemically controlled conditions. *Fuel* 2000;79:617-26, [https://doi.org/10.1016/S0016-2361\(99\)00185-4](https://doi.org/10.1016/S0016-2361(99)00185-4).
- [29] Kapteijn F, Peer O, Moulijn JA. Kinetics of the alkali carbonate catalysed gasification of carbon: 1. CO₂ gasification. *Fuel* 1986;65:1371-6, [https://doi.org/10.1016/0016-2361\(86\)90107-9](https://doi.org/10.1016/0016-2361(86)90107-9).
- [30] Li Q, Zhao C, Chen X, Wu W, Li Y. Comparison of pulverized coal combustion in air and in O₂/CO₂ mixtures by thermo-gravimetric analysis. *J Anal Appl Pyrolysis* 2009;85:521-8, <https://doi.org/10.1016/j.jaap.2008.10.018>.
- [31] Kim YT, Seo DK, Hwang J. Study of the effect of coal type and particle size on char CO₂ gasification via gas analysis. *Energy Fuels* 2011;25:5044-54, <https://doi.org/10.1021/ef200745x>.
- [32] Chin G, Kimura S, Tone S, Otake T. Gasification of coal char with steam. part 3. effect of potassium carbonate catalyst on the rate of gasification. *Int Chem Eng* 1984;24:346-54.
- [33] Kovacic G, Chambers A, Özüm B. CO₂ gasification kinetics of two Alberta coal chars. *Can J Chem Eng* 1991;69:811-5, <https://doi.org/10.1139/v91-120>.
- [34] Fogler HS. *Elements of Chemical Reaction Engineering*. 4th ed. New York: Prentice Hall PTR; 2006.
- [35] Levenspiel O. *Chemical Reaction Engineering*. 3rd ed. New York: Wiley; 1999.
- [36] Szekely J. *Gas-Solid Reactions*. 4th ed. Saint Louis : Elsevier Science, 2014.
- [37] Petersen EE. Reaction of porous solids. *AIChE J* 1957;3:443-8, <https://doi.org/10.1002/aic.690030405>.

-
- [38] Hashimoto K, Silveston PL. Gasification: Part I. Isothermal, kinetic control model for a solid with a pore size distribution. *AIChE J* 1973;19:259-68, <https://doi.org/10.1002/aic.690190209>.
- [39] Bhatia SK, Perlmutter DD. A random pore model for fluid-solid reactions: I. Isothermal, kinetic control. *AIChE J* 1980;26:379-86, <https://doi.org/10.1002/aic.690260308>.
- [40] Gavals GR. A random capillary model with application to char gasification at chemically controlled rates. *AIChE J* 1980;26:577-85, <https://doi.org/10.1002/aic.690260408>.
- [41] Fernández AM, Barriocanal C, Alvarez R. The effect of additives on coking pressure and coke quality. *Fuel* 2012;95:642-7, <https://doi.org/10.1016/j.fuel.2011.11.046>.
- [42] Grigore M, Sakurovs R, French D, Sahajwalla V. Coke gasification: The influence and behavior of inherent catalytic mineral matter. *Energy Fuels* 2009;23:2075-85, <https://doi.org/10.1021/ef8006728>.
- [43] Kim R, Hwang C, Jeon C. Kinetics of coal char gasification with CO₂: Impact of internal/external diffusion at high temperature and elevated pressure. *Appl Energy* 2014;129:299-307, <https://doi.org/10.1016/j.apenergy.2014.05.011>.
- [44] Kajitani S, Hara S, Matsuda H. Gasification rate analysis of coal char with a pressurized drop tube furnace. *Fuel* 2002;81:539-46, [https://doi.org/10.1016/S0016-2361\(01\)00149-1](https://doi.org/10.1016/S0016-2361(01)00149-1).
- [45] Dhaneswar SR, Pisupati SV. Oxy-fuel combustion: The effect of coal rank and the role of char-CO₂ reaction. *Fuel Process Technol* 2012;102:156-65, <https://doi.org/10.1016/j.fuproc.2012.04.029>.
- [46] Sircar I, Sane A, Wang W, Gore JP. Experimental and modeling study of pinewood char gasification with CO₂. *Fuel* 2014;119:38-46, <https://doi.org/10.1016/j.fuel.2013.11.026>.
- [47] Sing KSW. Characterization Of Porous solids: An introductory survey. *Studies in Surf Sci Catal* 1991;62:1-9, [https://doi.org/10.1016/S0167-2991\(08\)61303-8](https://doi.org/10.1016/S0167-2991(08)61303-8).
- [48] Enke D, Friedel F, Janowski F, Hahn T, Gille W, Müller R *et al*. Ultrathin porous glass membranes with controlled texture properties. *Surf Sci Catal* 2002;144:347-54, [https://doi.org/10.1016/S0167-2991\(02\)80154-9](https://doi.org/10.1016/S0167-2991(02)80154-9).
- [49] Okolo GN, Everson RC, Neomagus HWJP, Roberts MJ, Sakurovs R. Comparing the porosity and surface areas of coal as measured by gas adsorption, mercury intrusion and SAXS techniques. *Fuel* 2015;141:293-304, <https://doi.org/10.1016/j.fuel.2014.10.046>.

- [50] Roess LC. A simple method of obtaining a particle mass distribution by inverting the X-Ray intensity scattered at small angles. *J Chem Phys* 1946;14:695-7, <https://doi.org/10.1063/1.1724086>.
- [51] Roess LC, Shull CG. X-Ray scattering at small angles by finely-divided solids. II. Exact Theory for Random Distributions of Spheroidal Particles. *J Appl Phys* 1947;18:308-13, <https://doi.org/10.1063/1.1697651>.
- [52] Şenel İG, Gürüz AG, Yücel H, Kandas AW, and Sarofim AF, Characterization of pore structure of Turkish coals. *Energy Fuels*, 2001. 15(2):331-338, <https://doi.org/10.1021/ef000081k>.
- [53] Mares TE, Radliński AP, Moore TA, Cookson D, Thiyagarajan P, Ilavsky J, and Klepp J, Assessing the potential for CO₂ adsorption in a subbituminous coal, Huntly Coalfield, New Zealand, using small angle scattering techniques. *Int J Coal Geol*, 2009. 77(1-2):54-68, <https://doi.org/10.1016/j.coal.2008.07.007>.
- [54] Cohaut N, Blanche C, Dumas D, Guet JM, Rouzaud JN. A small angle X-ray scattering study on the porosity of anthracites. *Carbon* 2000;38:1391-400, [https://doi.org/10.1016/S0008-6223\(99\)00274-2](https://doi.org/10.1016/S0008-6223(99)00274-2).
- [55] Radliński AP, Mastalerz M, Hinde AL, Hainbuchner M, Rauch H, Baron M *et al.* Application of SAXS and SANS in evaluation of porosity, pore size distribution and surface area of coal. *Int J Coal Geol* 2004;59:245-71, <https://doi.org/10.1016/j.coal.2004.03.002>.
- [56] Radliński AP, Busbridge TL, Gray EMA, Blach TP, Cookson DJ. Small angle X-ray scattering mapping and kinetics study of sub-critical CO₂ sorption by two Australian coals, *Int J Coal Geol* 2009;77:80-9. <https://doi.org/10.1016/j.coal.2008.09.015>.
- [57] Bale HD, Carlson ML, Kalliat M, Kwak CY, Schmidt PW. Small-Angle X-Ray scattering of the submicroscopic porosity of some low-rank coals. *Am Chem Soc*; 1984, p. 79-94.
- [58] Calo JM, Hall PJ, Antxustegi M. Carbon porosity characterization via small angle neutron scattering. *Colloids Surf Physicochem Eng Aspects* 2001;187–188:219-32, [https://doi.org/10.1016/S0927-7757\(01\)00635-5](https://doi.org/10.1016/S0927-7757(01)00635-5).
- [59] Calo JM, Hall PJ, Houtmann S, Castello DL, Winans RE, Seifert S. “Real time” determination of porosity development in carbons: a combined SAXS/TGA approach. *Sur Sci Catal* 2002;144:59-66, [https://doi.org/10.1016/S0167-2991\(02\)80220-8](https://doi.org/10.1016/S0167-2991(02)80220-8).

- [60] Antxustegi MM, Hall PJ, Calo JM. Development of Porosity in Pittsburgh No. 8 Coal Char as investigated by contrast-matching small-angle neutron scattering and gas adsorption techniques. *Energy Fuels* 1998;12:542-6, <https://doi.org/10.1021/ef970153g>.
- [61] Diduszko R, Swiatkowski A, Trznadel BJ. On surface of micropores and fractal dimension of activated carbon determined on the basis of adsorption and SAXS investigations. *Carbon* 2000;38:1153-62, [https://doi.org/10.1016/S0008-6223\(99\)00236-5](https://doi.org/10.1016/S0008-6223(99)00236-5).
- [62] Foster MD, Jensen KF. Small angle X-ray scattering investigations of pore structure changes during coal gasification. *Fuel* 1990;69:88-96, [https://doi.org/10.1016/0016-2361\(90\)90263-P](https://doi.org/10.1016/0016-2361(90)90263-P).
- [63] Foster MD, Jensen KF. SAXS investigation of model carbon pore structure and its change with gasification. *Carbon* 1991;29:271-82, [https://doi.org/10.1016/0008-6223\(91\)90077-V](https://doi.org/10.1016/0008-6223(91)90077-V).
- [64] Pfeifer, P., Ehrburger-Doller, F., Rieker, T., Schmidt, P. W., Voss, D.J., Rodriguez-Reinoso, F., Molina-Sabio, M and Gonzalez, M.T. Fractal networks of carbon nanopores. *Carbon conference Proceedings – 23rd Biennial Conference* 1997;23.
- [65] Luo L, Liu J, Zhang Y, Zhang H, Ma J, You Y *et al.* Application of small angle X-ray scattering in evaluation of pore structure of superfine pulverized coal/char. *Fuel* 2016;185:190-8, <https://doi.org/10.1016/j.fuel.2016.07.111>.

Chapter 2.

Coal procurement, and coal and char sample preparation

Coal origin and procurement is discussed in this chapter, along with a detailed outline of the coal and char sampling process and characterisation.

2.1. Coal origin

Large scale coal deposits were first discovered in South Africa by George William Stow in 1879 [1]. In Figure 2.1, the known commercially viable coalfields of South Africa are shown [2]:

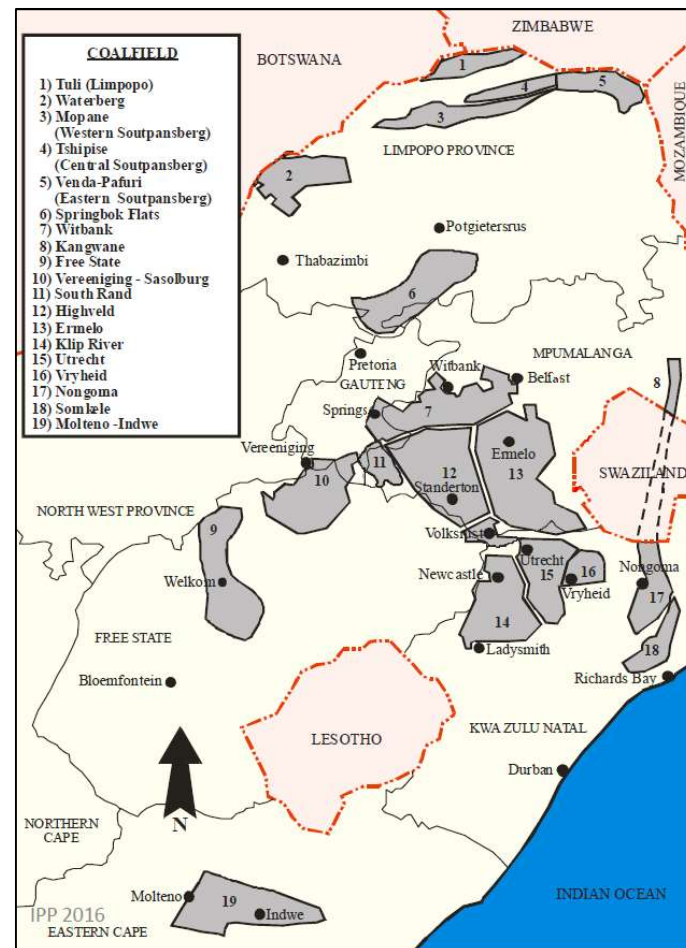


Figure 2.1: Coalfields of South Africa (taken from [2]).

In Figure 2.1, it is observed that most of the coalfields are in the northern part of South Africa, with most (7, 10 - 16) located in the central basin. The Witbank coalfield (coalfield 7 in Figure 2.1) is responsible for 40% of the total coal production in South Africa and is widely reported as South Africa's most important coalfield [3]. In Figure 2.2, the composite stratigraphic columns of the 5 seams of coal found in the Witbank coalfield are given [4].

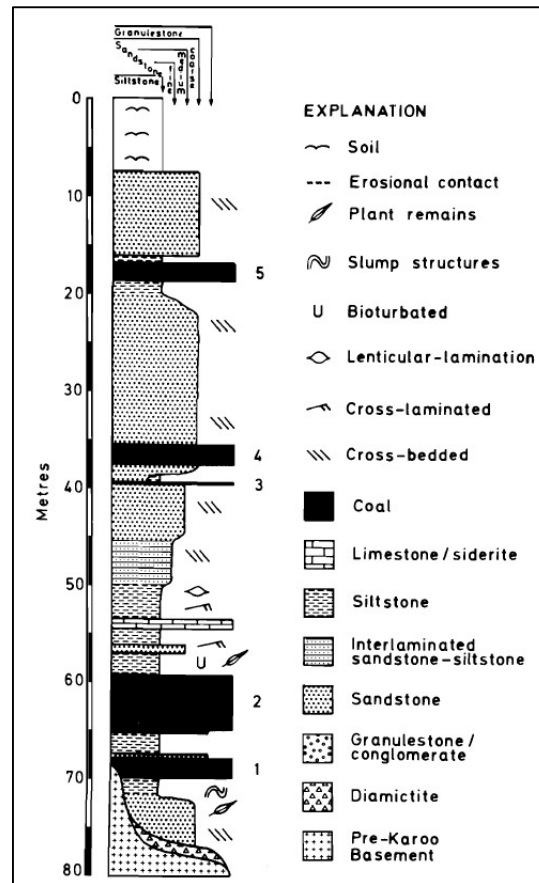


Figure 2.2. Composite stratigraphic columns of Witbank coalfields (taken from[4]).

The Witbank coalfield is more complex in some areas, which is not apparent in Figure 2.2, with seam-splitting observed for seam 1, seam 2 and seam 4, while the seams in other areas are completely eroded [4]. Seam 2 is the most mined seam due to greater seam stability and thickness, with seam 4 also mined extensively in the Witbank coalfield. Seam 1 and 5 are mined to a lesser extent, with this coal mined and processed mainly for the metallurgical industry [1]. In general, coals from the Witbank area have a low sulphur content (< 1 wt%) [5], low phosphorous content [6], are inertinite-rich [7-9] and have high ash values (up to 40 wt%) [1].

Coal with a low mineral matter content was selected for this study, to reduce the influence of mineral matter on pore development. A typical South African coal with low ash, from the Witbank coalfield, was selected using characterisation results from Bulletin 114 [10].

2.2. Coal procurement and sample preparation

Witbank Seam 4 coal is continuously mined at the Umlalazi mini-pit and sent to Landau colliery for processing, where the coal is crushed, screened and density separated. The coal mined at Umlalazi is processed specifically to produce export quality steam coal, resulting in coarse coal particles with low amounts of mineral matter. For this study, a 300 kg belt-cut sample of + 30 mm coal particles (density < 1500 kg/m³) was selected, with the product specified as small nuts of grade A steam coal. The 300 kg sample was transported in 220 L plastic drums to Potchefstroom, North West Province, where it was stored in a nitrogen atmosphere until further processing. In Figure 2.3, a detailed schematic of coal sample selection and preparation is shown.

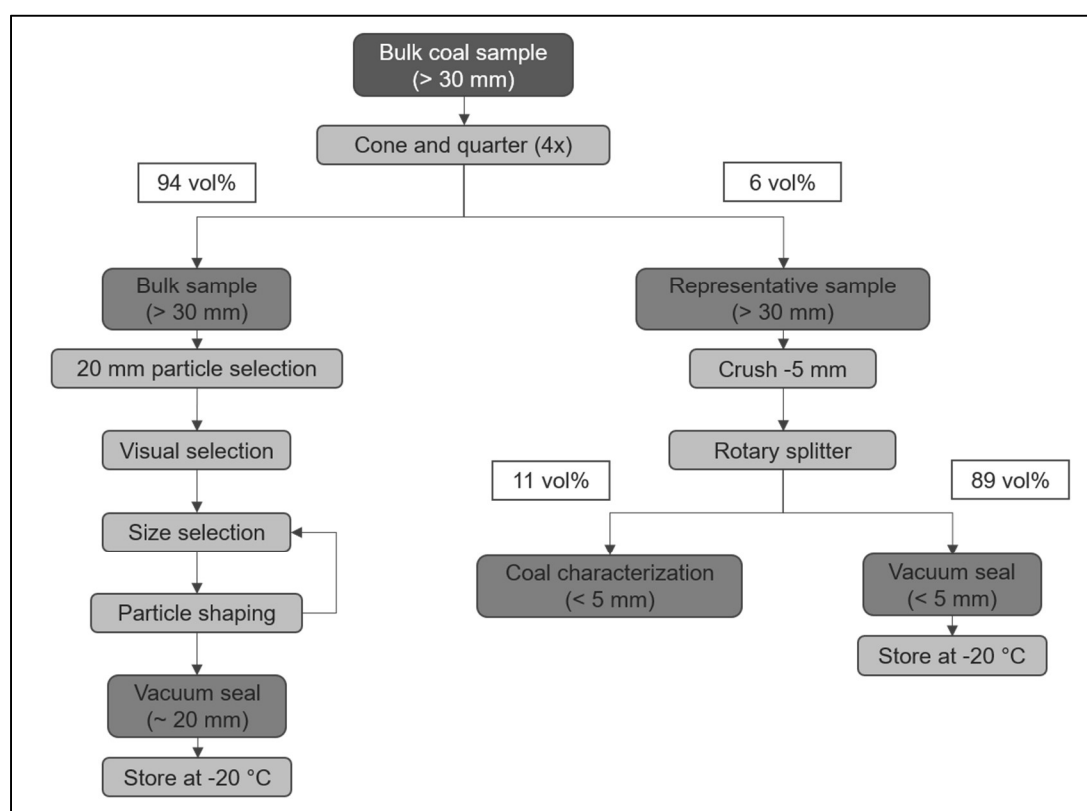


Figure 2.3: Coal sample selection and preparation.

The 300 kg coal sample was cone and quartered (as described in ASTM D2013-72) 4 times to obtain an ~ 18kg representative sample (> 30 mm), where the smaller representative sample of the bulk coal was used for coal characterisation and experimental samples. The sample was crushed in a gyratory crusher (Samuel Osborne (SA) LTD, Model: 66YROLL), with mill gap set to produce an average particle size of < 5 mm. The crushed sample was further split using a 6-sample rotary riffle splitter. Representative samples (18 kg, < 5 mm)

were loaded into the hopper (~ 3 kg hopper) and split into 6 equal volume samples. Diagonally opposite samples were mixed and kept separate, with the procedure repeated until the entire representative sample was split into 3 equal volume samples (~ 6 kg). The process was repeated for each 6 kg sample to obtain a total of 9 representative samples of equal volume, approximately 2 kg in weight. Each sample was vacuum sealed and refrigerated at - 20°C.

Single 20 mm coal samples were hand selected from the remaining bulk sample (Figure 2.3), with particles selected based on visual, dimensional and shape criteria. Single coal particles were firstly screened based on visual appearance, where particles with a bright appearance and no visible mineral bands selected. Dimensional selection was done using grid paper, with particles larger than 20 mm selected which allowed trimming of overlapping edges to increase sphericity. In Figure 2.4, a typical particle selected for reshaping, before and after being physically shaped, is shown. Particles were shaped using pliers, and stored in vacuum sealed plastic bags at - 20°C

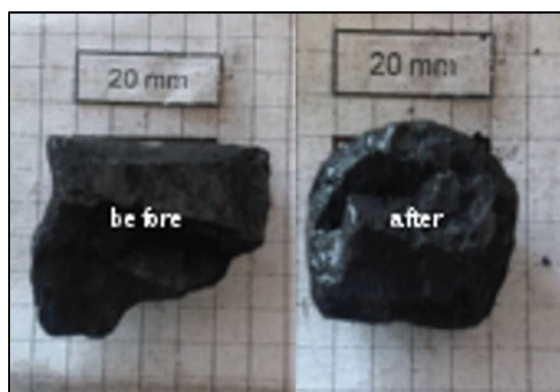


Figure 2.4: Dimensional selection and particle shaping of a typical 20 mm particle.

2.3. Parent coal characterisation

Representative samples were sent to various laboratories for parent coal characterisation. In Table 2.1, the various analyses, laboratories and standards are summarised. Chemical and mineralogy, and petrographic analyses were conducted according to international standard procedures.

Table 2.1: Summary of parent coal characterisation analyses and procedures.

Property	Analysis	Laboratory	Standard
Chemical and mineralogy	Sample preparation		ISO 13909-4: 2001
	Gross calorific value		ISO 1928: 2009
			ISO11722: 1999
	Proximate analysis	Bureau Veritas Testing and Inspection	ISO 1171: 2010
			ISO 562: 2010
	Ultimate analysis		ISO 29541: 2010
	Total sulphur		ISO 19579: 2006
	XRF		ASTM D4326 XRF
Petrography	Block preparation	SABS	ISO 7404 - 2, 1985
	Vitrinite random reflectance	Petrographics	ISO 7404 - 5, 1994
	Group macerals	SA Laboratory	ISO 7404 - 3, 1994

Parent coal characterisation results are shown in Table 2.2, and compared to results of similar Witbank seam 4 coals. The results in Table 2.2 show that the parent coal has a relative low ash and high calorific value. The ultimate analysis results show characteristically high oxygen content for Witbank seam 4 coal, which is known to be as a result of dolomite intrusions throughout the coalfield [1]. The chemical and mineralogy results for the parent coal compares well to literature, with the petrographic results showing negligible differences compared to reported results of seam 4 coal originating from Umlalazi [12-14]. The parent coal results shown in Table 2.2 are typical values for Witbank seam 4 washed coal, specifically resulting in a low ash coal with high calorific value, and petrographic analysis classifying the parent coal sample as an inertinite-rich, medium rank C bituminous coal.

Table 2.2: Parent and reported coal characterisation results.

Analysis	Parent coal	Umlalazi seam 4 [12-14]	Witbank seam 4 [15,16]
Gross calorific value (MJ/kg)	28.5	27.7	27.7
Proximate analysis (wt%, a.d.b)			
Moisture	2.3	2.8	3.6
Ash	13.4	14.8	25.8
Volatile matter	25.7	24.5	23.9
Fixed carbon	58.6	57.9	46.7
Ultimate analysis (wt% d.m.m.f.b)			
Carbon	83.2	83.8	78.5
Hydrogen	4.5	4.3	4.7
Nitrogen	2.0	2.1	1.9
Sulphur	0.9	1.0	0.6
Oxygen (by difference)	9.4	11.5	14.3
Petrographic			
Total Maceral (vol%, m.m.f.b)			
Vitrinite	29	25	26
Liptinite	4	3	10
Inertinite	67	72	64
Vitrinite random reflectance	0.78	0.81	0.68
Total maceral reflectance	1.38	ND	ND
Rank	Medium Rank C bituminous coal	Medium Rank C bituminous coal	Medium Rank C bituminous coal
XRF (wt%, d.b.)			
SiO ₂	45	38	42
Al ₂ O ₃	36	26	36
CaO	5.9	18.8	10.5
Fe ₂ O ₃	4.1	5.9	ND
K ₂ O	0.8	0,55	1.8
MgO	0.7	1.5	1.4
Na ₂ O	0.1	ND	0.2

ND- not determined

2.4. Char sample preparation

Chars were prepared in a vertical tube furnace supplied by Elite Thermal Systems Ltd. (TSV 12/50/300), with 52 mm internal diameter heating tube. Baseline 5 nitrogen (supplied by Afrox Pty Ltd. South Africa) was used as inert gas at 10 L/min, and supplied to the heating tube using a Sierra Smart Trak 50 Series mass flow controller. A multi-step temperature profile was used to create chars, where the samples were initially heated from ambient temperature to maximum gasification temperature (1000°C for this study), at a rate of 10°C/min. This was followed by a 1.0 hr dwelling period to allow for isothermal conditions to be obtained within the particles. Char preparation parameters, with the exception of holding time, were selected to mimic FBDB gasification conditions. The final char sample preparation step was controlled cooling at a rate of 5°C/min. In Table 2.3, the experimental conditions for the char preparation procedures are summarised. A graphical representation of the coal sampling procedure used to produce different sized chars is shown in Figure 2.5.

Table 2.3: Experimental conditions used for char preparation.

Variable	Specification
Nitrogen flow (L/min)	10
Argon purity	Afrox baseline 5
Temperature profile	Non-isothermal
Temperature (°C)	1000
Heating rate (°C/min)	10
Holding time (hr)	1.0
Cooling rate (°C/min)	5.0
Temperature (°C)	1000

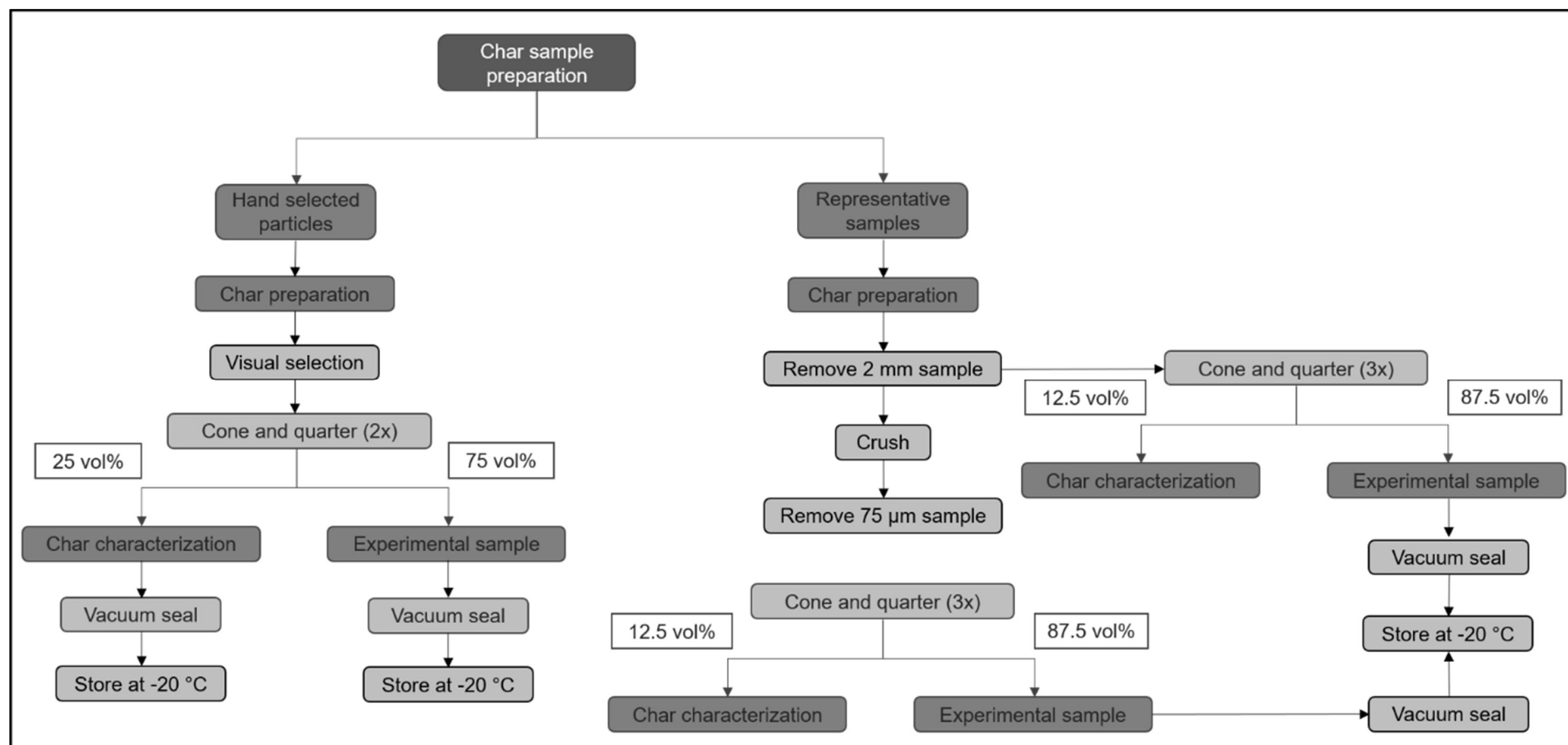


Figure 2.5: Sample preparation for different sized chars.

Three char size classifications (75 μm , 2mm and 20 mm) were selected for this study, with 75 μm mainly selected for entrained flow technologies, 2mm utilised in fluidised bed technologies and 20 mm the preferred size for fixed bed technologies. Chars for 75 μm and 2 mm particles were prepared using the smaller representative coal samples, detailed in Figure 2.5. Representative samples (5 randomly selected samples) were batch charred (~ 1 kg batches), and 2 mm particles removed using a narrow particle size range ($- 2.8 + 1.6$ mm). The remainder of the char sample was mixed by hand and crushed using a rotary ball mill, with the crushed sample screened to obtain the 75 μm fraction. The 75 μm and 2 mm samples were cone and quartered 3 times, with the bulk sample used for partial converted char preparation and the smaller sample used for char characterisation analysis.

As shown in Figure 2.5, chars for the 20 mm particles were produced using the hand selected lump coal particles. Charred particles were further inspected for swelling, large crack formation, and/or disintegration. Chars were re-selected on dimensional bases, where particles showing signs of swelling or large crack formations were discarded. Selected particles were cone and quartered twice, with the bulk sample used for partial converted char preparation and the smaller sample used for char characterisation analysis.

In Table 2.4, the particle size classification and corresponding particle size ranges selected for this evaluation are given, and the given coding is further used throughout the thesis..

Table 2.4: Particle size classification and corresponding particle size range.

Classification	Particle size range
75 μm	- 75 + 38 μm
2 mm	- 2.8 + 1.6 mm
20 mm	20 $\pm$ 3 mm

2.5. Char characterisation

Physical structure analysis was conducted in-house at the North-West University. A Micromeritics ASAP 2020 surface area and porosity analyser was used for low pressure CO_2 gas adsorption measurement. Samples (~ 200 mg) were dried at 85°C for 24 hours and degassed at < 10 $\mu\text{m Hg}$ (at 50°C) for 2 days, before gas adsorption analyses were conducted. On-line data acquisition was acquired using ASAP 2020 v4.0 software during low pressure CO_2 gas adsorption measurements ($0 < P/P_0 \leq 0.032$), with ASAP 2020 v4.0 software automatically determining physical structure properties by implementing Dubinin-

Radushkevich (D-R) and Horvath-Kawazoe (H-K) models based on per gram sample (ash content). Micropore surface area and volume, reported by the ASAP 2020 v4.0 software, were corrected to per gram carbon using Equations 2.1 and 2.2.

$$S\left(\frac{m^2}{g_{\text{carbon}}}\right) = \frac{S\left(\frac{m^2}{g_{\text{sample}}}\right) \times (X_{\text{char,ash}} + X_{\text{char,volatile}} + X_{\text{char,carbon}}(1-X))}{X_{\text{char,carbon}}(1-X)} \quad \text{Eq 2.1}$$

$$V\left(\frac{m^3}{g_{\text{carbon}}}\right) = \frac{V\left(\frac{m^3}{g_{\text{sample}}}\right) \times (X_{\text{char,ash}} + X_{\text{char,volatile}} + X_{\text{char,carbon}}(1-X))}{X_{\text{char,carbon}}(1-X)} \quad \text{Eq 2.2}$$

In Table 2.5 the char characterisation results for the three particle sizes are given.

Table 2.5: Char characterisation results.

Analysis	75 μm	2 mm	20 mm	Witbank seam 4 [15]
Proximate analysis (wt%, d.b)				
Ash	18.8	17.6	17.0	34.7
Volatile matter	2.2	1.9	2.3	1.2
Fixed carbon	79.0	80.5	80.7	64.1
Fuel ratio	35.9	42.3	35.1	53.4
Ultimate analysis (wt% d.m.m.f.b)				
Carbon	95.8	95.9	96.2	96.4
Hydrogen	0.2	0.2	0.2	0.1
Nitrogen	1.9	1.8	1.7	1.5
Sulphur	0.8	0.6	0.5	0.5
Oxygen	1.4	1.5	1.4	1.5
Physical analysis (CO₂ gas adsorption)				
Surface area (m ² /g _c)	124	143	170	148
Pore volume (mL/g _c)	0.089	0.107	0.158	ND
XRF analysis (wt%)				
SiO ₂	46	45	45	ND
Al ₂ O ₃	36.8	35.8	35.9	ND
CaO	4.5	5.1	5.9	ND
Fe ₂ O ₃	4.1	4.6	4.3	ND
K ₂ O	0.8	0.8	0.7	ND
MgO	0.5	0.5	0.6	ND
Na ₂ O	0.1	0.1	0.1	ND
Alkali index	2.2	2.6	2.5	ND

ND- not determined

For chars created here, as seen from Table 2.5, values obtained from the proximate and ultimate analysis do not differ significantly with particle size. Further, it is evident that ash values do also not differ significantly with particle size, with ash values comparing well to parent coal ash values when normalising to a volatile matter and moisture free basis. In order to quantify the small deviations in inherent catalytic minerals and ash composition, the alkali index as defined by Sakawa *et al.* [17] was calculated, with the alkali index ranging from 2.2 to 2.6 for the three particle sizes, with no apparent dependence on particle size. Generally, it is concluded that the chemical composition of the three particle sizes does not differ significantly. Large particle char characterisation results for the sample originating from the Witbank seam 4 sample is shown in Table 2.5 [15], for samples charred at 1050°C. A low ash coal is observed for the char samples when compared to the work of Van Wyk *et al.* [15], with ensuing decreased fixed carbon observed for Van Wyk *et al.* [15]. An increased fuel ratio is observed for Van Wyk *et al.* [15] and could be ascribed to higher charring temperature which resulted in the greatest degree of volatile release. Hattingh *et al.* [12-14] and Van Wyk *et al.* [15,16] reported ash composition of parent coal only, with a calculated alkali index for the parent coal sample of 6.2 and 4.6, respectively, with the higher reported alkali index ascribed due to greater calcium contribution to mineral matter.

Comparing micropore surface area and pore volume in Table 2.5, particle size dependent char physical characteristics are observed. An increase in micropore surface area and pore volume is observed as particle size increases, which agrees with previous evaluations [18-23]. Particle size dependent pore development is proposed to be as a result of increasing heat and mass transfer gradients occurring with increasing particle size. Increased transient temperature gradients observed inside larger particles causes greater mechanical stress, and increased residence time for volatiles inside larger particles promotes reaction with carbonaceous material, both suggested to result in increasing pore formation.

2.6. Nomenclature

Symbols:

S- Micropore surface area (m^2/g_C or m^2/g_{sample})

V- Micropore volume (m^3/g_C or m^3/g_{sample})

X- Char conversion (-)

Abbreviations

a.d.b.- Air dry basis

d.b.- Dry basis

d.m.m.f.b.- Dry mineral matter free basis

m.m.f.b.- Mineral matter free basis

vol%- Volume percentage

wt%- Weight percentage

XRF- X-ray fluorescence

2.7. Chapter References

- [1] Hancox PJ, Götz AE. South Africa's coalfields — A 2014 perspective. *International Int J Coal Geol* 2014;132:170-254, <https://doi.org/10.1016/j.coal.2014.06.019>.
- [2] Prevost X. Underground coal gasification. *Inside Mining* 2009;September:7-9.
- [3] Keneilwe R, Nembahe R. 2018: South African energy sector report. Department of Energy 2018:56.
- [4] Cairncross B, Cadle AB. Palaeoenvironmental control on coal formation, distribution and quality in the Permian Vryheid Formation, East Witbank Coalfield, South Africa. *Int J Coal Geol* 1988;9:343-70, [https://doi.org/10.1016/0166-5162\(88\)90031-6](https://doi.org/10.1016/0166-5162(88)90031-6).
- [5] Mehliiss, A. T. M., South Africa., Minerals Bureau.,. Sulphur in South African coal. Johannesburg: The Bureau, 1987.
- [6] Xaba DS. Evaluate the remaining resources of low phosphorus coal in Mpumalanga Province. CSIR Miningtek 2004;Coaltech 2020 Task 1.2.1:39.
- [7] Holland MJ, Cadle AB, Pinheiro R, Falcon RMS. Depositional environments and coal petrography of the Permian Karoo Sequence: Witbank Coalfield, South Africa. *Int J Coal Geol* 1989;11:143-69.
- [8] Boshoff HP, Bergh CE, Kruszewska KJ. Analyses of coal product samples of producing South African collieries. Pretoria, Republic South Africa: CSIR, 1991.
- [9] Glasspool IJ. Hypautochthonous–allochthonous coal deposition in the Permian, South African, Witbank Basin No. 2 seam; a combined approach using sedimentology, coal petrology and palaeontology. *Int J Coal Geol* 2003;53:81-135, [https://doi.org/10.1016/S0166-5162\(02\)00193-3](https://doi.org/10.1016/S0166-5162(02)00193-3).
- [10] Pretorius CC, Boshoff HP, Pinheiro HJ. Analyses of coal product samples of South African Collieries. SABS 2002;Bulletin 114:97.
- [11] Allen T, Khan AA. Critical evaluation of powder sampling procedures. *Chem Eng* 1970;238:108-112.
- [12] Hattingh BB, Everson RC, Neomagus HWJP, Bunt JR, van Niekerk D, Jordaan JHL *et al.* Elucidation of the Structural and Molecular Properties of Typical South African Coals. *Energy Fuels* 2013;27:3161-72, <https://doi.org/10.1021/ef400633d>.

-
- [13] Hattingh BB, Everson RC, Neomagus HWJP, Bunt JR, van Niekerk D, Ashton BP. Modeling the nonisothermal devolatilization kinetics of typical South African coals. *Energy Fuels* 2014;28:920-33, <https://doi.org/10.1021/ef402124f>.
- [14] Bean NC, Bunt JR, Strydom CA, Neomagus HWJP, van Niekerk D, Hattingh BB. Influence of additives on the devolatilization product yield of typical South African coals, and effect on tar composition. *J S Afr Inst Min Metall* 2018;118:395-407, <http://dx.doi.org/10.17159/2411-9717/2018/v118n4a10>.
- [15] Van Wyk S, Neomagus HWJP, Bunt JR, Everson RC. Coal reactivity and selection for solid-based pre-reduction of sponge iron. *Int J Coal Prep Util* 2017:1-14, <https://doi.org/10.1080/19392699.2017.1384729>.
- [16] Van Wyk S. Coal evaluation and reactivity for direct solid based pre-reduction of sponge iron. 2016.
- [17] Sakawa M, Sakurai Y, Hara Y. Influence of coal characteristics on CO₂ gasification. *Fuel* 1982;61:717-20, [https://doi.org/10.1016/0016-2361\(82\)90245-9](https://doi.org/10.1016/0016-2361(82)90245-9).
- [18] Agrawal RK, Gandhi F, McCluskey RJ. Low-pressure pyrolysis of newsprint. *J Anal Appl Pyrol* 1984;6: 325-38, [https://doi.org/10.1016/0165-2370\(84\)80026-1](https://doi.org/10.1016/0165-2370(84)80026-1).
- [19] Stubington JF, Sumaryono. Release of volatiles from large coal particles in a hot fluidized bed. *Fuel* 1984, 63 (7): 1013-19, [https://doi.org/10.1016/0016-2361\(84\)90327-2](https://doi.org/10.1016/0016-2361(84)90327-2).
- [20] Solomon PR, Hamblen DG. Chapter 5: Pyrolysis: Schlosberg R.H. (Ed.), *Chemistry of Coal Conversion*, Plenum Press, New York (1985), pp. 121-251
- [21] Devanathan N, Saxena SC. Transport model for devolatilization of large nonplastic coal particles: the effect of secondary reactions. *Ind Eng Chem Res* 1987, 26 (3): 539-48, <https://doi.org/10.1021/ie00063a021>.
- [22] Stubington JF, Linjewile TM The effects of fragmentation on devolatilization of large coal particles. *Fuel* 1989, 68 (2) (1989), pp. 155-160, [https://doi.org/10.1016/0016-2361\(89\)90316-5](https://doi.org/10.1016/0016-2361(89)90316-5).
- [23] Stubington J.F., Huang G., Scaroni A.W. Devolatilization times of mm-size coal particles. *Fuel*, 70 (9): 1105-08, [https://doi.org/10.1016/0016-2361\(91\)90268-F](https://doi.org/10.1016/0016-2361(91)90268-F).

Chapter 3.

Partially converted char sample preparation and gas adsorption measurements

The experimental setup and procedures used to generate partially converted chars are detailed in this chapter, along with the low-pressure CO₂ gas adsorption results for these specific char samples.

3.1. Introduction

The partial conversion of the different char samples is discussed here. The experimental equipment, experimental procedure and time required for partial converted char preparation are given in Section 3.2 - 3.4. Low pressure CO₂ gas adsorption measurement results of partially converted chars are discussed in Section 3.5.

3.2. Thermogravimetric analyser setup

A thermogravimetric analyser (TGA) designed, constructed and commissioned in-house at the North-West University, was used to prepare partially converted char samples [1-3]. In Figure 3.1, a schematic of the TGA setup is shown.

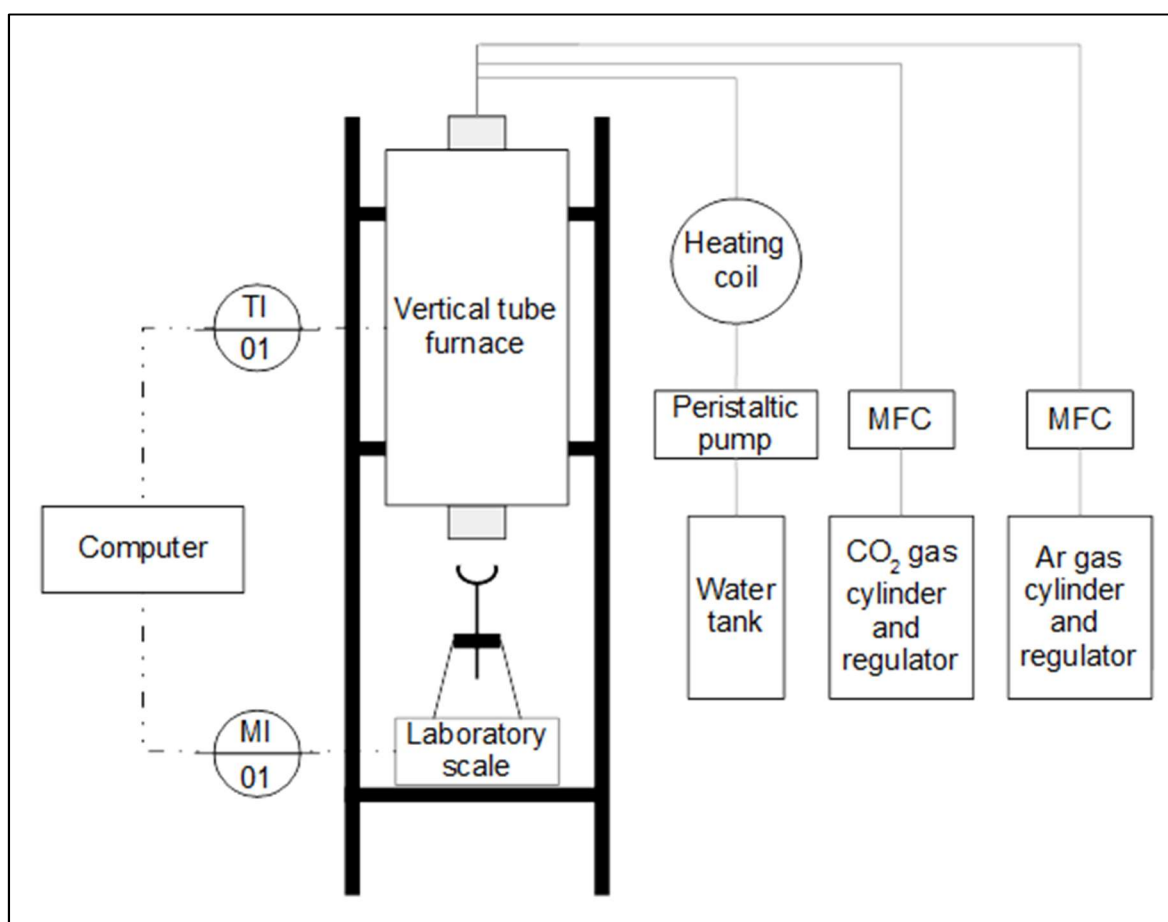


Figure 3.1: Schematic representation of the TGA equipment used for char conversion experiments.

As given in Figure 3.1, the experimental setup consists of a vertical tube furnace, mass flow controllers, steam generator, laboratory scale and data acquisition system. An Elite Thermal Systems Ltd. vertical tube furnace with tube inner pipe diameter of 50 mm was used. The

reaction zone temperature was measured using a 1 mm, K-type thermocouple and data was continuously logged using Adam modules. The atmosphere of the reaction zone was controlled using mass flow controllers and a steam generator. Brooks 0254 mass flow controllers were used to give a constant supply of argon and CO₂ to the furnace. The steam generator consists of a 10 litre stainless steel buffer tank, peristaltic pump (323 S/D Watson-Marlow Bredel high-performance variable speed pump), and stainless-steel coils mounted inside a heating mantel. A constant supply of steam is fed to the furnace by pumping deionised water to the temperature-controlled heating coils at a constant rate using the peristaltic pump.

The sample mass is continually measured using an Adam precision balance (ADAM PGW 453e milli balance), with the coal sample placed in a sample holder comprising of an aluminium tripod and quartz coal stand, with the quartz coal stand designed to increase the gas flow around the sample. For the 75 µm and 2 mm experiments, the particles were placed on a quartz-wool layer to prevent the particles from falling through openings in the sample holder. The various equipment used for the experimental setup is summarised in Table 3.1.

Table 3.1: Summary of equipment used.

Variable	Supplier	Model
Vertical tube furnace	Elite Thermal systems Ltd	TSV 15/50/180
Thermocouple	Wika instruments (Pty.) Ltd.	Wika K-type, 1 mm
Temperature logging	Wika instruments (Pty.) Ltd.	ADAM 4011 and ADAM 4056S
Mass flow controllers	Aveng ACS	Brooks 0254
Peristaltic pump	Watson-Marlon Bredel (Pty.) Ltd	323 S/D high-performance pump
Laboratory scale	Lenton (Pty.) Ltd	PGW 453e milli balance

3.3. Experimental procedure

The reaction temperature and gas concentrations were set on the furnace, mass flow controllers and steam generator, respectively. Once the furnace temperature was stable, an additional hour was allowed to arrive at constant gas temperatures. After temperature stabilisation, the sample holder was placed on the balance and the furnace lowered into position. Once the mass reading from the laboratory scale was stable, the mass balance was tared to eliminate the influence of gas flow on weight measurement. The pre-weighed char sample was loaded into the sample holder, after which the furnace was lowered immediately,

and the sample was allowed to reach isothermal conditions (30 minutes) in an argon atmosphere. After, the reaction gas was introduced to the furnace, data logging was initiated.

Fully converted chars were produced by gasifying char samples until sample mass reduced to expected ash values. The reagent gas was then switched off and air was introduced into the furnace until no significant mass changes was detected anymore. After complete conversion of the char, air was switched off and reagent gas reintroduced into the furnace to determine the final ash mass.

Partially converted chars were produced by gasifying char samples for a specific time to achieve a predetermined conversion. Once gasification has commenced for specific time and sample mass is at approximated weight, the reaction gas was shut-off and the argon gas flow increased from 1.0 to 10 L/min to flush any remaining reaction gas. The furnace was immediately lifted to position the sample in $\sim 150^{\circ}\text{C}$ temperature zone (furnace temperature profile shown in Appendix A.1), to terminate reaction of the sample. The sample was left to cool inside the furnace tube, for 15 minutes, to ensure that the sample was not in contact with atmospheric air. After being cooled, the sample was removed and stored for later use.

Argon flow rate and sample weight (shown in Table 3.2) were experimentally chosen to ensure that total gas flow (Appendix A.2) and sample weight (Appendix A.3) did not influence reactivity experiments, which experimentally shows negligible effect of external mass transfer limitations. The lowest gasification temperature chosen for CO_2 and steam gasification was experimentally proven to be chemical reaction controlled for $75\text{ }\mu\text{m}$ char particles (Appendix A.4). The highest gasification temperature was chosen as 150°C higher than the selected lowest gasification temperature, as previous research showed mass transfer limitations observed for particle sizes $> 1\text{ mm}$ at the two respective temperatures [4-6]. The Experimental conditions for the preparation of partially devolatilised chars is summarised in Table 3.2.

Table 3.2: Experimental conditions used for converted char preparation.

Variable	Specification
Argon flow (NL/min, STP)	1.0
Argon purity	Afrox baseline 5
Temperature profile	Isothermal
Conversion (%)	10, 25, 35, and 50
Sample weight	
75 μm (g)	± 1.0
2 mm (g)	± 1.0
20 mm	Single particle
CO₂ gasification	
CO ₂ concentration (mol%)	10
CO ₂ purity	Afrox technical grade
Temperature (°C)	850 and 1000
Steam gasification	
Steam concentration (mol%)	20
Water used	Deionised
Temperature (°C)	800 and 950
Heating mantel temperature (°C)	400

3.4. Determination of gasification durations

To determine the specific gasification time required to prepare partially converted chars, multiple samples were first fully converted. In Figure 3.2, the data process steps used to obtain specific gasification times for the CO₂ gasification of 75 μm at 1000°C is presented as an example.

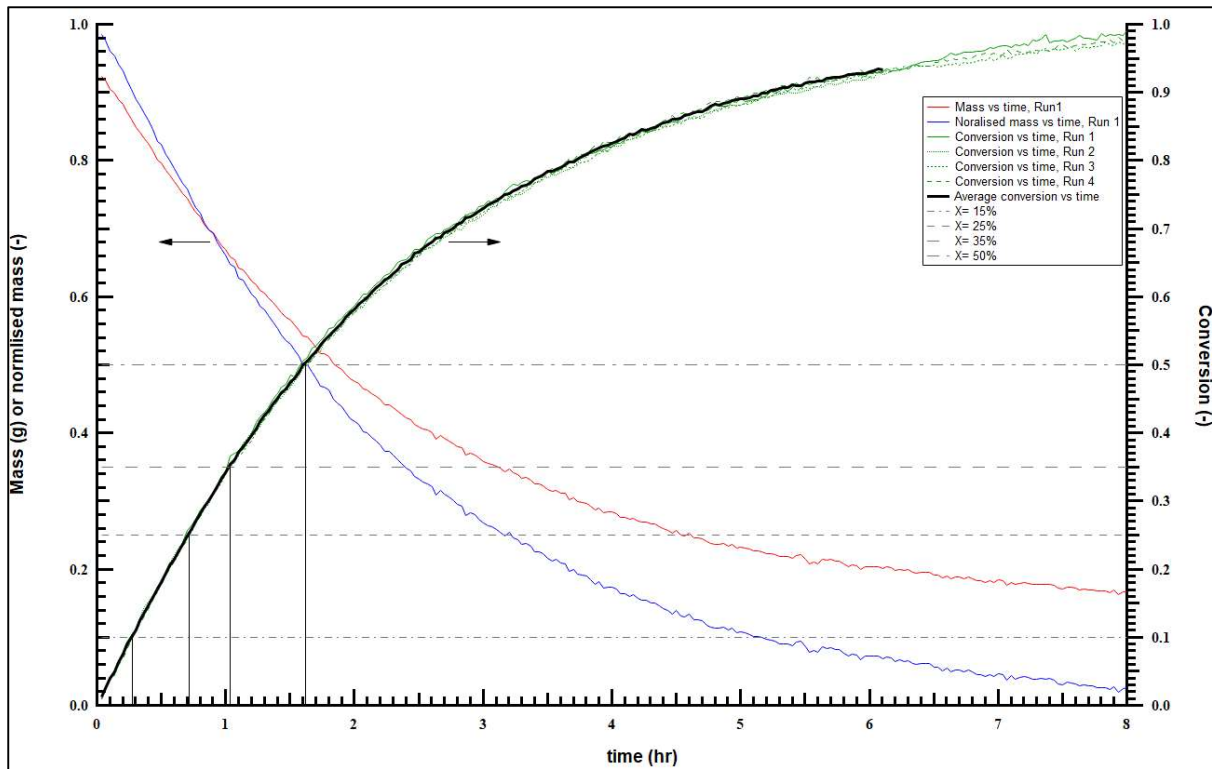


Figure 3.2: Data processing and specific gasification time for CO₂ gasification of 75 μm sample at 1000°C.

Conversion for each experiment was calculated using Equation 3.1:

$$X = \frac{M_{t=0} - M_t}{M_{t=0} - M_{ash}} \quad \text{Eq 3.1}$$

The average conversion at each time interval was determined for the repeat runs, with average data used to determine the time required to convert chart to a specific conversion. In Table 3.3, the resulting time required for partially converted chars for all samples is listed.

Table 3.3: Gasification time required for partially converted char samples.

		CO ₂ gasification		Steam gasification	
		850°C	1000°C	800°C	950°C
75 µm	10%	9 hr 50 min	16 min	1 hr 54 min	6 min
	25%	26 hr 22 min	42 min	5 hr 14 min	16 min
	35%	38 hr 58 min	62 min	7 hr 54 min	22 min
	50%	61 hr 18 min	100 min	12 hr 52 min	34 min
2 mm	10%	24 hr (18%)	1 hr 12 min	4 hr 42 min	14 min
	25%	ND	3 hr 8 min	10 hr 16min	22 min
	35%	48 hr	4 hr 32 min	13 hr 44 min	34 min
	50%	72 hr	6 hr 56 min	19 hr 2 min	1 hr 8 min
20 mm	10%	ND	3 hr 30 min	ND	38 min
	25%	ND	8 hr 16 min	ND	1hr 38 min
	35%	ND	11hr 20 min	ND	2 hr 22 min
	50%	ND	16 hr 6 min	ND	3 hr 36 min

ND- sample not generated

Samples for lowest gasification temperature of 20 mm particles were not generated as reaction times were too long for practical purposes.

3.5. Low pressure CO₂ gas adsorption of partially converted chars

Low pressure CO₂ gas adsorption measurements, using the procedure described in Section 2.5, were conducted on all partially converted chars. CO₂ gas adsorption measurements probe the micropore volume and surface area, with micropore structure parameters used to calibrate pore volume and surface area of SAXS measurements. The surface area development of the 75 µm samples are shown in Table 3.4.

Table 3.4: Surface area (m^2/g_c) development for 75 μm gasified samples.

X (%)	Surface area (m^2/g_c)			
	CO ₂ gasification		Steam gasification	
	850°C	1000°C	800°C	950°C
0	124			
10	222	190	338	311
25	287	252	595	519
35	360	299	703	628
50	454	339	808	707

It can be observed from Table 3.4, for both CO₂ and steam gasified chars at all temperatures, that an increase in micropore surface area is observed with an increase in conversion, where this increasing trend indicates that pore growth is more significant than pore coalescence up to 50% conversion for both CO₂ and steam gasification. High conversions required for pore coalescence is typical for bituminous coal and is reported to be due to low char porosity [7-10]. For both CO₂ and steam gasification it is also observed that a decrease in temperature results in an increase in micropore surface area at a specific conversion, and this trend has also previously been reported [7,11,12].

Table 3.5: Surface area measurements (m^2/g_c) for 2 and 20 mm partially converted samples.

X (%)	Surface area (m ² /g _c)			
	2 mm		20 mm	
	CO ₂ gasification			
	850°C	1000°C	1000°C	
0	144		171	
10	ND	181	193	
18	219	ND	ND	
25	ND	269	269	
35	382	364	483	
50	531	499	647	
	Steam gasification			
	800°C	950°C	950°C	
	10	296	314	370
	25	508	453	529
	35	588	584	631
	50	957	870	870

ND - sample not generated

The general trends observed for 75 μm (Table 3.4) are also observed for 2 and 20 mm particles, as shown in Table 3.5. Results indicate that no significant pore coalescence is observed for conversion up to 50% for all particle sizes. Further, an increase in micropore surface area is observed with a decrease in gasification temperature for all particle sizes. Evaluating the influence of particle size on pore development for CO₂ gasification shows an increase in micropore surface area development with an increase in particle size, at constant temperature and conversion. A comparable trend is also observed for steam gasification.

In light of the preliminary low pressure CO₂ gas adsorption results, it is clear that further investigation into pore structure development during gasification is required. To further elucidate the influence of gasification reagent, gasification temperature and particle size on pore development during gasification, the pore structure of the partially converted chars will be determined using small angle X-ray scattering measurements (SAXS). In Chapter 4 a detailed discussion on the evaluation of gasification reagent on pore development using 75

μm particles is presented, with the influence of particle size on pore development evaluated in Chapter 5. Evaluating pore structure development over a wider pore size range using SAXS will further elucidate the observed influence using low pressure CO_2 gas adsorption results.

3.6. Nomenclature

Symbols:

M_{ash} - Sample weight after combustion (g)

$M_{t=0}$ - Initial sample mass (g)

M_t - Specific time sample mass (g)

X- Char conversion (-)

Abbreviations

SAXS- *Small Angle X-ray Scattering*

STP- *Standard temperature and pressure*

TGA- *Thermogravimetric analyser*

3.7. Chapter references

- [1] Coetzee S, Neomagus HWJP, Bunt JR, Everson RC. Improved reactivity of large coal particles by K_2CO_3 addition during steam gasification. *Fuel Processing Technology* 2013;114:75-80. <http://dx.doi.org/10.1016/j.fuproc.2013.03.041>.
- [2] Kühn T, Bunt JR, Neomagus HWJP, Piketh SJ, Everson RC, Coetzee S. Coal-derived low smoke fuel assessment through coal stove combustion testing. *Journal of Analytical and Applied Pyrolysis* 2017;126:158-68. <https://dx.doi.org/10.1016/j.jaap.2017.06.012>
- [3] Van Wyk S, Neomagus HWJP, Bunt JR, Everson RC. Coal reactivity and selection for solid-based pre-reduction of sponge iron. *International Journal of Coal Preparation and Utilization* 2017:1-14. <https://dx.doi.org/10.1080/19392699.2017.1384729>.
- [4] Hanson S, Patrick JW, Walker A. The effect of coal particle size on pyrolysis and steam gasification. *Fuel* 2002;81:531-7. [http://dx.doi.org/10.1016/S0016-2361\(01\)00153-3](http://dx.doi.org/10.1016/S0016-2361(01)00153-3).
- [5] Huang J, Watkinson AP. Coal gasification in a stirred bed reactor. *Fuel* 1996;75:1617-24. [http://dx.doi.org/10.1016/S0016-2361\(96\)00133-0](http://dx.doi.org/10.1016/S0016-2361(96)00133-0).
- [6] Löwenthal G, Mühlen H-, van Heek KH A Novel Kinetic Approach to predict the Gasification Rates of Larger Particles. In: Ltd, International Energy Agency Coal Research, editor. 1991 International Conference on Coal Science Proceedings. : Butterworth-Heinemann, 1991:291-4.
- [4] Su JL, Perlmutter DD. Effect of pore structure on char oxidation kinetics. *AIChE J* 1985;31:973-81. <https://doi.org/10.1002/aic.690310614>
- [5] Feng B, Bhatia SK. Variation of the pore structure of coal chars during gasification. *Carbon* 2003;41:507-23. [http://dx.doi.org/10.1016/S0008-6223\(02\)00357-3](http://dx.doi.org/10.1016/S0008-6223(02)00357-3)
- [6] Tilghman MB, Mitchell RE. Coal and biomass char reactivities in gasification and combustion environments. *Combustion and Flame* 2015;162:3220-35. <https://doi.org/10.1016/j.combustflame.2015.05.009>
- [7] Liu L, Cao Y, Liu Q. Kinetics studies and structure characteristics of coal char under pressurized CO_2 gasification conditions. *Fuel* 2015;146:103-10. <https://doi.org/10.1016/j.fuel.2015.01.002>
- [8] Molina-Sabio M, Gonzalez MT, Rodriguez-Reinoso F, Sepúlveda-Escribano A. Effect of steam and carbon dioxide activation in the micropore size distribution of activated carbon. *Carbon* 1996;34(4):505-9. [http://dx.doi.org/10.1016/0008-6223\(96\)00006-1](http://dx.doi.org/10.1016/0008-6223(96)00006-1)

- [9] Rodríguez-Reinoso F, Molina-Sabio M, González MT. The use of steam and CO₂ as activating agents in the preparation of activated carbons. *Carbon* 1995;33(1):15-23. [http://dx.doi.org/10.1016/0008-6223\(94\)00100-E](http://dx.doi.org/10.1016/0008-6223(94)00100-E)
- [10] Arenas E, Chejne F. The effect of the activating agent and temperature on the porosity development of physically activated coal chars. *Carbon* 2004;42(12-13):2451-5. <http://dx.doi.org/10.1016/j.carbon.2004.04.041>
- [11] González JF, Román S, González-García CM, Nabais JMV, Ortiz AL. Porosity development in activated carbons prepared from walnut shells by carbon dioxide or steam activation. *Ind Eng Chem Res* 2009;48(16):7474-81. <http://dx.doi.org/10.1021/ie801848x>

Chapter 4.

Pore development during gasification of South African inertinite-rich chars evaluated using small angle X-ray scattering

G. Hennie Coetzee, Richard Sakurovs, Hein W.J.P Neomagus, Leigh Morpeth, Raymond C. Everson, Jonathan P. Mathews, John R. Bunt

Pore development arising from steam and CO₂ gasification of a char, ~ 75 µm, was evaluated using small angle X-ray scattering. A novel ratio analysis technique was developed to study the pore development data, and used to evaluate the influence of steam and CO₂ thereon.

Findings reported in this chapter are published as *Carbon* **2015**, 95, 250-260.

DOI: doi.org/10.1016/j.carbon.2015.08.030

Abstract

Pore development arising from steam and CO₂ gasification of a char, prepared from an inertinite-rich Witbank Seam 4 coal, was investigated using small angle X-ray scattering. The char, ~ 75 µm, was gasified to specific conversions (10, 25, 35 and 50%) using two gasification reagents, CO₂ and steam. A novel ratio analysis technique was developed to study the pore development from experimental data. Differently sized pores grow at different rates with the difference not being simply due to gas accessibility. In particular, the pores between 1 and 40 nm in size showed more pore growth than larger or smaller sizes. Steam gasification created a more porous char with increased pore growth of pore sizes between 1 and 40 nm than CO₂ gasification. The pore generation rate of steam was up to a factor 7 times faster than CO₂, compared at the highest gasification temperatures. For the smaller pores, < 1 nm, it was found that the rate of pore generation was slower compared to larger pores, though was still evident with the critical cross over pore size for CO₂ to be 1 nm compared to 0.6 nm for steam. This may be a direct consequence of CO₂'s greater kinetic diameter.

4.1. Introduction and background

The conversion of coal with oxidising media such as CO₂ and steam is used to increase the economic potential of feedstocks, generating products including: syngas, electricity and activated carbon. During industrial gasification, coal undergoes several stages of transformation such as dewatering, pyrolysis, gasification, and combustion resulting in physical and chemical changes. A fundamental understanding of these changes is key to the design of coal gasifiers [1]. For the gas-solid reactions, it is reported that the reaction rate is dependent on the change in physical char structure as conversion progresses [2-5], and has widely been studied for coal chars [6-10]. The physical changes that are observed during gasification can also be directly used to describe the surface area development in the production of activated carbon from waste material [11-16]. In general, pore structure development during steam and CO₂ gasification under comparable conditions is different. Steam gasification yields an increase in all pore sizes from the onset of gasification, and increases the mesoporosity to a greater extent than CO₂. While CO₂ tends to produce a relatively narrow micropore structure with broadening of microporosity only after extensive activation [6, 7, 12, 13]. However, contradictory trends are reported regarding which gasification agent results in maximum micropore development (maximum reported for CO₂ [11, 13, 14] and for steam [17-19]), with the deviations being attributed to the diversity of the char structures used. These findings are based on combining measurements made by gas adsorption (typically, CO₂ at 273 K and N₂ at 77 K), mercury porosimetry, and also adsorption of organic vapours with differing molecular diameters. While useful, the influence of time-temperature histories on the char behaviour and differences between techniques complicate using a combination of different methods to determine pore size variations due to gasification [20].

Small Angle X-ray Scattering (SAXS) can be used to evaluate pore sizes over a wide range using a single measurement. The intensity of the X-ray beam is determined as a function of scattering angle. The scattering angle is converted to the scattering vector Q , which can be used to determine pore radius, R , by the approximate relationship $R = \sim 2.5/Q$ [16]. If the pore size distribution follows fractal behaviour, the Porod plot ($\log(\text{Intensity}(Q))$ versus $\log(Q)$) results in a straight line, and the pore size distribution follows strict scaling laws. However, if the slope varies with Q , the material is not fractal and more complex modelling is required. In this case models require estimation of fixed input parameters (electron density difference and form factor) and variable fitting parameters (pore number or volume distribution) [21]. SAXS has been used to investigate coal pore structures [21-26], with the recent SAXS studies

focused on how gas is sorbed and released from the coal structure [27-31]. SAXS data show that there is a wide distribution of pore sizes in chars. A summary of the research conducted on pore development during gasification using Small Angle Scattering (SAS) is shown in Table 4.1.

Table 4.1: Summary of research on the pore development during carbon conversion using SAS.

Reference	Source	Reagent	Temperature (°C)	Analysis
Bale <i>et al.</i> [32]	Lignite	O ₂	240	SAXS
Calo <i>et al.</i> [33]	Subbituminous coal & Phenolic resin char	O ₂	400, 470	SANS* with contrast matching
Calo <i>et al.</i> [34]	Saran char, raw and calcium-loaded cellulose	O ₂	340, 425, 560	SAXS
Antxustegi <i>et al.</i> [35]	Argonne Premium Pittsburgh No. 8	O ₂	400	SANS with contrast matching
Diduszko <i>et al.</i> [36]	Activated carbon (hard coal)	Steam	-	SAXS, benzene adsorption
Foster and Jensen [37]	Anthracite	CO ₂	825	SAXS
Foster and Jensen [38]	Carbosieve-S	CO ₂	825	SAXS
Pfeifer <i>et al.</i> [39]	Olive stone	Steam	750	SAXS

*Small Angle Neutron Scattering

Although the pore development during carbon conversion has been studied previously using SAXS, the authors have found no systematic study comparing the pore development during steam and CO₂ gasification using this technique. The comparison of pore development from CO₂ and steam using SAXS will combine the effects observed using established techniques (gas adsorption and porosimetry) with the added benefits of SAXS [32-39]. Here the pore development during gasification of char made from an South African inertinite-rich, Witbank seam 4 coal, using steam and CO₂, is evaluated using SAXS.

4.2. Experimental section

4.2.1. Sample preparation and characterisation

The bulk coal sample (300 kg) was + 30 mm particle size, Witbank seam 4 export steam coal (washed at specific gravity < 1.5). Witbank seam 4 coal is inertinite-rich, see Table 4.2, which exhibits different properties to most Northern Hemisphere coals. The sample was cone-and-quartered 4 times and the representative sample crushed to - 5 mm. Char preparation was

carried out in a nitrogen atmosphere controlled oven at 1000°C (heating rate of 10°C/min) with a holding time of 1 hr (flow rate of 2 L/min, STP). The sample was obtained by, crushing the char sample and collecting a narrow size fraction (- 75 + 38 µm). The parent coal and char characterisations are shown in Table 4.2.

Table 4.2: The characterisation results of the parent coal and char.

	Parent coal	Char
Proximate analysis (wt% d.b.)		
Ash	13.7	17.6
Volatile matter	26.3	2.2
Carbon	60.0	80.2
Ultimate analysis (wt% d.a.f.)		
Carbon	83.5	95.9
Hydrogen	4.5	0.2
Nitrogen	2.0	1.9
Sulphur	0.9	0.8
Oxygen (by difference)	9.3	1.3
Petrography		
Macerals (vol% m.m.f.)		
Vitrinite	29	
Liptinite	4	
Inertinite	67	
Rr (%)	0.78	
Rsc (%)	1.38	
Rank:	Medium rank C	

The char was gasified in a TGA (details in Coetzee *et al.* [40]) using either steam (20 mol%) or CO₂ (10 mol%) with an Argon balance. The converted char preparation was carried out using two gasification temperatures (800 and 950°C for steam, 850 and 1000°C for CO₂). The particle size and gasification temperatures were chosen to reduce external mass transfer limitations and to allow acceptable reactivity times (50% conversion within 3 days). The TGA was pre-heated to the set gasification temperature, using inert conditions, after which the char sample was inserted and the gasification reagent was introduced once isothermal conditions were reached.

4.2.2. SAXS measurement

The SAXS measurements were performed at the Australian Synchrotron in Melbourne; a detailed discussion on the beamline is discussed in Kirby *et al.* [40]. The beam energy, -

wavelength and -size used was 11 keV, 1.127 Å and 250 x 150 µm, respectively. A Pilatus 1M detector was used for data acquisition, with exposure time of 1 second and two detector positions (denoted as short and long SAXS). The two positions resulted in a Q-range probed from $1.698 \cdot 10^{-3}$ to 0.8333 Å^{-1} , which corresponds to assumed pore diameter between 0.25 and 147 nm.

The gasified samples were mounted in a washer (inner diameter of 10 mm and a thickness of 300 µm) using M3 Scotch® transparent tape. The weight and thickness of the mounted char samples was measured. Two secondary standards, glassy carbon (300 µm thick), were used for absolute intensity calibration of the SAXS datasets. A raster grid of $\sim 0.7 \times 0.7 \text{ mm}$ was collected using 18 scans (3 x 6) for each sample and both detector positions.

The experimental repeatability of the measurements was calculated using repeat scans (18 mapped scans) of the short SAXS setting of 75 µm char particle. The average 95% confidence interval experimental error over the full Q-range was calculated as $< 1\%$. The sample variance for the char (over the entire Q-range, after merging camera position data) was determined using a mapped scan (18 scans) which covered a total area of $\sim 0.5 \text{ mm}^2$, with sample variance calculated as $< 8\%$. All samples were scanned using a similar 18 scan map, with sample variance showing comparable results. Larger errors were observed at the extreme ends of the Q-range. The statistical difference between results was determined using the t-test method (for two-tail 95% confidence interval).

4.2.3. Data processing

Scatterbrain 2.3 and Irena 2.56 software [42] were used for data processing steps. Scatterbrain was used to: calculate 1D datasets (Intensity versus Q) from the 2D collected data, summation of the raster grid scans and calculation of the total incident (I_0) and beam stop (I_{BS}) intensities. The sample data was then corrected for transmission and background scattering, then normalised for thickness and converted to absolute-intensity following the procedure of Zhang *et al.* [43]. The correction factors of 187 (short SAXS) and 15 913 (long SAXS) were obtained for the absolute-intensity calibration of the glassy carbon. The glassy carbon scans were used to inspect scattering data for anomalously low or high data points and no artifacts were found. The absolute intensity calibrated data (cm^{-1}) of the short and long SAXS is combined using an auto-scale factor with an averaged factor of 0.85 ± 0.04 , resulting in an additional uncertainty if calculating absolute parameters. The scaling factor procedure was used to process all sample data to obtain absolute intensity plots. Irena 2.56 was also

used to determine the pore number distribution using polydisperse model of spherical voids and flat background subtraction using the IPG/TNNLS fitting method [42]. In this study: features $< 3 \text{ \AA}$ are assumed to be influenced by molecular structure features (such as lattice interspacing) and are not included in surface area and pore volume calculations.

Three separate ratios were calculated from the SAXS data to compare results of different scans: scaled intensity, intensity conversion ratio (ICR) and scaled conversion intensity ratio (SCIR). For scaled intensity, the scaling factor was chosen as the reciprocal of the absolute intensity at $Q = 1.698 \cdot 10^{-3} \text{ \AA}^{-1}$ which corresponds to the largest probed pore size (pore diameter of $\sim 147 \text{ nm}$). The scaled intensity allows direct comparison of changes in pore size distributions. The ICR was calculated by dividing the scattering intensity of the gasified char at each measurement point (all Q) by that of the unreacted char. The SCIR was calculated by dividing the scaled intensity of the gasified char with the scaled intensity of the char (at each Q) to qualitatively compare the relative extent to which the number of pores at different sizes is affected by conversion, gasification agent and gasification temperature. Porosity is defined as the porosity obtained from the probed pore size range, and is not the absolute total porosity. The cross-over pore size is defined as the micro pore size where the SCIR reduce below 1, which indicates a slower pore growth rate for micro pores smaller than the cross-over pore size, compared to larger pores.

Low pressure CO_2 gas adsorption was used to obtain the micropore surface area with the equipment and procedures as detailed in Okolo *et al.* [20]. The CO_2 gas adsorption results were used to scale the calculated SAXS surface area for the comparable pore size range (0.3 to 0.5 nm) resulting in SAXS surface area corrected for mineral matter influence on the scattering. The micro- (3 $\text{\AA}$ to 2 nm), meso- (2 to 50 nm), and macropore ($> 50 \text{ nm}$) surface area and porosity is calculated and converted to surface area per gram carbon (m^2/g_c) (in this approach, it is assumed that all pores measured using SAXS are accessible to CO_2 for gas adsorption measurements and that the mineral matter porosity is negligible, CO_2 gas adsorption surface area for ash is measured as $10 \text{ m}^2/\text{g}_{\text{ash}}$). The calculated surface area and porosity is divided into 10 pore bins (logarithmic scaling) for further comparison. The Surface area ratio (SAR) for the 10 bins is calculated by dividing the specific bin surface area at a specific conversion with the specific char bin surface area.

4.3. Results and Discussions

4.3.1. Char

Figure 4.1 shows the absolute intensity scattering curve and pore size frequency (PSF) of the char.

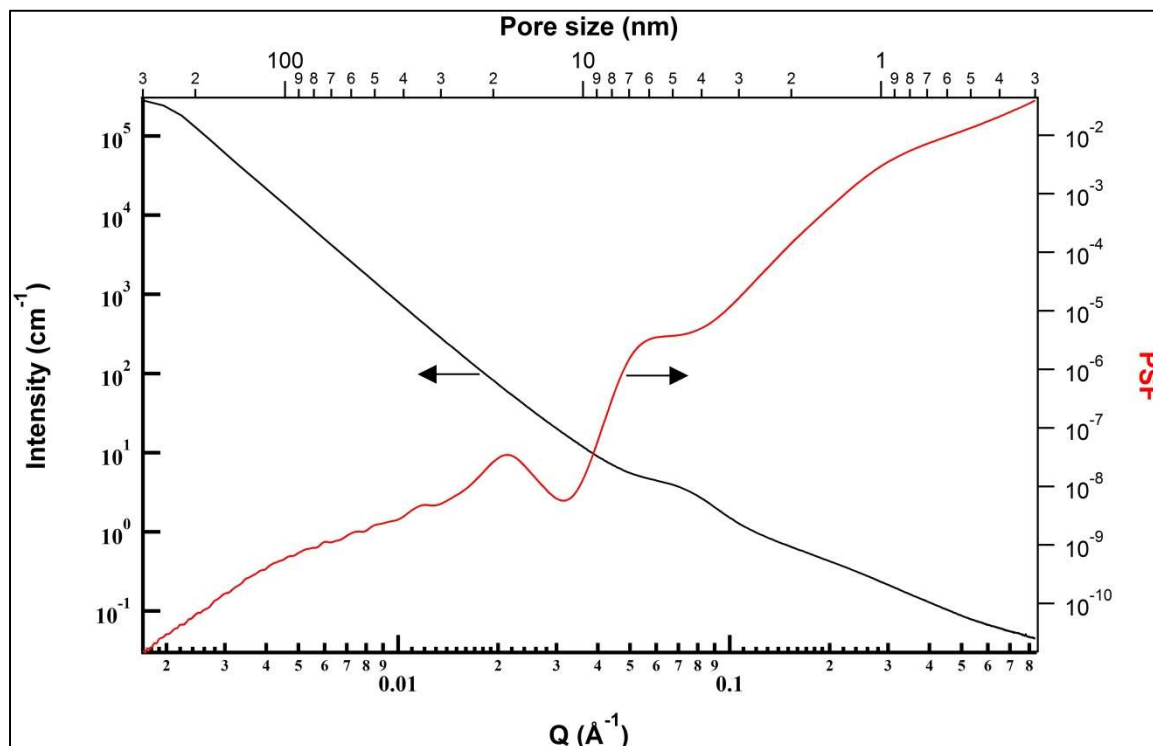


Figure 4.1: Absolute intensity and PSF for the char sample.

The slope of the Porod plot for intensity is not constant over the whole Q -range. Nevertheless, a linear, Porod region is observed at the low Q -range, which turns into a Guinier (non-linear) region in the mid Q -range ($0.03 < Q(\text{\AA}^{-1}) < 0.2$) and is followed by another Porod region at the high Q -range ($> 0.2 \text{ \AA}^{-1}$). The low- Q Porod region has a slope of approximately -3.5, compared to the high- Q Porod regime with a shallower slope (-1.8). The Porod region at low Q indicates that some pores are present in the char structure that are larger than probed in the SAXS measurement, which are confirmed by the model results. Since the slope changes with Q , simple fractal models are inadequate to describe the porosity of chars, and for this study a polydisperse model was used to determine the pore number. The log-log PSF plot showed the prevalence of small pores and non-linear pore size frequency, specifically for pore size ranging from 3 to 10 nm. The observed non-linearity for pore size from 3 to 10 nm is not a measurement artefact as the non-linearity was detected at both camera positions, overlapped

Q-range for two positions range from $0.04 \text{ \AA}^{-1}$ to $0.2 \text{ \AA}^{-1}$. The non-linear region is also not due to mineral matter, as non-linearity is reduced while mineral matter content increases as conversion progress as see in Figure 4.4. Since the non-linearity is reduced as conversion progress, it is proposed that this is a direct result of char carbon structure and that molecular characterisation and modelling of carbon structure should be used in future studies to further elucidate these observations. Figure 4.2 shows the cumulative pore surface area and individual pore size surface area of the char.

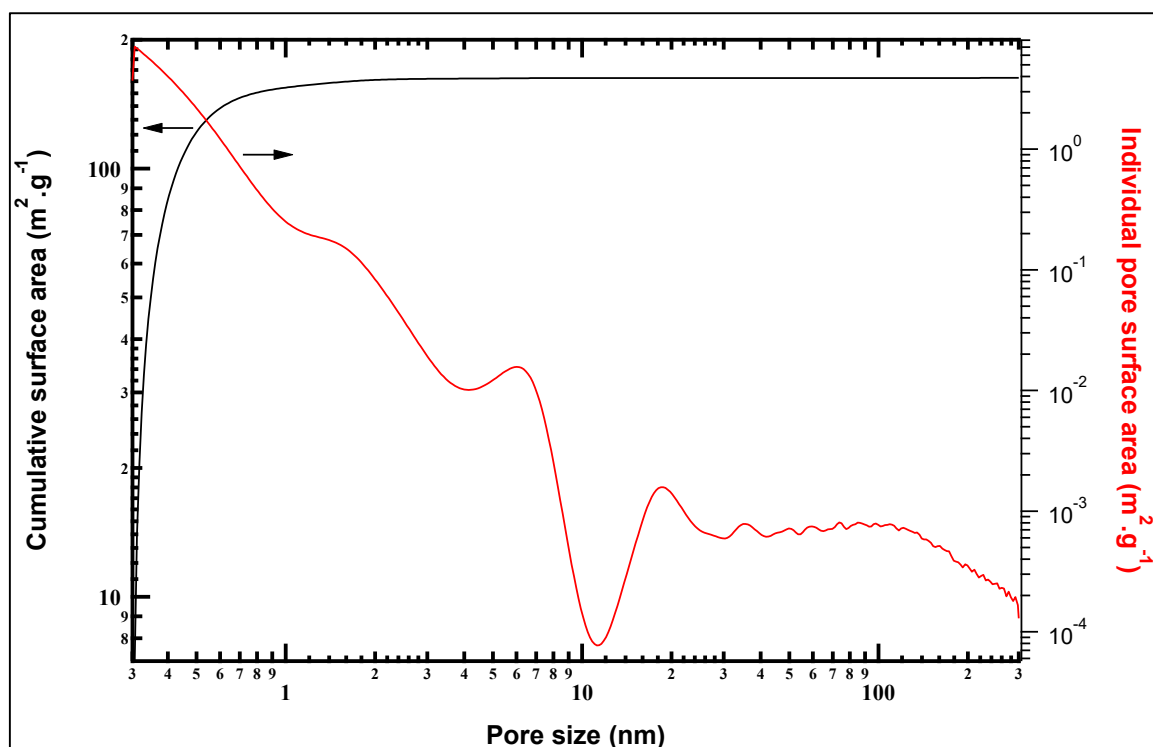


Figure 4.2: Cumulative surface area and individual pore surface area for the char sample.

The cumulative pore surface area shows that 95% of the pore surface area is found in the micropore pore size range ($< 2 \text{ nm}$). The individual pore surface area distribution is usually accepted as a smooth power law distribution (from fractal assumption), with the phenomena not seen for this char. Figure 4.3 shows the cumulative pore volume and individual pore size volume and shows a clear bimodal pattern (maxima at 1 and 100 nm), with comparatively few pores in the intermediate region.

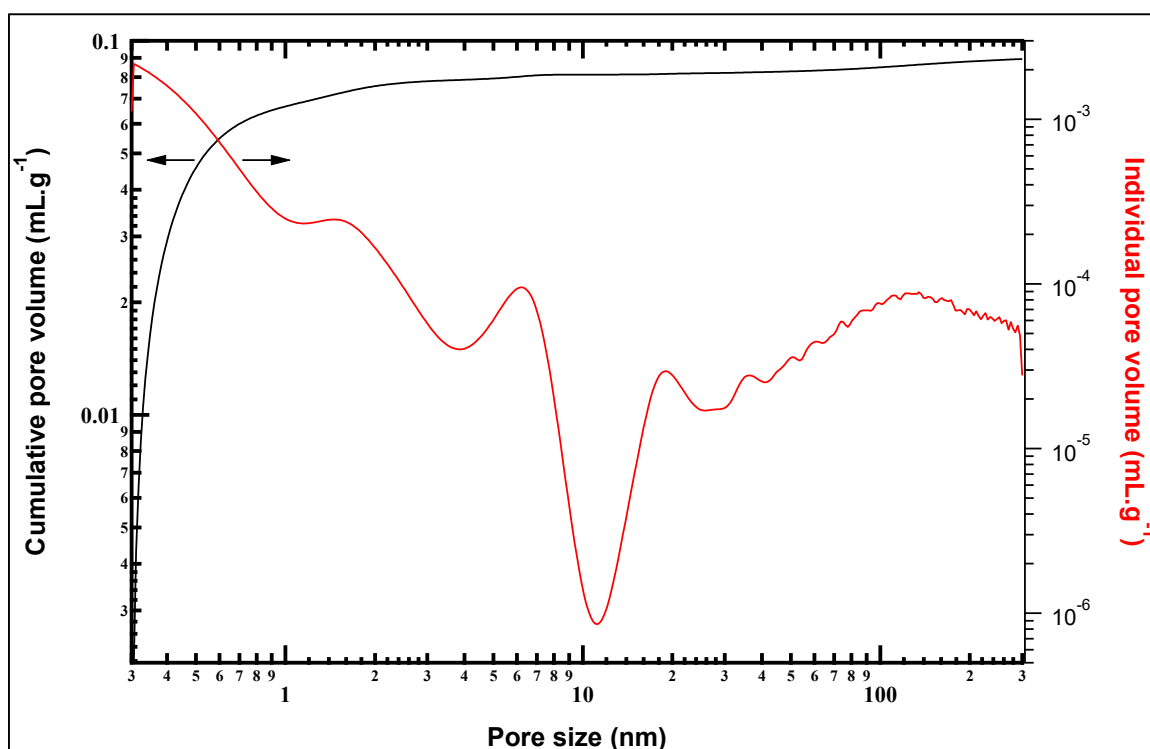


Figure 4.3: Cumulative volume and individual pore volume for the char sample.

The cumulative pore volume obtained translates to 15% porosity for the probed pore size range. The cumulative pore surface area and bimodal porosity distribution observations are comparable to literature for coal chars using gas adsorption measurements [44-51].

4.3.2. Gasified chars

Figure 4.4 shows the absolute intensity data for the chars after CO₂ gasification (all conversions) at 1000°C. Generally, the absolute scattering intensity increases over the entire Q-range as the conversion progress, indicating that the numbers of pores at all sizes increase, even at the smallest sizes observed. The increase in number of pores per unit volume at each size range is due to smaller pores – which are more numerous than larger pores – increasing in size on gasification and does not imply new pores are created, except possibly at the smallest resolvable scale. This also means that any pore coalescence is overshadowed by pore growth at these conversions, since pore coalescence would lead to a decrease in pore numbers, and thus scattering intensity. The SAXS surface area and pore volume (per gram carbon) for the micro-, meso-, and macropores are shown in Table 4.3.

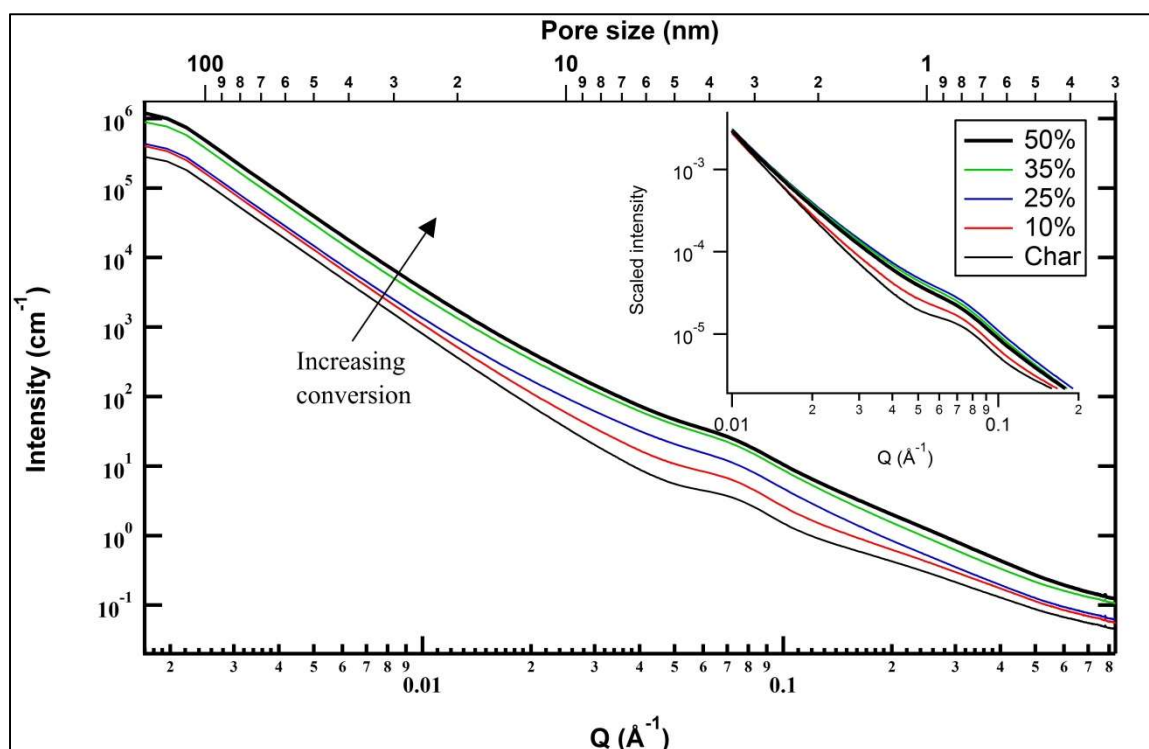


Figure 4.4: Absolute intensity data for all conversions at 1000°C for CO₂.

Table 4.3: SAXS surface area and pore volume for micro-, meso- and macropores based on gram carbon for CO₂.

	Pore volume (mL/g _c)			Surface area (m ² /g _c)		
	Micropore	Mesopore	Macropore	Micropore	Mesopore	Macropore
0	0.47	0.026	0.066	161	1.65	0.47
10	0.61	0.045	0.096	257	3.57	1.15
25	0.67	0.083	0.136	343	7.46	2.49
35	1.28	0.153	0.271	379	7.53	2.57
50	1.57	0.184	0.341	435	8.68	2.85

The pore development of micropores follows similar trends as reported in literature [6, 11, 13, 14], with CO₂ gasification opening the microporosity from onset of gasification. Broadening of meso-, and macropores is observed here from the onset of gasification; it was previously only observed at high conversions [6, 11, 13, 14]. Because pores of all sizes are generated during gasification under these conditions, it can be concluded that the gases have access to most, if not all, of the pore sizes. Table 4.4 and Figure 4.5 shows the SAR and SCIR plot, respectively, for the different conversions of CO₂ gasification at 1000°C.

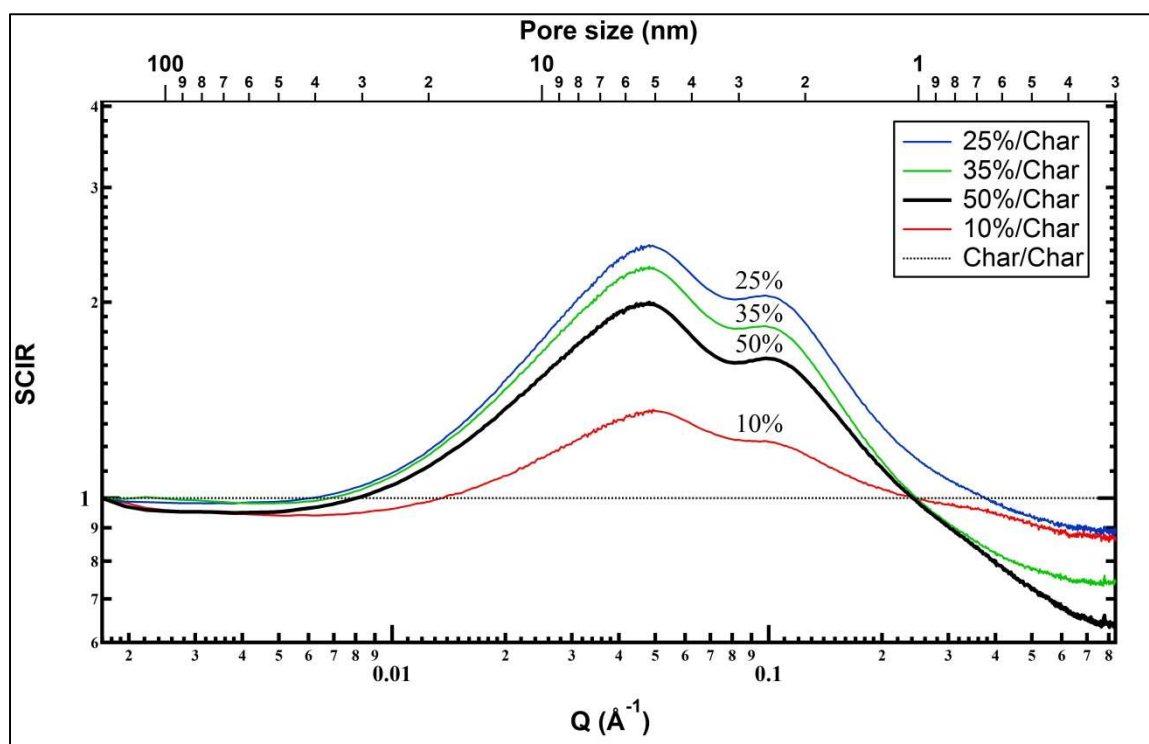


Figure 4.5: SCIR and SAR of gasified char for CO₂ at 1000°C.

Table 4.4: Ratio of surface area at various pore sizes gasified char at 1000°C for CO₂ gasification compared to original char.

	Pore size range (nm)	SAR (10%)	SAR (25%)	SAR (35%)	SAR (50%)
Bin 1	0.3-0.6	1.5	2.1	2.4	2.7
Bin 2	0.6-1.2	2.0	2.6	2.0	2.4
Bin 3	1.2-2.4	1.8	2.6	2.8	4.0
Bin 4	2.4-4.8	2.6	6.5	6.4	7.4
Bin 5	4.9-9.5	2.5	5.5	5.6	6.1
Bin 6	9.7-19.1	3.3	11	11	12
Bin 7	19-38	2.1	3.6	3.9	4.7
Bin 8	39-76	1.9	2.7	2.9	3.5
Bin 9	78-153	1.7	2.1	2.5	3.2
Bin 10	155-300	1.6	2.1	2.5	3.3

From Figure 4.5, for pore size > 40 nm, the SCIR is observed to be close to 1. A SCIR value close to 1 indicates that pore sizes are modified at approximately the same rate as the largest pores. All of the larger pores appear to grow at the same rate. For pore sizes between 1 and 40 nm, the intensity ratio is > 1, showing that the rate of pore growth for these sized pores is greater than those of the larger pore sizes. For pore sizes < 1 nm, the SCIR ratio reduces to < 1, indicating that smaller pores are less affected by conversion than the largest pores. The same observations can be made using the SI subplot in Figure 4.4. The observation of pore

development observed using SCIR and SI, is verified and quantified using SAR calculated from polydisperse modeling. For pore sizes > 40 nm, the increase in SAR of different bins (at a specific conversion) follows similar trends as conversion progress which indicates that pore sizes are modified at the same rate. For the intermediate pore size range, 1.2 nm to 38 nm, a larger increase in the SAR per pore bin is observed as conversion progress, indicating an increase rate of pore generation when compared to other pore sizes. For pore sizes < 1.2 nm, generally, the SAR is observed to be the smallest, indicating the lowest rate of pore generation. The SCIR in Figure 4.4 shows a decreasing trend as conversion increases ($> 25\%$), indicating a relative increasing growth rate of larger pores (> 40 nm) compared to small pores. The overlap in SI, SCIR and SAR observations shows that the novel ratio analysis (SI and SCIR) will give indicative changes into pore development using experimental results without the necessity of complex modelling.

The observation from SCIR, SI and SAR further shows that individual sized pores inside the larger lumped bins (IUPAC pore size classification) grow at different rates with the difference not explained by gas accessibility alone and require further investigation using advanced molecular characterisation and modelling. The largest growth in surface area is observed for pore bin 5 (9 to 19 nm), with a factor increase up to 4. This observation has direct implications with regards to activated carbon production and usage, carbon (coal and biomass) reaction modelling and industrial scale operations. Increased resolution on a pore scale can be accomplished by increasing the number of bins, with 10 bins only arbitrarily used here to ease data representation. There are several possible explanations for the apparent differences in the rate of pore generation for pore size during gasification, which include:

- Chemical controlled reactivity is a surface phenomenon in gas-solid reactions and since the surface area distribution is not constant over the pore size scale, with an increase surface area observed for the smaller pore sizes, the selective increase to < 50 nm could be due to this.
- The nature of the surface in smaller pores is different to that in larger pores, allowing greater reactivity. For example, reactivity of carbon in aromatic structures is greater at the edges than the centre of the structure [52-55]. If the smaller pores have more exposed edge carbons this would increase the apparent reactivity. Alternatively, if the aromatic planes are more distorted at smaller pore sizes, due to the smaller radius of curvature, the higher energy would reduce the activation energy of the reaction.

- The large pores being equally reactive as the smaller pores, but pore coalescence being more prevalent at the larger size scale.
- A change in mass transport mechanism for pores below 25 nm.

The conclusions and general trends discussed for CO₂ gasification, in Figure 4.4 and 4.5, are also applicable to the steam gasification results.

4.3.3. CO₂ and steam comparison

Table 4.5 and Figure 4.6 show the pore development parameters and scattering intensity of all converted chars using steam gasification at 950°C, respectively.

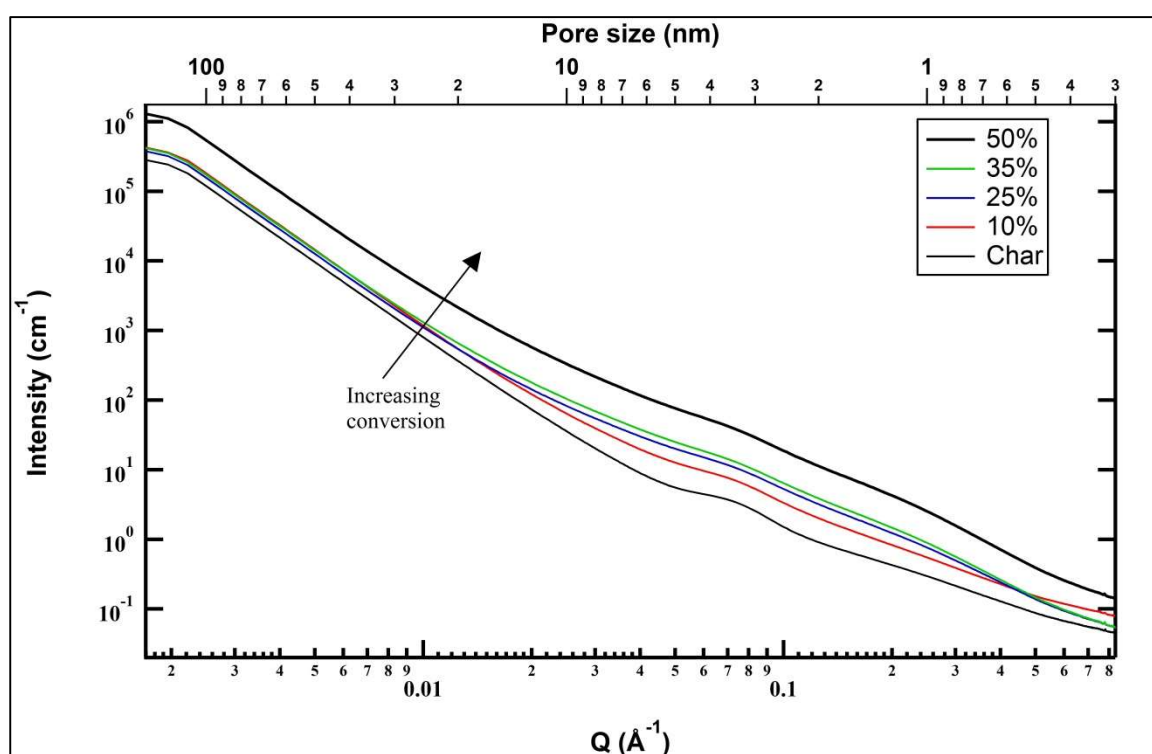


Figure 4.6: Absolute intensity data for all conversions at 950°C for steam.

Table 4.5: SAXS surface area and porosity for micro-, meso- and macropores based on gram carbon for steam gasification at 950°C.

	Pore volume (mL/g _c)			Surface area (m ² /g _c)		
	Micropore	Mesopore	Macropore	Micropore	Mesopore	Macropore
0	0.48	0.026	0.066	161	1.65	0.47
10	0.89	0.064	0.10	402	5.14	1.25
25	0.63	0.11	0.12	832	31.8	6.53
35	0.66	0.13	0.14	1052	48.7	9.83
50	1.96	0.40	0.43	1089	48.2	9.90

The scattering intensity for steam gasified char (Figure 4.6), over the entire Q -range, is greater than that of CO_2 gasified char (Figure 4.4) for the same conversion (Figure 4.4), indicating that the number of pores for a specific converted char using steam is greater than CO_2 . From Table 4.5 it is observed that widening of micro-, meso-, and macropores occurs from the onset of gasification. Comparing Table 4.3 and 4.5, it is also seen that the pore volume and surface area for steam gasification is larger than for CO_2 . This is consistent with the differences between steam and CO_2 gasification effects on porosity and surface area previously observed [6, 11, 13, 14]. Table 4.6 and Figure 4.7 shows the SAR and SCIR plot, respectively, for steam gasification at 950°C .

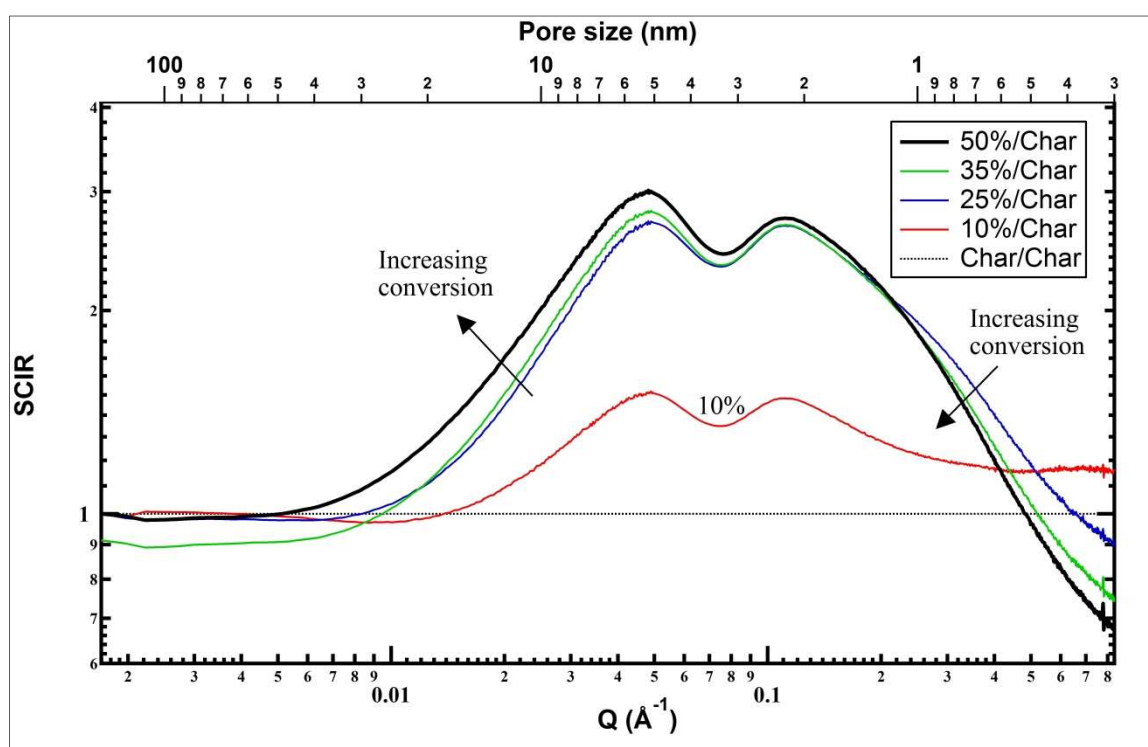


Figure 4.7: SCIR for steam gasification at 950°C .

Table 4.6: SAR of gasified char at 1000°C for CO₂ gasification.

	Pore size range (nm)	SAR (10%)	SAR (25%)	SAR (35%)	SAR (50%)
Bin 1	0.3-0.6	2.5	4.3	5.4	6.0
Bin 2	0.6-1.2	2.5	10	13	10
Bin 3	1.2-2.4	2.3	14	21	21
Bin 4	2.4-4.8	3.7	23	34	33
Bin 5	4.9-9.5	2.7	14	22	21
Bin 6	9.7-19.1	4.3	30	49	52
Bin 7	19-38	2.0	8.1	13	14
Bin 8	39-76	2.1	7.0	9.7	10
Bin 9	78-153	1.8	5.2	7.2	7.8
Bin 10	155-300	1.7	5.2	7.3	7.9

As for CO₂ gasification, in steam gasification different pore sizes grow at different rates. However, differences in pore selectivity between steam and CO₂ are observed when the micro-, meso and macroporosity are considered separately for the SCIR and SAR. For the macropores (> 50 nm) there is no systematic change in the SCIR, indicating that all large pores are equally affected by steam and CO₂. The SCIR in Figure 4.5 shows an increasing trend as conversion increases, indicating a relative decreased growth rate of larger pores (> 40 nm) compared to smaller pores, with an opposite trend observed for CO₂ gasification. From the SAR it is observed that the macropore growth for steam gasification is larger compared to CO₂, as expected from the intensity comparison. Within the pore size range of 2 to 50 nm; the SCIR and SAR for steam is greater than CO₂, with the second maxima for steam gasification (seen in Figure 4.7) also larger than what is observed for CO₂ (Figure 4.5). The same pore bin (bin 5) showed the maximum rate of pore generation for CO₂ gasification. The larger ratio increase and higher peaks observed for steam gasification indicates that the rate of pore generation of sizes between 2 and 50 nm are greater for steam than CO₂. Comparing SAR at the different conversion for the highest gasification temperatures, shows that pore growth from steam is up to a factor 7 faster than CO₂. The SCIR for pores probed below 2 nm also shows different behaviour for steam compared to CO₂. For CO₂, the SCIR decreases rapidly from the second maxima to < 1, with the cross over pore size ~ 1 nm, indicating that the rate of pore generation reduce drastically. From the SAR, steam shows a definite increase in pore reactivity between 0.6 and 2 nm compared to CO₂, with the cross-over pore size for steam being ~ 0.6 nm. The difference in cross over pore size between steam and CO₂ is likely due to the critical pore size, for each reagent gas, where surface diffusion becomes the dominant mass transport mechanism. The quantification of the specific cross-over pore size for CO₂ and steam can directly be used to improve reactivity and flux models developed by authors [56-58] which assumed the minimum pore size for mass transfer influence to be ~ 2

nm. It is reported in literature that the inert gas used to dilute the CO₂ and steam affects the measured gasification rates [59-62]. Because it is found here that even very fine pores are affected by gasification, the presence of the diluent gas may itself slow access to ultrafine pores of a size comparable with the molecular diameter of the diluent gas even if it is not adsorbed onto the char surface. If so, then the 'crossover' pore size may be affected by the choice of diluent gas; this is suggested as a possibility for future examination.

The difference between pore development during CO₂ and steam gasification is summarised as follows: The difference in micro-, meso-, and macropore development observed during steam and CO₂ gasification using SAXS, generally agree with trends observed using gas adsorption techniques and mercury porosimetry [6-10,15,17-19]. The increased intensity observed for steam shows that steam creates a greater probed-porosity than CO₂. Compared to steam gasification, CO₂ conversion produces a more uniform increase in pore numbers at all pore sizes, concluded from the smaller SCIR and SAR seen for CO₂. The change in macropore development between CO₂ and steam is comparable; the SAR of the different pore bins follow similar trends. Steam has an increased macropore generation rate when compared to CO₂. However, the overall contribution of macropore development for CO₂ gasification is greater compared to steam. For the mesopore size range, an increase in the selective pore reactivity is observed for steam compared to CO₂. The individual pore size growth of pores < 25 nm is larger for steam than CO₂, with the greatest selective pore growth seen for pores ranging between 1.2 and 19 nm. The greatest selectivity for steam is seen for pore range 0.6 to 2.4 nm. The selective increase in opening of specific pore fraction (< 25 nm) by steam could be due to its deeper penetration into the pore structure compared to CO₂ which is consistent with smaller kinetic diameter (2.65 Å for steam and 3.3 Å for CO₂ [63]). If so, the greater number of pores accessible by steam may accentuate the faster reactivity of steam compared to CO₂ observed in kinetic studies. The increased accessible surface area available to steam and different pore growth rates during reactivity should be taken into consideration when comparing the intrinsic reaction rate between steam and CO₂ (reporting reactivity on the basis of total surface area).

4.3.4. Temperature influence

Figure 4.8 shows the temperature influence, using the ICR, on the pore development for CO₂ and steam gasification, respectively. The effects of temperature are much smaller than the other effects examined, at least over the temperature range investigated. For CO₂ gasification, in general, the ICR at 850°C is slightly lower than the ratio at 1000°C. This will

result in less probed pores at 850°C compared to 1000°C, which could be due to the greater contribution of pore > 147 nm reactivity and particle surface reactivity for the lower gasification temperature. The opposite trend is seen for steam gasification, where generally, the intensity ratio of 800°C is greater than at 950°C. The lack of definable temperature effects on the pore development, over the entire pore range probed, shows that all pores are penetrated to the same extent independently of the gasification temperatures studied.

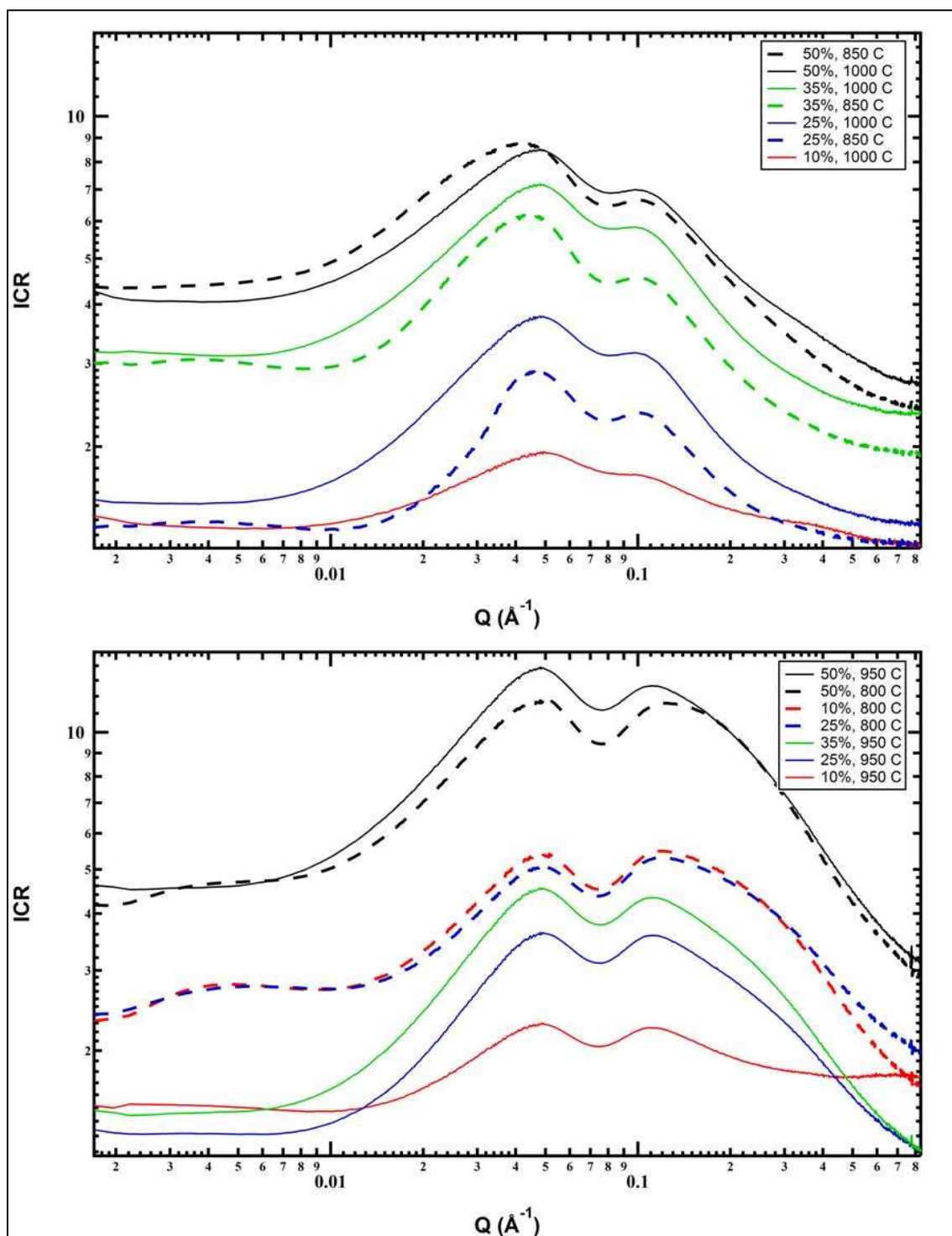


Figure 4.8: ICR results for all the gasification temperatures for a) CO_2 and b) steam.

4.4. Conclusions

In this work the pore development of chars gasified by CO₂ and steam using SAXS is evaluated. The sample used for this investigation was char prepared from an inertinite-rich South African coal, Witbank seam 4. The use of an inertinite-rich sample adds to the maceral and international diversity of coal data in literature. This work further demonstrates the utility of SAXS studies of gasified chars, with the added resolution supplementing understanding of the complex system. A novel ratio analysis method (SI, ICR and SCIR), using scatter intensity data only without requiring modelling, was developed to describe pore growth to compare steam and CO₂ gasification. The main findings of the pore development during CO₂ and steam gasification of ~ 75 µm particle size were:

- The general trends observed using large lumped pore ranges (IUPAC) from SAXS results compares well to literature. With the only exception being the broadening of meso- and macropores from onset of CO₂ gasification, which was not found with the other chars and likely to be maceral related.
- The ratio analysis of intensity plots showed that different sized pores grow at different rates and differences within these sections were also seen. This was further quantified using modelling and the calculation of SAR. The following trends were observed:
 - Pore sizes > 40 nm were equally effected by gasification
 - Pore sizes ranging from critical cross over to 40 nm shows an increased rate of pore generation
 - Pore sizes < critical cross over pore size showed to have a decrease rate of pore generation when compared to larger pore sizes
- The differences in individual sized pore growth cannot be explained by gas accessibility alone.
- Steam creates more pores for a given conversion, and also shows increased selectivity of pore growth for the pore size range between 0.6 and 40 nm, when compared to CO₂ gasification. The increase was quantified by comparing SAR for each conversion at the highest gasification temperature of steam to CO₂. The increase was up to a factor 7, with the largest increase seen for the pore range 0.6 to 2.4 nm.
- The rate of pore generation below 1 nm was found to be slower than the larger pore sizes with the critical cross over pore size for CO₂ being 1 nm, compared to 0.6 nm for steam. The greater critical cross over value for CO₂ may be a direct consequence of CO₂'s greater kinetic diameter.

The differences in pore growth rate seen at different sizes is an additional complexity that needs to be addressed in reaction rate models of gasification of carbons and production of activated carbon. These fundamental understanding can be incorporated into single particle models in order to quantify the gasification rate. The influence of the inert diluent gas on the pore development should be investigated in future evaluations to determine its effect.

4.5. Nomenclature

Symbols:

d_p - Pore diameter [nm]

I_0 - Total incident intensities

I_{BS} - Beam stop intensities

Q - Scattering vector [$\text{\AA}^{-1}$]

Abbreviations

ICR– Intensity conversion ratio

IPG-TNNLS – Internal point gradient – total non-negative least square

PSF– Pore size frequency

R_r- Vitrinite random reflectance

R_{sc}- Total maceral reflectance

SAS- Small Angle Scattering

SANS- Small Angle Neutron Scattering

SAR – Surface area ratio

SAXS- Small Angle X-ray Scattering

SCIR- Scaled conversion intensity ratio

TGA-Thermogravimetric analyser

4.6. Chapter References

- [1] Lee S. Coal gasification: Synthesis of syngas, fuels, and petrochemicals. In Williams C, Prescott M, editors. *Alternative Fuels*. District of Columbia: Taylor & Francis; 1996, p. 95-164.
- [2] Dhaneswar SR, Pisupati SV. Oxy-fuel combustion: The effect of coal rank and the role of char-CO₂ reaction. *Fuel Process Technol* 2012;102:156-65.
<http://dx.doi.org/10.1016/j.fuproc.2012.04.029>
- [3] Grigore M, Sakurovs R, French D, Sahajwalla V. Coke Gasification: The influence and behavior of inherent catalytic mineral matter. *Energy Fuels* 2009;23(4):2075-85.
<http://dx.doi.org/10.1021/ef8006728>
- [4] Kajitani S, Hara S, Matsuda H. Gasification rate analysis of coal char with a pressurized drop tube furnace. *Fuel* 2002;81(5):539-46. [http://dx.doi.org/10.1016/S0016-2361\(01\)00149-1](http://dx.doi.org/10.1016/S0016-2361(01)00149-1)
- [5] Kim YT, Seo DK, Hwang J. Study of the effect of coal type and particle size on char-CO₂ gasification via gas analysis. *Energy Fuels* 2011;25(11):5044-54.
<http://dx.doi.org/10.1021/ef200745x>
- [6] Arenas E, Chejne F. The effect of the activating agent and temperature on the porosity development of physically activated coal chars. *Carbon* 2004;42(12-13):2451-5.
<http://dx.doi.org/10.1016/j.carbon.2004.04.041>
- [7] Huo W, Zhou Z, Wang F, Wang Y, Yu G. Experimental study of pore diffusion effect on char gasification with CO₂ and steam. *Fuel* 2014;131:59-65.
<http://dx.doi.org/10.1016/j.fuel.2014.04.058>
- [8] Huo W, Zhou Z, Wang F, Yu G. Mechanism analysis and experimental verification of pore diffusion on coke and coal char gasification with CO₂. *Chem Eng J* 2014;244:227-33.
<http://dx.doi.org/10.1016/j.cej.2014.01.069>
- [9] Linares-Solano A, Salinas-Martínez dL, Cazorla-Amorós D, Martín-Gullón I. Porosity development during CO₂ and steam activation in a fluidized bed reactor. *Energy Fuels* 2000;14(1):142-9. <http://dx.doi.org/10.1021/ef9900637>
- [10] Feng B, Bhatia SK. Variation of the pore structure of coal chars during gasification. *Carbon* 2003;41(3):507-23. [http://dx.doi.org/10.1016/S0008-6223\(02\)00357-3](http://dx.doi.org/10.1016/S0008-6223(02)00357-3)

- [11] González JF, Román S, González-García CM, Nabais JMV, Ortiz AL. Porosity development in activated carbons prepared from walnut shells by carbon dioxide or steam activation. *Ind Eng Chem Res* 2009;48(16):7474-81.
<http://dx.doi.org/10.1021/ie801848x>
- [12] Molina-Sabio M, Gonzalez MT, Rodriguez-Reinoso F, Sepúlveda-Escribano A. Effect of steam and carbon dioxide activation in the micropore size distribution of activated carbon. *Carbon* 1996;34(4):505-9. [http://dx.doi.org/10.1016/0008-6223\(96\)00006-1](http://dx.doi.org/10.1016/0008-6223(96)00006-1)
- [13] Pastor-Villegas J, Durán-Valle CJ. Pore structure of activated carbons prepared by carbon dioxide and steam activation at different temperatures from extracted rockrose. *Carbon* 2002;40(3):397-402. [http://dx.doi.org/10.1016/S0008-6223\(01\)00118-X](http://dx.doi.org/10.1016/S0008-6223(01)00118-X)
- [14] Rodríguez-Reinoso F, Molina-Sabio M, González MT. The use of steam and CO₂ as activating agents in the preparation of activated carbons. *Carbon* 1995;33(1):15-23. [http://dx.doi.org/10.1016/0008-6223\(94\)00100-E](http://dx.doi.org/10.1016/0008-6223(94)00100-E)
- [15] Román S, González JF, González-García CM, Zamora F. Control of pore development during CO₂ and steam activation of olive stones. *Fuel Process Technol* 2008;89(8):715-20. <http://dx.doi.org/10.1016/j.fuproc.2007.12.015>
- [16] San Miguel , Guillermo, Fowler GD, Sollars CJ. A study of the characteristics of activated carbons produced by steam and carbon dioxide activation of waste tyre rubber. *Carbon* 2003;41(5):1009-16. [http://dx.doi.org/10.1016/S0008-6223\(02\)00449-9](http://dx.doi.org/10.1016/S0008-6223(02)00449-9)
- [17] Serrano-Talavera B, Muñoz-Guillena MJ, Linares-Solana A, Salinas-Martínez de Lecea C. Activated carbons from Spanish coals. 3. Preoxidation effect on anthracite activation. *Energy and Fuels* 1997;11(4):785-791. <http://dx.doi.org/10.1021/ef960105g>
- [18] Wigmans, T. Fundamentals and practical implications of activated carbon production by partial gasification of carbonaceous materials. In: Figueiredo J, Moulijn J, editors. *Carbon and coal gasification*; NATO/ASI, Series E; Alvor: Portugal, 1985; p 559-599
- [19] Kühl H, Kashani-Motlagh MM, Mühlen HJ, van Heek KH. Controlled gasification of different carbon materials and development of pore structure. *Fuel* 1992;71(8), 879-882. [http://dx.doi.org/10.1016/0016-2361\(92\)90236-H](http://dx.doi.org/10.1016/0016-2361(92)90236-H)
- [20] Okolo GN, Everson RC, Neomagus HWJP, Roberts MJ, Sakurovs R. Comparing the porosity and surface areas of coal as measured by gas adsorption, mercury intrusion and SAXS techniques. *Fuel* 2015;141:293-304. <http://dx.doi.org/10.1016/j.fuel.2014.10.046>

- [21] Radliński AP, Mastalerz M, Hinde AL, Hainbuchner M, Rauch H, Baron M *et al.* Application of SAXS and SANS in evaluation of porosity, pore size distribution and surface area of coal. *Int J Coal Geol* 2004;59(3-4):245-71. <http://dx.doi.org/10.1016/j.coal.2004.03.002>
- [22] Cohaut N, Blanche C, Dumas D, Guet JM, Rouzaud JN. A small angle X-ray scattering study on the porosity of anthracites. *Carbon* 2000;38(9):1391-400. [http://dx.doi.org/10.1016/S0008-6223\(99\)00274-2](http://dx.doi.org/10.1016/S0008-6223(99)00274-2)
- [23] László K, Czakkel O, Dobos G, Lodewyckx P, Rochas C, Geissler E. Water vapour adsorption in highly porous carbons as seen by small and wide angle X-ray scattering. *Carbon* 2010;48(4):1038-48. <http://dx.doi.org/10.1016/j.carbon.2009.11.023>
- [24] Liu J, Jiang X, Huang X, Wu S. Morphological characterization of super fine pulverized coal particle. Part 4. Nitrogen adsorption and small angle X-ray scattering study. *Energy Fuels* 2010;24(5):3072-85. <http://dx.doi.org/10.1021/ef100142t>
- [25] Liu J, Jiang X, Huang X, Shen J, Wu S. Investigation of the diffuse interfacial layer of superfine pulverized coal and char particles. *Energy Fuels* 2011;25(2):684-93. <http://dx.doi.org/10.1021/ef101307a>
- [26] Zhao Y, Liu S, Elsworth D, Jiang Y, Zhu J. Pore structure characterization of coal by synchrotron small-Angle X-ray scattering and transmission electron microscopy. *Energy Fuels* 2014;28(6):3704-11. <http://dx.doi.org/10.1021/ef500487d>
- [27] Mares TE, Radliński AP, Moore TA, Cookson D, Thiyagarajan P, Ilavsky J *et al.* Assessing the potential for CO₂ adsorption in a subbituminous coal, Huntly Coalfield, New Zealand, using small angle scattering techniques. *Int J Coal Geol* 2009;77(1-2):54-68. <http://dx.doi.org/10.1016/j.coal.2008.07.007>
- [28] Melnichenko YB, He L, Sakurovs R, Kholodenko AL, Blach T, Mastalerz M *et al.* Accessibility of pores in coal to methane and carbon dioxide. *Fuel* 2012;91(1):200-8. <http://dx.doi.org/10.1016/j.fuel.2011.06.026>
- [29] Mastalerz M, He L, Melnichenko YB, Rupp JA. Porosity of coal and shale: Insights from gas adsorption and SANS/USANS techniques. *Energy Fuels* 2012;26:5109-20. <http://dx.doi.org/10.1021/ef300735t>
- [30] Radliński AP, Busbridge TL, Gray EMA, Blach TP, Cookson DJ. Small angle X-ray scattering mapping and kinetics study of sub-critical CO₂ sorption by two Australian coals. *Int J Coal Geol* 2009;77(1-2):80-9. <http://dx.doi.org/10.1016/j.coal.2008.09.015>

-
- [31] Sakurovs R, He L, Melnichenko YB, Radliński AP, Blach T, Lemmel H *et al.* Pore size distribution and accessible pore size distribution in bituminous coals. *Int J Coal Geol* 2012;100:51-64. <http://dx.doi.org/10.1016/j.coal.2012.06.005>
- [32] Bale HD, Carlson ML, Schobert HH. Thermal modification of the pore structure of a North Dakota lignite. *Fuel* 1986;65(9):1185-9. [http://dx.doi.org/10.1016/0016-2361\(86\)90227-9](http://dx.doi.org/10.1016/0016-2361(86)90227-9)
- [33] Calo JM, Hall PJ, Antxustegi M. Carbon porosity characterization via small angle neutron scattering. *Colloids Surf Physicochem Eng Asp* 2001;187–188:219-32. [http://dx.doi.org/10.1016/S0927-7757\(01\)00635-5](http://dx.doi.org/10.1016/S0927-7757(01)00635-5)
- [34] Calo JM, Hall PJ, Houtmann S, Castello DL, Winans RE, Seifert S. “Real time” determination of porosity development in carbons: a combined SAXS/TGA approach. Extended abstracts, 6th International Symposium on the characterization of porous solids. Alicante, Spain: Studies in Surface Science and Catalysis, 2002; p.59-66. [http://dx.doi.org/10.1016/S0167-2991\(02\)80220-8](http://dx.doi.org/10.1016/S0167-2991(02)80220-8)
- [35] Antxustegi MM, Hall PJ, Calo JM. Development of porosity in Pittsburgh No. 8 coal char as investigated by contrast-matching small-angle neutron scattering and gas adsorption techniques. *Energy Fuels* 1998;12(3):542-6. <http://dx.doi.org/10.1021/ef970153g>
- [36] Diduszko R, Swiatkowski A, Trznadel BJ. On surface of micropores and fractal dimension of activated carbon determined on the basis of adsorption and SAXS investigations. *Carbon* 2000;38(8):1153-62. [http://dx.doi.org/10.1016/S0008-6223\(99\)00236-5](http://dx.doi.org/10.1016/S0008-6223(99)00236-5)
- [37] Foster MD, Jensen KF. Small angle X-ray scattering investigations of pore structure changes during coal gasification. *Fuel* 1990;69(1):88-96. [http://dx.doi.org/10.1016/0016-2361\(90\)90263-P](http://dx.doi.org/10.1016/0016-2361(90)90263-P)
- [38] Foster MD, Jensen KF. SAXS investigation of model carbon pore structure and its change with gasification. *Carbon* 1991;29(2):271-82. [http://dx.doi.org/10.1016/0008-6223\(91\)90077-V](http://dx.doi.org/10.1016/0008-6223(91)90077-V)
- [39] Pfeifer, P., Ehrburger-Doller, F., Rieker, T., Schmidt, P. W., Voss, D.J., Rodriguez-Reinoso, F., Molina-Sabio, M and Gonzalez, M.T. Fractal networks of carbon nanopores. Extended abstracts, 23rd Biennial conference on carbon. University Park (Pennsylvania, USA): American Carbon Society, 1997; p. 350-1.
- [40] Coetzee S, Neomagus HWJP, Bunt JR, Everson RC. Improved reactivity of large coal particles by K₂CO₃ addition during steam gasification. *Fuel Process Technol* 2013;114:75-80. <http://dx.doi.org/10.1016/j.fuproc.2013.03.041>

-
- [41] Kirby NM, Mudie ST, Hawley AM, Cookson DJ, Mertens HDT, Cowieson N *et al.* A low-background-intensity focusing small-angle X-ray scattering undulator beamline. *J Appl Crystallogr* 2013;46:1670-80. <http://dx.doi.org/10.1107/S002188981302774X>
- [42] Ilavsky J, Jemian PR. Irena: tool suite for modeling and analysis of small-angle scattering. *J Appl Crystallogr* 2009;42:347-53. <http://dx.doi.org/10.1107/S0021889809002222>
- [43] Zhang F, Ilavsky J, Long G, Quintana JG, Allen A, Jemian P. Glassy carbon as an absolute intensity calibration standard for small-angle scattering. *Metal Mater Trans A* 2010;41(5):1151-8. <http://dx.doi.org/10.1007/s11661-009-9950-x>
- [44] Joyner LG, Barrett EP, Skold R. The determination of pore volume and area distributions in porous substances. II. Comparison between nitrogen isotherm and mercury porosimeter methods. *J Am Chem Soc* 1951;73(7):3155-8. <http://dx.doi.org/10.1021/ja01151a046>
- [45] Hashimoto K, Miura K, Yoshikawa F, Imai I. Change in pore structure of carbonaceous materials during activation and adsorption performance of activated carbon. *Ind Eng Chem Proc Des Dev* 1979;18(1):72-80. <http://dx.doi.org/10.1021/i260069a010>
- [46] Dombrowski RJ, Hyduke DR, Lastoskie CM. Pore size analysis of activated carbons from Argon and Nitrogen porosimetry using Density Functional Theory. *Langmuir* 2000;16(11):5041-50. <http://dx.doi.org/10.1021/la990827a>
- [47] Liu G, Benyon P, Benfell KE, Bryant GW, Tate AG, Boyd RK *et al.* The porous structure of bituminous coal chars and its influence on combustion and gasification under chemically controlled conditions. *Fuel* 2000;79(6):617-26. [http://dx.doi.org/10.1016/S0016-2361\(99\)00185-4](http://dx.doi.org/10.1016/S0016-2361(99)00185-4)
- [48] Lorenz H, Carrea E, Tamura M, Haas J. The role of char surface structure development in pulverized fuel combustion. *Fuel* 2000;79(10):1161-72. [http://dx.doi.org/10.1016/S0016-2361\(99\)00259-8](http://dx.doi.org/10.1016/S0016-2361(99)00259-8)
- [49] Li Q, Zhao C, Chen X, Wu W, Lin B. Properties of char particles obtained under O₂/N₂ and O₂/CO₂ combustion environments. *Chem Eng Process: Process Intensif* 2010;49(5):449-59. <http://dx.doi.org/10.1016/j.cep.2010.03.007>
- [50] Lee D, Bae J, Park S, Lee Y, Hong J, Choi Y. The pore structure variation of coal char during pyrolysis and its relationship with char combustion reactivity. *Ind Eng Chem Res* 2012;51(42):13580-8. <http://dx.doi.org/10.1021/ie301927v>

- [51] Tang Y, Ma X, Lai Z, Lin H, Wu J. Char characteristics of municipal solid waste prepared under N_2 and CO_2 atmospheres. *J Anal Appl Pyrol* 2013;101:193-8. <http://dx.doi.org/10.1016/j.jaap.2013.01.010>
- [52] Frankcombe TJ, Bhatia SK, Smith SC. Ab initio modelling of basal plane oxidation of graphenes and implications for modelling char combustion. *Carbon* 2002;40(13):2341-9. [http://dx.doi.org/10.1016/S0008-6223\(02\)00147-1](http://dx.doi.org/10.1016/S0008-6223(02)00147-1)
- [53] Montoya A, Mondragón F, Truong TN. Formation of CO precursors during char gasification with O_2 , CO_2 and H_2O . *Fuel Process Technol* 2002;77-78:125-30. [http://dx.doi.org/10.1016/S0378-3820\(02\)00013-9](http://dx.doi.org/10.1016/S0378-3820(02)00013-9)
- [54] Sendt K, Haynes BS. Density functional study of the chemisorption of O_2 on the zig-zag surface of graphite. *Combust Flame* 2005;143(4):629-43. <http://dx.doi.org/10.1016/j.combustflame.2005.08.026>
- [55] Castro-Marcano F, Kamat AM, Russo Jr. MF, van Duin ACT, Mathews JP. Combustion of an Illinois No. 6 coal char simulated using an atomistic char representation and the ReaxFF reactive force field. *Combust Flame* 2012;159(3):1272-85. <http://dx.doi.org/10.1016/j.combustflame.2011.10.022>
- [56] Singer SL, Ghoniem AF. Comprehensive gasification modeling of char particles with multi-modal pore structures. *Combust Flame* 2013;160(1):120-37. <http://dx.doi.org/10.1016/j.combustflame.2012.09.007>
- [57] Wang FY, Bhatia SK. A generalised dynamic model for char particle gasification with structure evolution and peripheral fragmentation. *Chem Eng Sci* 2001;56:3683-97. [http://dx.doi.org/10.1016/S0009-2509\(01\)00060-4](http://dx.doi.org/10.1016/S0009-2509(01)00060-4)
- [58] Biggs MJ, Agarwal PK. The CO/CO_2 product ratio for a porous char particle within an incipiently fluidized bed: a numerical study. *Chem Eng Sci* 1997;52:941-52. [http://dx.doi.org/10.1016/S0009-2509\(96\)00489-7](http://dx.doi.org/10.1016/S0009-2509(96)00489-7)
- [59] Walker PL, Pentz L, Biederman DL, Vastola FJ. The influence of “inert” diluent gases on the rate of carbon gasification. *Carbon* 1977;15(3):165-8. [http://dx.doi.org/10.1016/0008-6223\(77\)90051-3](http://dx.doi.org/10.1016/0008-6223(77)90051-3)
- [60] Britten JA, Falconer JL. Effect of nonreacting gases on the desorption of reaction-created CO from graphite. *Carbon* 1985;23(6):627-33. [http://dx.doi.org/10.1016/0008-6223\(85\)90222-2](http://dx.doi.org/10.1016/0008-6223(85)90222-2)

- [61] Ahmed S, Back MH. The effect of water vapor and inert gases on the carbon-oxygen reaction. *Carbon* 1987;25(6):783-9. [http://dx.doi.org/10.1016/0008-6223\(87\)90152-7](http://dx.doi.org/10.1016/0008-6223(87)90152-7)
- [62] Zang L, Calo JM. The "inert gas effect" on carbon reactivity. *Proceedings of the 1995 - 22nd Biennial Carbon Conference*. University of California, San Diego USA; p.602-3.
- [63] Barbieri G, Bernardo P. GRACE: Experimental evaluation of hydrogen production by membrane reaction. In: Thomas DC, Benson SM, Editors. *Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO₂ Capture Project*, vol 2, Amsterdam: Elsevier; 2005, p. 385-408.

Chapter 5.

Particle size influence on the pore development of nanopores in coal gasification chars: from micron to millimeter particles

G. Hennie Coetzee, Richard Sakurovs, Hein W.J.P Neomagus, Leigh Morpeth, Raymond C. Everson, Jonathan P. Mathews, John R. Bunt

The pore development arising from steam and CO₂ gasification for three particle sizes (75 µm, 2 and 20 mm) was evaluated using small angle X-ray scattering. A novel application of radial SAXS measurement was developed to obtain pore development profiles for the 20 mm gasified chars.

Findings reported in this chapter are published as

Carbon **2017**, 112, 37-46.

DOI: doi.org/10.1016/j.carbon.2016.10.088

Abstract

The influence of particle size on the growth of nanopores arising from gasification of a South African coal-char was investigated using small angle X-ray scattering. Three different char sizes (75 μm , 2 and 20 mm) were gasified between 800 and 1000°C to specific conversions up to 50% and the pore development during CO₂ and steam gasification was compared. For the CO₂ gasified chars studied here, particle size influenced the rates of individual pore growth for all pore sizes and an increased development of micro-, and macropores was observed as particle size increased. For the steam gasified chars studied here, particle size only influenced the rates of individual pore growth for larger pores, with prevalence of macropore development. A novel application of monitoring pore development as a function of distance from the surface was applied to the 20 mm gasified char, spanning the surface to the interior of the spherical particle. The portion closest to the surface, showed the greatest pore development over the entire pore range, followed by the interior and center. The radial changes in growth rate for individual pore sizes demonstrated intra-particle mass transfer limitations for the 20 mm particle studied here under these conditions.

5.1. Background and Introduction

In coal conversion processes, gas-solid reactions play an important role [1]. The description of gas-solid reactions, at the particle level includes both reactive and mass transfer processes. A complete chemical reaction controlled process is Regime I, and Regime II is associated with conversions where intra-particle mass transfer affects the reaction rate [2]. The change in reaction rate, compared to chemical reaction control, is lumped into the effectiveness factor, the theory of which originates from gas-solid catalytic systems [3]. The effectiveness factor is often evaluated on the assumption of constant pore size during conversion. In contrast to catalytic systems where pore size does not change, carbonaceous material, when converted, undergoes changes in the porous structure. This influences the diffusion rate, the effectiveness factor and hence conversion rates. This process is further complicated by varying chemical composition for coal from different areas.

The pore development of activated carbon and coal, reacted by steam, CO₂, and O₂, has been evaluated by means of gas adsorption, mercury porosimetry, and X-ray and neutron angle scattering [4-12]. These pore development studies were used to generate pore parameter models, including (modifications of) the capillary- and random pore model, originally developed to predict structural change as conversion progresses for chemical reaction controlled reactions [13-16]. The influence of changes in structure with conversion, with reactivity limited by internal mass transfer, was recognised by several authors and incorporated into advanced dynamic particle models [17-21]. Pore development models of gasified chars in Regime II, superimpose pore development from chemical controlled reactions onto varying local conversions - due to concentration gradients within the particle [22,23]. Large particle feed introduce increasing mass transfer limitations within coal conversion processes [24-27].

The effect of particle size on the initial char structure (including surface area and pore volume) has previously been explored [28-33]; generally surface area and pore volume are found to increase as particle size increases. However, limited research has been conducted on the influence of particle size on the char structure development as conversion progresses. Kawahata and Walker [34] studied three particle sizes (105 – 150 μm , 212 - 355 μm and 0.85 -1 mm) at 900 °C using CO₂ gasification. They found decreasing pore development with an increase in particle size from the onset of gasification, proposed to be due to increased mass transfer limitations for the larger particles. Satya Sai *et al.* [35,36] also studied the pore development of three particle sizes (550 μm , 1.1 and 1.55 mm) at 850°C using CO₂

gasification, and found a relative increasing pore development with an increase in particle size. This was ascribed to a greater extent of pore coalescence in the smaller particles. They also studied the pore size distribution change as conversion progressed, using Brunauer–Emmett–Teller (BET) isotherm measurements using N_2 and found an increase in micro (< 2 nm) and large pore (> 8 nm) development as particle size increases. In light of these contradictory results, it is clear that further investigation into the effect of particle size on pore development is warranted.

To further elucidate the influence of particle size and indirectly intra-particle diffusion on pore development, the influence of a wider particle size range on the pore development for chars prepared from Witbank seam 4 coal was studied. The use of Small Angle X-ray Scattering (SAXS) allows investigation of a wider pore size range (0.3 to 147 nm), compared to previous studies. Three particle sizes (approximately 75 μm , 2 and 20 mm) were used and both steam and CO_2 gasification experiments were performed, where the latter two represent the particle size used for fluidised- and fixed bed operation. Gasification was performed in a Thermogravimetric Analyser (TGA) at atmospheric pressure and under isothermal conditions.

In a previous article [37], the authors compared the influence of CO_2 to steam on the pore development of 75 μm char particles. There it was found that different pore sizes grow at different rates, with prevalence for pore growth ranging from 1 to 40 nm. It was also found that the growth of different sized pores was influenced by the reaction gas. Here we evaluate the influence of reagent gas, temperature and particle size on pore development, specifically evaluating the effects on the growth rate of individual sized pores. Mineral matter and gas concentration was not studied, with the main focus being the influence of particle. Further, the influence of reagent gas and temperature was evaluated radially on the pore growth rates of individual pore size of the 20 mm particles. While the use of SAXS has seen extensive research conducted on powders, it is rarely applied to large particles and lower grade coal that is used extensively in locations such as South Africa and India.

5.2. Experimental

5.2.1. Sample preparation and characterisation

The bulk (+ 30 mm) washed ($< 1500 \text{ kg.m}^{-3}$) coal originated from the Witbank coal fields (South Africa) and is classified as an export, grade A steam coal. Mineral matter will influence the pore development during char formation and reactivity, and it is not aimed to distinguish the

role of mineral matter (and ultimately ash) on the behaviour studied here. However, the removal of mineral matter from large particles is ineffective and may impact reactivity through retention of demineralisation acids [38]. Thus, to reduce sample variance for the different particle sizes, the following sampling procedure was used. The bulk sample was used to hand-pick 20 (± 2) mm particles where more spherical particles were selected. The remaining sample (300 kg) was cone-and-quartered 4 times to produce a representative sample. This was crushed to -5 mm before charring. The char was prepared in a nitrogen controlled atmosphere at 1000°C, by heating the sample from ambient temperature at a rate of 10°C/min, and a holding time of 1 hour. The 2 mm sample was removed from the charred representative sample, using a narrow size range (- 2.8 + 1.6 mm) and the remainder of the char sample was crushed to obtain the 75 μm fraction (- 75 + 38 μm). The hand-selected 20 mm char particles with no charring induced visible fracture were used. In Table 5.1, the characteristics of the parent coal and chars are shown.

Table 5.1: The characterisation results of the parent coal and chars.

	Parent coal	75 μm char	2 mm char	20 mm char
Proximate analysis (wt.% a.d. for coal, d.b. for char)				
Moisture	2.3	-	-	-
Ash	13.4	17.6	18.8	17.0
Volatile matter	25.7	2.2	1.9	2.2
Fixed carbon	58.6	80.2	79.3	80.8
Ultimate analysis (wt% d.m.m.f.)				
Carbon	83.4	95.8	95.9	96.1
Hydrogen	4.4	0.2	0.2	0.2
Nitrogen	2.0	1.9	1.8	1.7
Sulphur	0.9	0.8	0.6	0.5
Oxygen (by difference)	9.3	1.3	1.5	1.5
Petrography				
Macerals (vol% m.m.f.)				
Vitrinite	29			
Liptinite	4			
Inertinite	67			
Rr (%)	0.78			
Rsc (%)	1.38			
Rank:	Bituminous medium rank C			

The gasification equipment, process and conditions are discussed in detail in Coetzee *et al.* [37]. The TGA, designed and constructed in-house, consists of a movable vertical tube furnace which can be loaded with single or multiple particles including those with diameters

up to 40 mm. The chars were inserted into a pre-heated TGA furnace (850 and 1000 °C for CO₂ and 800 and 950 °C for steam), and after isothermal conditions were reached the reacting gas was introduced (10 mol% for CO₂ and 20 mol% for steam, with the balance Argon), where the different gasification temperatures for steam and CO₂ were chosen to produce comparable reaction times. The total flow rate was selected as 1.2 NL/min as to avoid external mass transfer limitations. The observed activation energies for 75 µm, 2 and 20 mm were 300/185/125 and 215/218/216 kJ/mol for CO₂ and steam, respectively. The samples were converted up to 50% weight loss, and for the 20 mm particles, only the highest gasification temperatures were considered. The 20 mm gasified particles were broken into smaller pieces which allowed selective sampling from both the surface and centre of the parent particle, with remainder of sample used for 20 mm converted char measurements. The approach used by Lozano-Castelló *et al.* [39] to obtain radial profile development was improved here by isolating radial samples. The surface, centre, and the interior of the 20 mm samples along with the 2 mm particles were crushed using a mortar and pestle and a narrow particle size range was extracted (+ 75 – 130 µm).

5.2.2. CO₂ gas adsorption measurements

Low pressure CO₂ gas adsorption measurements were used to obtain the micropore structural parameters, with the equipment and procedures as detailed in Okolo *et al.* [40]. The micropore results for low pressure CO₂ gas adsorption was used to scale the SAXS structural parameters in the pore range 3.3 to 5 Å, which allowed correction for the contribution of ash to SAXS scattering. It was assumed that all pores that are probed by SAXS (pore size from 3.3 to 5 Å) are also accessible to CO₂ for gas adsorption measurements and that the ash contribution to sorption is negligible (CO₂ gas adsorption measurements of the ash resulted in a micropore surface area of < 10 m²/g)

5.2.3. SAXS measurement and data processing

SAXS measurements were performed at the Australian Synchrotron in Melbourne, Australia. The SAXS measurements used two detector positions which corresponds to pore diameter probed, ranging from 0.25 to 147 nm (using the approximate relationship proposed by Radliński *et al.* [41]). The sample was scanned 18 times using a 3x6 raster grid (~ 0.7x0.7 mm). The sample data was corrected for transmission, background scattering, normalised for thickness and converted to absolute-intensity (using glassy carbon). The data collection and processing is discussed in detail in Coetzee *et al.* [37].

The possibility of multiple scattering effects affecting interpretation was judged to be unlikely because the transmission factors were determined as > 0.9 for all particle sizes. Irena 2.56 [42] was used for data processing, polydisperse modeling, and ratio calculations (scaled intensity (SI) and scaled conversion intensity ratio (SCIR)). The SI, which represents the intensity scaled to a specific Q value, is used for pore structure comparison without the need of complex modelling. In comparing the SI, a greater value at a particular pore size indicates more pore growth at that pore size. Due to oversaturation of the detector at low Q -range for the 20 mm gasified chars, the SI ratio was obtained using the intensity at $Q = 2.221 \cdot 10^{-3} \text{ \AA}^{-1}$ for scaling (pore size $\sim 110 \text{ nm}$). The SCIR represents the ratio of SI of the reacted to unreacted char over the entire Q -range, where SCIR values larger than 1, indicates an increased number of pores (associated with a given Q) compared to the change in number of pores at $Q = 2.221 \cdot 10^{-3} \text{ \AA}^{-1}$, while $SCIR(Q) < 1$ means the opposite.

MATLAB was used to calculate pore volumes, surface areas, and ensuing fractions from the modelled pore number (using a polydisperse Internal Point Gradient – Total Non-Negative Least Square (IPG-TNNLS) fitting model), with pore diameters $> 3 \text{ \AA}$ were used. The calculated surface area is divided into 10 pore bins using logarithmic scaling, where the surface area ratio (SAR) for the different bins are calculated using Equation 5.1.

$$SAR_i(X) = \frac{S_i(X)}{S_{i,0}} \quad \text{Eq 5.1}$$

The created ideal pore volume (mL/g_C , V_P^{id}) – *i.e.*, the volume of pores that are introduced by removal of carbon as conversion progresses if it is assumed that the particle size and carbon density (ρ_C , 2000 kg/m^3 [43]) remains constant is:

$$V_P^{id}(X) = \frac{V_{P,0} + \frac{X}{\rho_C}}{1-X} \quad \text{Eq 5.2}$$

The fraction of non-probed pore volume (f_{NPPV}) – *i.e.* pores whose sizes are outside the range probed in this experiment – was determined as the fraction of SAXS probed pore volume to ideal total pore volume, using Equation 5.3.

$$f_{NPPV}(X) = \left(1 - \frac{V_{SAXS}(X)}{V_P^{id}(X)} \right) \quad \text{Eq 5.3}$$

5.3. Results and discussion

5.3.1. Raw chars

The absolute intensity (presented as a Porod plot) and scaled intensity data for the 75 μm , 2 and 20 mm chars are compared in Figure 5.1.

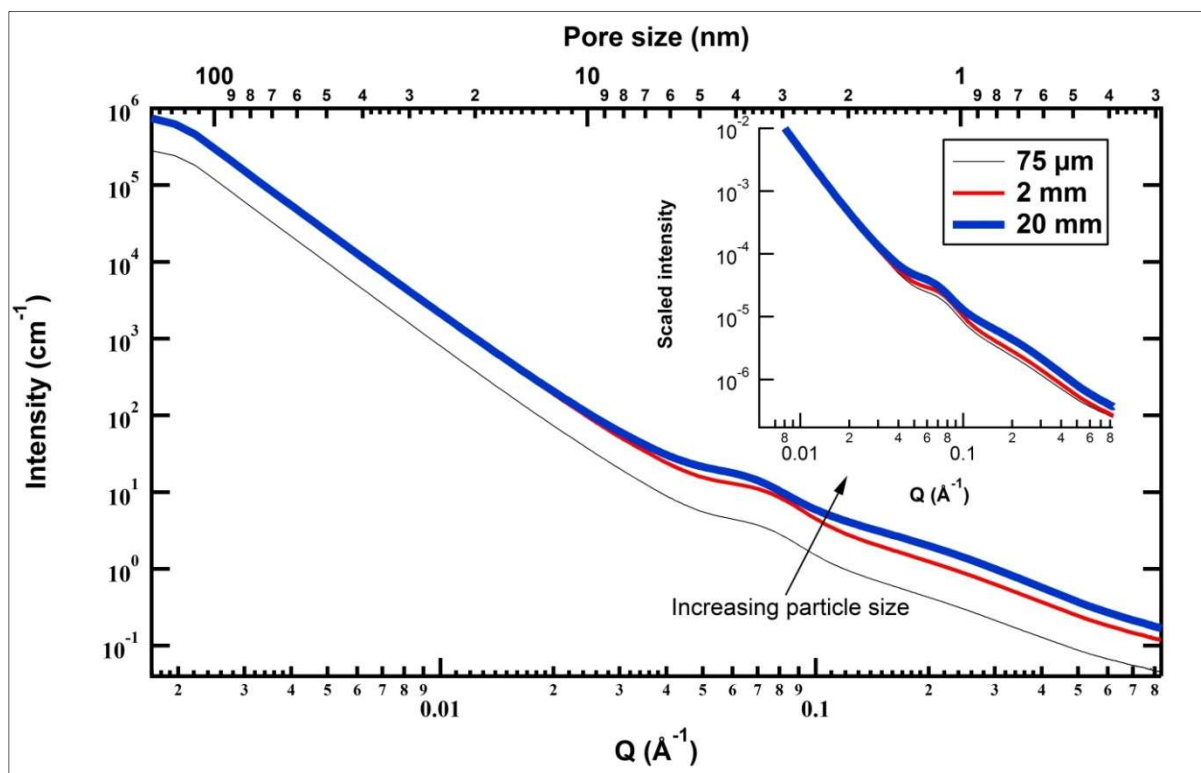


Figure 5.1: Absolute and scaled intensity data for 75 μm , 2 and 20 mm char.

From Figure 5.1, an increase in intensity is observed as particle size increases for pores < 10 nm, which indicates that the number of pores for pore size < 10 nm increases as char particle size increases. For the Porod plot, the absence of a Guinier region at low Q -range is also observed, which points toward a char structure that includes larger pore sizes than probed by the SAXS measurements (> 147 nm). The 2 and 20 mm Porod plots show similar variations in slope as previously observed for the 75 μm char [37], with the pore structures for all chars failing to accommodate a single fractal scaling law [44-46]. The SI subplot in Figure 5.1 shows that some of the curves overlap at low Q -range, but at high Q -range the SI values are greater for the larger particles, indicating a relative increased pore fraction observed for the corresponding Q -range.

The pore volume and surface area for the IUPAC proposed pore ranges, determined using the SAXS profiles, are shown in Table 5.2.

Table 5.2: Pore volume and surface area for micro-, meso- and macropores for the three chars.

	Pore volume (mL/g _c)			Surface area (m ² /g _c)		
	Micropore	Mesopore	Macropore	Micropore	Mesopore	Macropore
75 μm	0.075	0.007	0.006	160	1.6	0.06
2 mm	0.092	0.008	0.006	181	1.6	0.05
20 mm	0.140	0.010	0.006	218	1.8	0.04

Table 5.2 shows an increase in total pore volume and surface area (per unit of carbonaceous mass) for these chars as particle size increases, which agrees with previous evaluations [28-33]. From Table 5.2 it is also seen that the influence of particle size on pore structure development is mainly observed for micropore and mesopores. Previous research found that the reason for particle size influencing the pore structure development of chars, is due to more profound heat and mass transfer restrictions that occur with increasing particle size [28-33]. Heat transfer limitations lead to increased transient temperature gradients inside larger particles during heating, while mass transfer limitations will result in a larger residence time for volatiles inside larger particles. The relative longer residence time of volatiles (which include steam and CO₂) in larger particles, promotes reaction with the carbonaceous material causing additional pore growth.

5.3.2. Pore development during CO₂ gasification

The pore volume, and surface area for the particle sizes, gasification temperatures and reagents are shown in Table 5.3 and 5.4, respectively.

Table 5.3: SAXS pore volume (in mL/g_c) and fraction of non-probed pore volume (in brackets) for the gasified chars.

X (%)	75 μm		2 mm		20 mm
	CO ₂				
	850°C	1000°C	850°C	1000°C	1000°C
0	0.089		0.105		0.157
10	0.139(0.10)	0.161(-0.04)	-	0.142(0.19)	0.210(0.09)
18	-	-	0.150(0.38)	-	-
25	0.253(0.11)	0.222(0.22)	-	0.244(0.21)	0.285(0.25)
35	0.311(0.23)	0.248(0.39)	0.322(0.25)	0.400(0.07)	0.567(-0.11)
50	0.425(0.37)	0.286(0.58)	0.530(0.25)	0.628(0.12)	0.845(-0.04)
	Steam				
	800°C	950°C	800°C	950°C	950°C
10	0.434	0.233	0.302	0.276	0.374
25	0.697	0.719	0.520	0.600	0.662
35	0.728	0.953	0.694	0.765	0.772
50	1.19	0.986	1.74	1.31	1.70

Tables 5.3 and 5.4 show increasing total surface area and pore volume for CO₂ gasification as particle size increase occurred, which agrees with previous findings [35,36]. For 75 μ m CO₂ gasified chars at the same conversion extent, a greater pore volume and surface area is observed for gasification at 850°C than at 1000°C, which was not observed for 2 mm chars (35 and 50% conversion). From Tables 5.3 and 5.4, the 20 mm gasified chars particles show the largest pore volume and surface area.

Table 5.4: Total surface area (m^2/g_c) determined for gasified chars.

X (%)	75 μm		2 mm		20 mm
	CO ₂				
	850°C	1000°C	850°C	1000°C	1000°C
0	162		183		220
10	266	263	-	231	272
18	-	-	275	-	-
25	405	348	-	368	406
35	483	388	512	568	721
50	618	445	760	763	949
	Steam				
	800°C	950°C	800°C	950°C	950°C
	557	410	456	428	546
	915	866	880	730	920
	1000	1060	923	934	1000
	1310	1130	1690	1470	1780

The fraction of pore volume not probed by SAXS for 75 μm CO_2 gasified particles at 850°C is less than for 1000°C, with the non-probed fraction for both temperatures increasing as conversion progresses. The non-probed fraction for the larger gasified char particles shows a decreasing trend as conversion progresses. The positive values for non-probed fractions can be explained by the introduction or growth of pores larger than probeable by the SAXS measurement, or by a reduction of the char particle size, or collapse and realignment of the carbon structure of the pore walls during conversion [47-49]. The negative non-probed pore volumes can be explained by particle swelling, were Coetzee *et al.* [50] found that large particles show varying extent of swelling even for coals with a free swelling index of < 0.5 ; the char samples were prepared using individual single particles. If external surface area reaction and particle volume change are negligible during gasification, the porosity for a set char size conversion should be independent of temperature and reagent gas (Equation 2). Table 5.6 shows the micro-, meso-, and macropore surface area (determined from SAXS), which is used to ascertain the fractions shown in Figure 5.2.

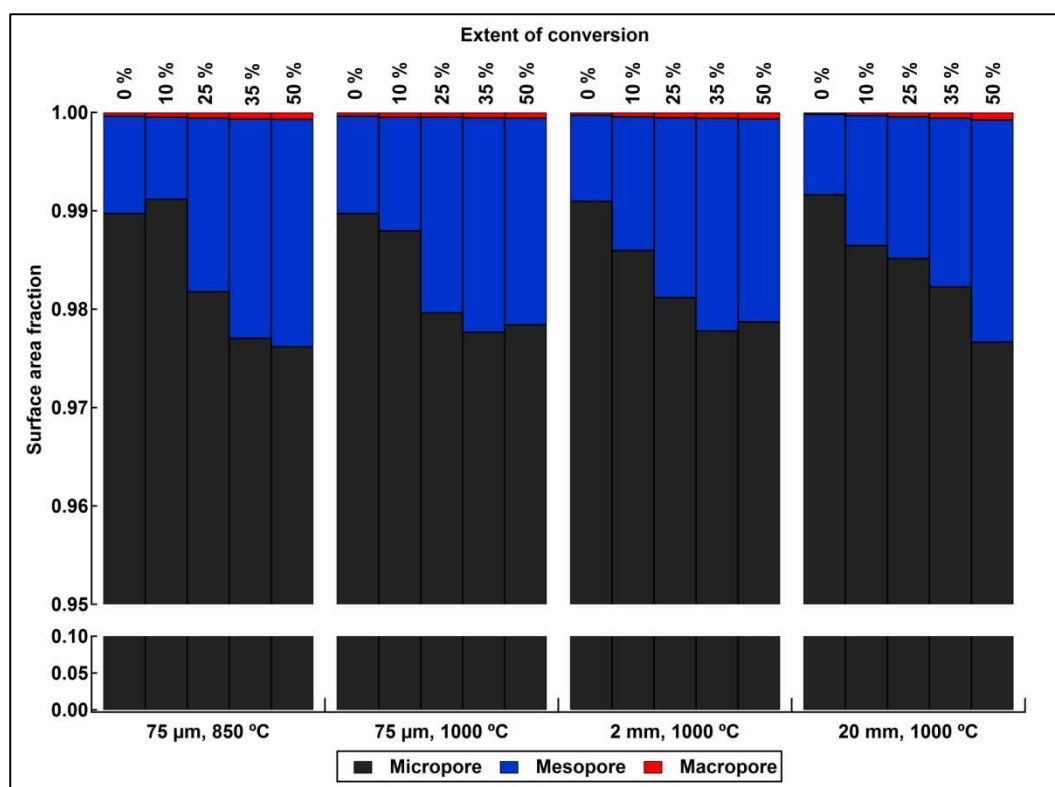


Figure 5.2: The micro-, meso-, and macropore cumulative surface area fraction for CO₂ gasification.

Figure 5.2 shows that for these samples there was an increase in contribution of meso-, and macropores to the total surface area from the onset of CO₂ gasified chars. For the 75 µm particles at 1000°C and extended conversions, the micropore fraction stabilises for higher conversions, with the same trend seen at higher conversion for the 2 mm (1000°C), but for the 20 mm particles were a steady increase in micropore fraction is observed.

5.3.3. Temperature influence on pore development of 75 µm CO₂ gasified char

Comparing the pore volume and surface area of 850 to 1000°C gasified chars (Table 5.3 and 5.4), a relative increase is seen for the probed pore range at 850°C. The increased non-probed fraction at 1000°C compared to 850°C, indicates a relative greater contribution of large pores (> 147 nm) to the total pore volume at 1000°C. In Figure 5.2, the pore fractions shows a systematic increase in meso-, and macropore fractions from onset of gasification, with a relative increased effect observed for 850°C compared to 1000°C. The temperature dependent trends in Figure 5.2 are not influence by pores that are inaccessible to gas due to restrictions, since the same starting structure is used. It is proposed that the temperature

dependent trends are due to an increase in intra-particle mass transfer limitations, with low gasification temperatures more selectively impacting micropore development.

5.3.4. Particle size influence on pore development during CO₂ gasification

Figure 5.3 shows the SCIR of the CO₂ gasified char at 1000°C for 25% conversion, with the observations at 25% being illustrative for all conversions.

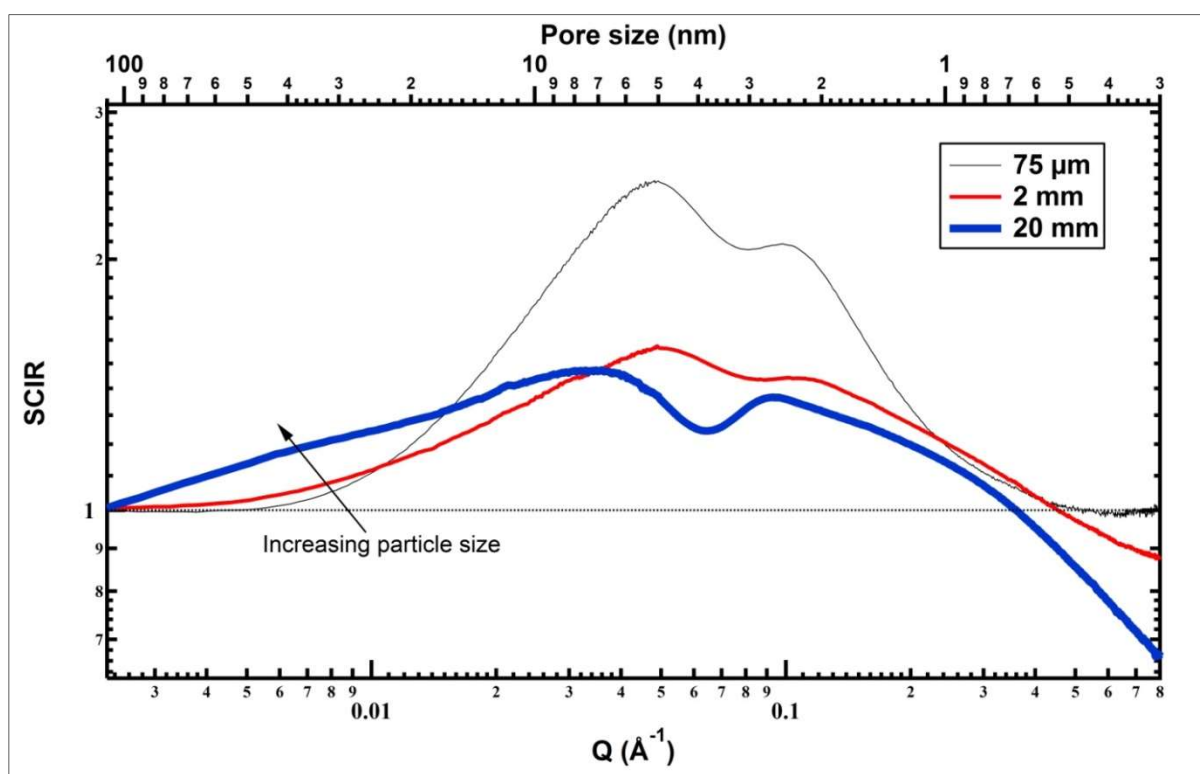


Figure 5.3: CO₂ gasified char SCIR at 25% conversion for all particle sizes.

Figure 5.3 shows that the SCIR for 75 μm gasified char (discussed in detail previously [37]) is approximately 1 for pore sizes > 40 nm, indicating that all pores > 40 nm grow at approximately the same rate. The SCIR is > 1 for pore sizes between 0.4 and 40 nm, indicating a faster growth rate at these pore sizes than at 110 nm. For pore sizes < 0.4 nm, the SCIR is < 1, indicating that these pores grow more slowly than those at 110 nm. The SCIR for 2 mm gasified char is > 1 for all pores > 0.5 nm, which indicates that the number of these pores grow more rapidly than those at 110 nm, with the opposite observed for pore sizes < 0.5 nm. Similar trends observed for the 2 mm gasified chars are seen for the 20 mm chars, with the cross-

over pore size for 20 mm gasified chars increasing to 0.7 nm compared to 0.4 and 0.5 nm for 75 μm and 2 mm gasified chars, respectively. Figure 5.3 shows that CO_2 gasification particle size influences the growth rate of individual pore sizes over the entire range probed by SAXS.

The SAR for CO_2 gasified chars at 1000 $^\circ\text{C}$ is shown in Table 5.5. The SAR allows qualitative comparison of individual pore size growth rate (reported in 10 bins, each covering a factor of two in pore size) for different samples.

Table 5.5: SAR for steam and CO₂ gasification chars.

	Pore diameter (nm)		CO ₂			Steam		
	Smallest	Largest	75 µm	2 mm	20 mm	75 µm	2 mm	20 mm
	25% conversion							
Bin 1	0.3	0.6	2.1	1.9	1.6	4.4	3.3	3.2
Bin 2	0.6	1.2	2.5	2.6	3.1	9.6	7.6	9.4
Bin 3	1.2	2.4	2.5	3.2	3.5	14	10	10
Bin 4	2.4	4.8	6.1	4.3	4.3	22	16	13
Bin 5	4.8	9.5	5.3	3.7	3.7	14	9.7	7.9
Bin 6	9.5	19.1	11	5.2	9.1	31	21	32
Bin 7	19.1	38.1	3.4	3.4	3.9	7.6	7.0	10
Bin 8	38.1	76.3	2.6	2.7	3.7	6.6	6.2	12
Bin 9	76.3	152	2.1	2.6	3.1	5.1	5.4	8.9
Bin 10	152	300	2.1	2.6	3.1	5.1	5.4	8.8
50% conversion								
Bin 1	0.3	0.6	2.7	3.6	3.8	5.9	6.4	5.5
Bin 2	0.6	1.2	2.4	7.1	6.1	10	16	22
Bin 3	1.2	2.4	3.9	10	8.8	21	26	28
Bin 4	2.4	4.8	7.2	13	14	33	47	47
Bin 5	4.8	9.5	6.2	11	18	21	23	18
Bin 6	9.5	19.1	12	12	30	53	60	87
Bin 7	19.1	38.1	4.7	10	17	14	21	18
Bin 8	38.1	76.3	3.5	7.6	14	10	18	20
Bin 9	76.3	152	3.3	7.9	13	7.9	15	14
Bin 10	152	300	3.3	8.2	14	8.0	15	15

Comparing the SAR of 2 mm to 75 μm at 25% conversion, an increased SAR for pore bin 2, 3, and 7 - 10 is observed, which indicates increased pore development for 2 mm gasified chars compared to 75 μm , with the opposite trends observed for the remaining pore bins. Comparison of 20 mm SAR pore bins with 75 μm shows similar pore bin trends observed for the 2 mm comparison. The SAR of 2 mm gasified chars show a decreased SAR for most pore bins (all except the smallest pore bin), compared to 20 mm. The quantitative SCIR and qualitative SAR trends show a prevalence of pore growth for larger pore sizes ($> 40 \text{ nm}$), with a decreasing pore growth of smaller pore sizes and an increasing cross over pore size as particle size increases. The increased contribution of large pore development could be ascribed to increased intra-particle mass transfer limitations introduced by increasing particle size. From fundamental gas-solid reaction theory, and the Thiele Modulus concept, it is known that a direct relationship exists between internal mass transfer limitation and particle size, with an increased gas concentration gradient observed as particle size increases. Increased intra-particle mass transfer limitations result in a decreased observed reaction rate since reagent gas access is not the same across the radius of the particle. The fundamental principles of Thiele Modulus can be directly applied to pores, as proposed by Gavalas [14], with the mass transfer coefficient directly proportionate to pore size when assuming Knudsen diffusion for smaller pores. It is proposed here that the prevalence of pore growth for larger pores, as particle size increases, is due to increased inter-particle mass transfer limitations and the effect thereof on the observed reactivity of smaller pores affected by the increased internal gas concentration gradients along the length of the pore. It stands to reason that observed reactivity of smaller pores has a relative decrease in pore growth due observed increasing in critical pore size and decreasing SCIR and SAR for smaller pores, with a relative increase in large pore contribution to overall conversion.

Comparison of SAR at 50%, shows an increased pore development for all pore bins, as particle size increases, which suggests a decreasing influence of pore coalescence as particle size is increased. The decreasing effect of coalescence as particle size increases corresponds to findings by Satya Sai *et al.* [35,36].

5.3.5. The radial CO_2 gasified pore development for 20 mm

Figure 5.4 shows the surface area fraction of the meso-, and macropores for the surface, interior and centre samples of 1000°C , and 75 μm gasified char at 850°C .

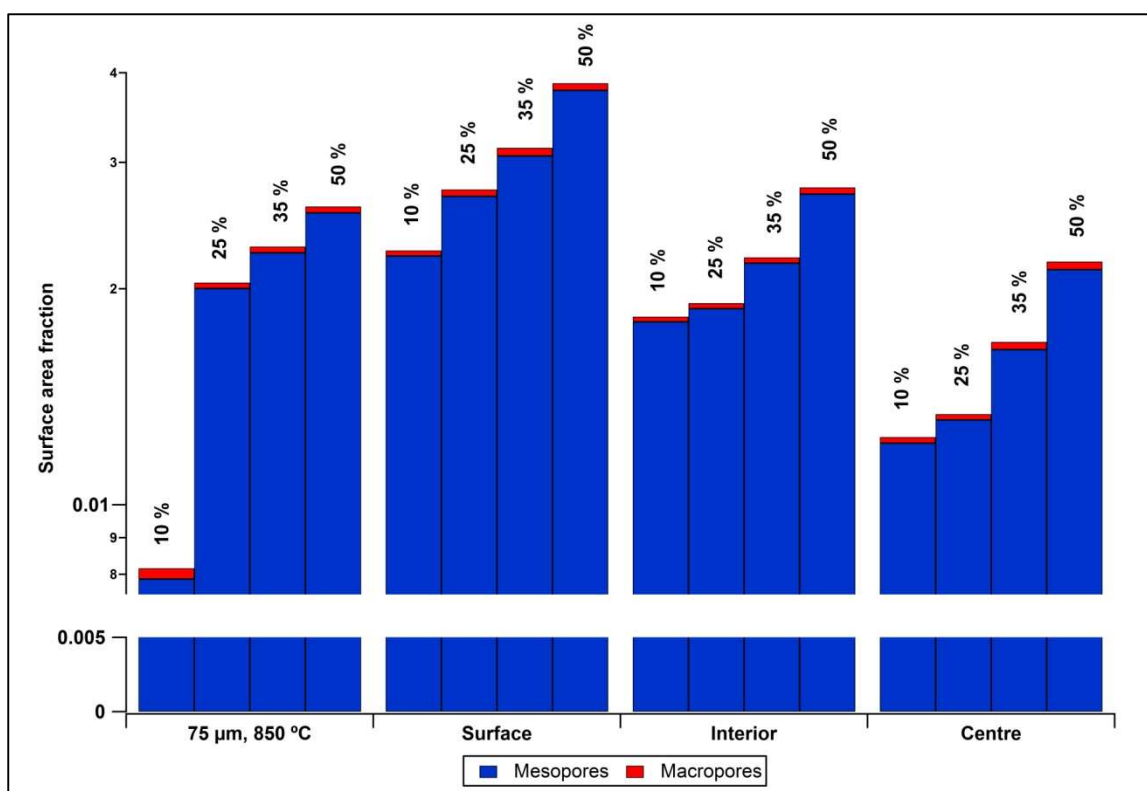


Figure 5.4: Meso-, and macropore surface area fraction for 75 µm (at 850°C) and 20 mm (surface, interior and centre) CO₂ gasification.

For a given conversion, the combined meso-, and macropore fraction of the 20 mm gasified chars is greater at the particle surface than for the other samples. A decreasing trend in the pore fraction is also observed when comparing the surface sample to the interior, and centre samples. These trends show a greater large pore development for the surface sample than for the centre sample. The CO₂ gasified char SCIR for 20 mm particles (centre, surface and interior) at 1000°C is shown in Figure 5.5.

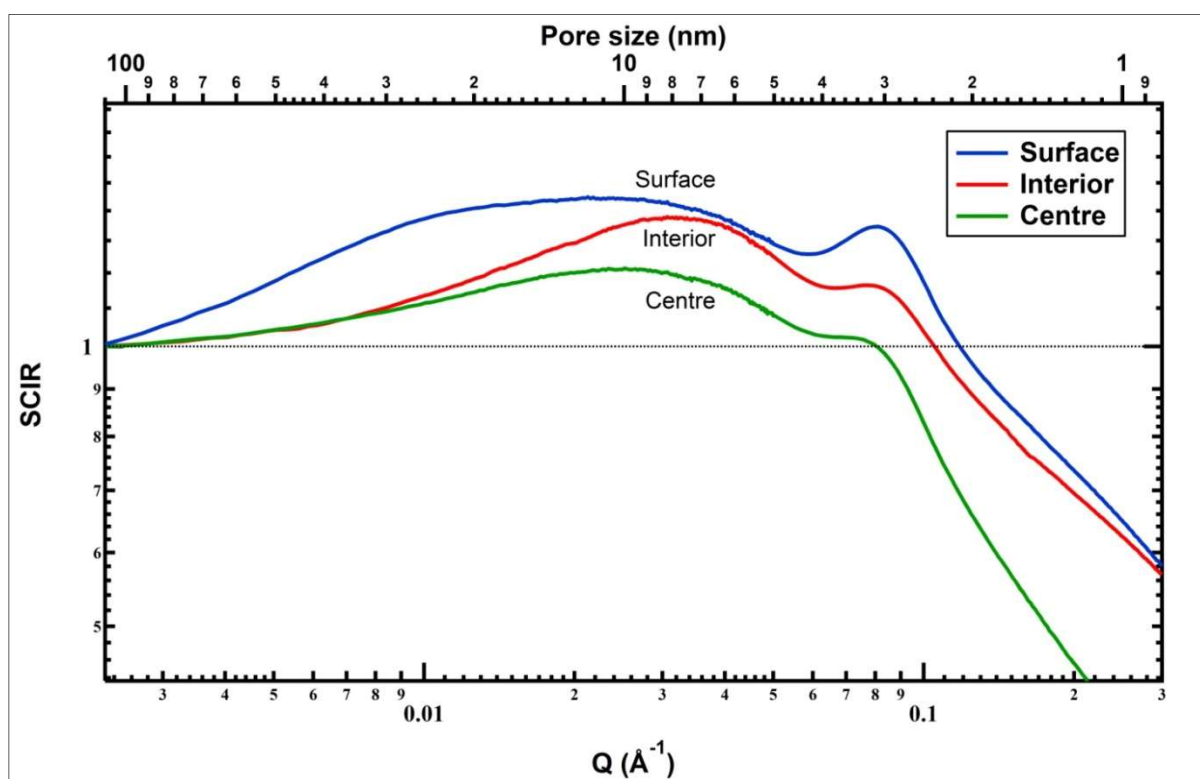


Figure 5.5: SCIR for CO₂ gasified chars at 50% conversion.

Figure 5.5 shows that the subsamples taken from the surface of the particles showed greatest pore development for the pore range > 25 nm, with this difference also observed for all other conversions. A decreasing SCIR (pores < 25 nm) is observed in the order of $75 \mu\text{m} > \text{surface} > \text{interior} > \text{centre}$. The SCIR plot shows radial differences in individual pore growth rates for the 20 mm gasified chars, with an increasing critical pore size observed when compared to surface sample. Compared to surface sample, the smaller SCIR for pores < 110 nm shows prevalence of larger pore growth (> 110 nm) for interior and centre samples. The overall increased contribution observed for larger pores (surface $<$ interior $<$ centre) combined with increased critical pore size (surface $<$ interior $<$ centre), concurs with the findings in Section 5.3.4. These trends indicate that reaction in the finest pores is slowed by mass transfer restrictions. The fractional surface area grouping (Figure 5.4) and SCIR (Figure 5.5) shows radial deviation in the growth rate of individual sized pores, within the 20 mm particles, which is proposed to be due to the different intra-particle gas concentration profiles.

Table 5.6: Micro-, meso-, and macropore pore volume and surface area for CO₂ gasification chars of all particle sizes.

X (%)	Pore volume (mL/g _c)						Surface area (m ² /g _c)					
	Micropore		Mesopore		Macropore		Micropore		Mesopore		Macropore	
	850°C	1000°C	850°C	1000°C	850°C	1000°C	850°C	1000°C	850°C	1000°C	850°C	1000°C
75 μm												
0	0.075		0.007		0.006		161		1.58		0.06	
10	0.120	0.132	0.010	0.017	0.009	0.011	264	260	2.10	3.77	0.07	0.10
25	0.200	0.172	0.036	0.037	0.017	0.014	397	340	8.11	7.92	0.15	0.12
35	0.235	0.190	0.051	0.040	0.025	0.018	472	379	10.84	8.33	0.21	0.15
50	0.311	0.219	0.077	0.045	0.038	0.022	602	436	15.76	9.43	0.32	0.18
2 mm												
0	0.092	0.008	0.006	181	1.56	0.05	181		1.6		0.05	
10	-	0.117	-	0.016	-	0.010	-	228	-	3.12	-	0.08
18	0.130	-	0.011	-	0.008	-	272	-	2.46	-	0.07	-
25	-	0.199	-	0.029	-	0.016	-	362	-	6.09	-	0.13
35	0.258	0.309	0.040	0.061	0.024	0.030	503	553	8.60	14.7	0.20	0.25
50	0.423	0.481	0.068	0.093	0.039	0.055	744	744	15.0	18.7	0.31	0.39
20 mm												
0	0.140		0.010		0.006		218		1.80		0.040	
10	0.172		0.026		0.012		267		4.89		0.080	
25	0.235		0.033		0.016		399		7.63		0.133	
35	0.452		0.074		0.040		705		15.7		0.287	
50	0.619		0.144		0.083		922		25.7		0.554	

5.3.6. Particle size influence on pore development for steam gasified chars

Comparison of the pore volume and surface area development of the 75 μm steam gasified chars (Table 5.3 and 5.4), shows greater development (surface area and volume) at 800°C than for the 950°C, which is similar to what was observed for the 75 μm CO₂ gasification. The pore volume and surface area at a fixed conversion also increased with increasing particle size, which is consistent with previous findings by Satya Sai *et al.* [35,36]. The 75 μm pore volume is comparable to the ideal pore volumes from onset of gasification, resulting in a much smaller non-probed pore volume compared to the 75 μm CO₂ gasified chars examined here. The smaller non-probed pore volume indicates that the relative contribution of external surface area and large pore (> 147 nm) reactivity occurs to a lesser extent for steam than for CO₂. Comparing the SAR for steam gasified chars to CO₂ gasified chars (Table 5.5) shows greater SAR (all bins) for all steam gasified chars, indicating greater pore development for all pores for steam.

The micro-, meso-, and macropore surface area (determined from SAXS) for steam gasification at all conversions, is shown in Table 5.7 and is used to ascertain the fractions shown in Figure 5.6.

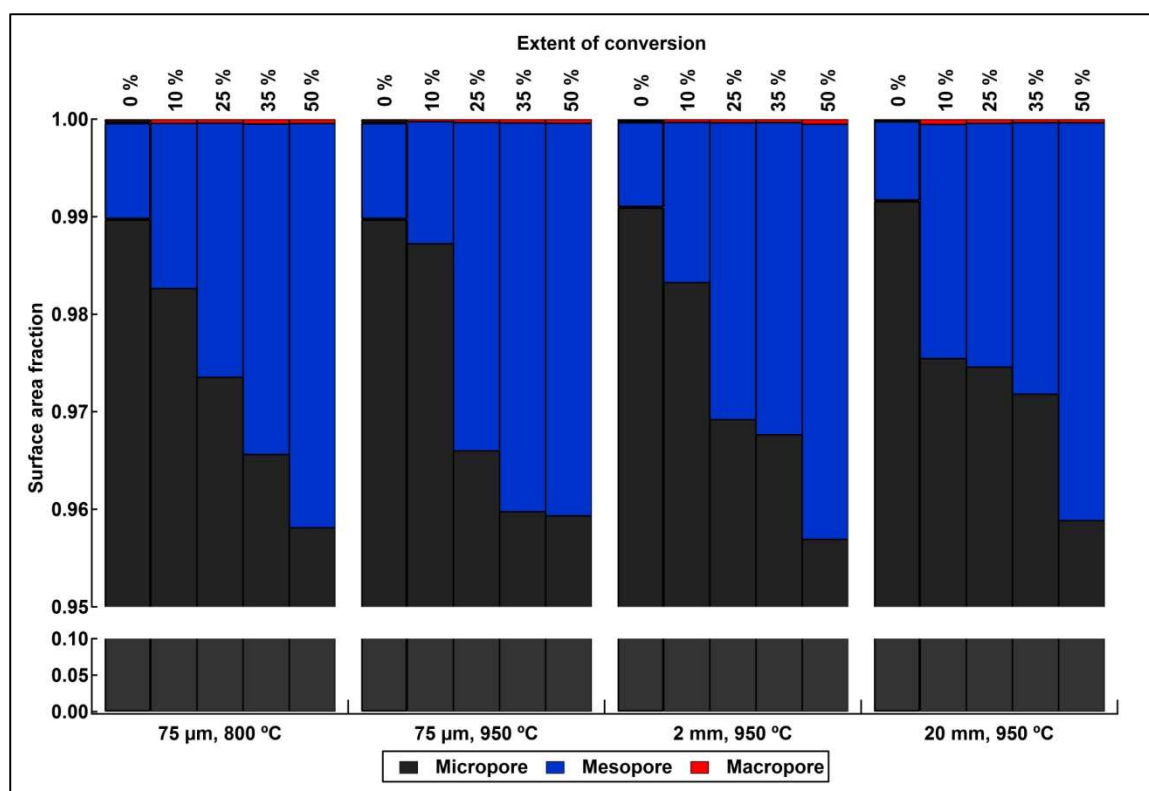


Figure 5.6: The micro-, meso-, and macropore cumulative surface area fraction for steam gasification chars.

The cumulative surface area fraction in Figure 5.6 shows a systematic increase in meso-, and macropore fraction from the onset of gasification for these samples. The systematic increase in meso-, and macropore fraction for steam is comparable to CO_2 (Figure 5.2), with greater meso-, and macropore development observed from onset of gasification for steam, compared to CO_2 .

Comparing the SAR for the steam gasified chars of 2 mm to 75 μm at 25% conversion shows greater ratios for pore bin 9 and 10, indicating increased pore development for the 2 mm steam gasified chars for these pore bins. For all other pore bins, the SAR indicates greater pore development for the 75 μm compared to the 2 mm. For the 20 mm SAR comparison to the 75 μm , increased pore development for pore bins > 5, is seen which indicates greater development for the 20 mm gasified chars in these pore bins. The SAR trends show the prevalence of pore development for large pore sizes, which is more profound as particle size increased for these samples. The prevalence of pore development for large pore sizes is similar to what was observed for CO_2 gasified chars, with the prevalence of smaller pores (bin 2 and 3) observed for CO_2 not seen for steam gasified chars, indicating that for steam gasified chars particle size influences the pore development of large pore sizes only, which could be

attributed to the smaller kinetic diameter of water, compared to CO₂. The smaller kinetic diameter of water could result in a larger fraction of surface area available in small pores, reducing the observed influence of steam gasification for smaller pores compared to CO₂.

Figure 5.7 shows the SCIR plots for steam gasification at 25% conversion of 20 mm centre, surface, and interior at 950 °C.

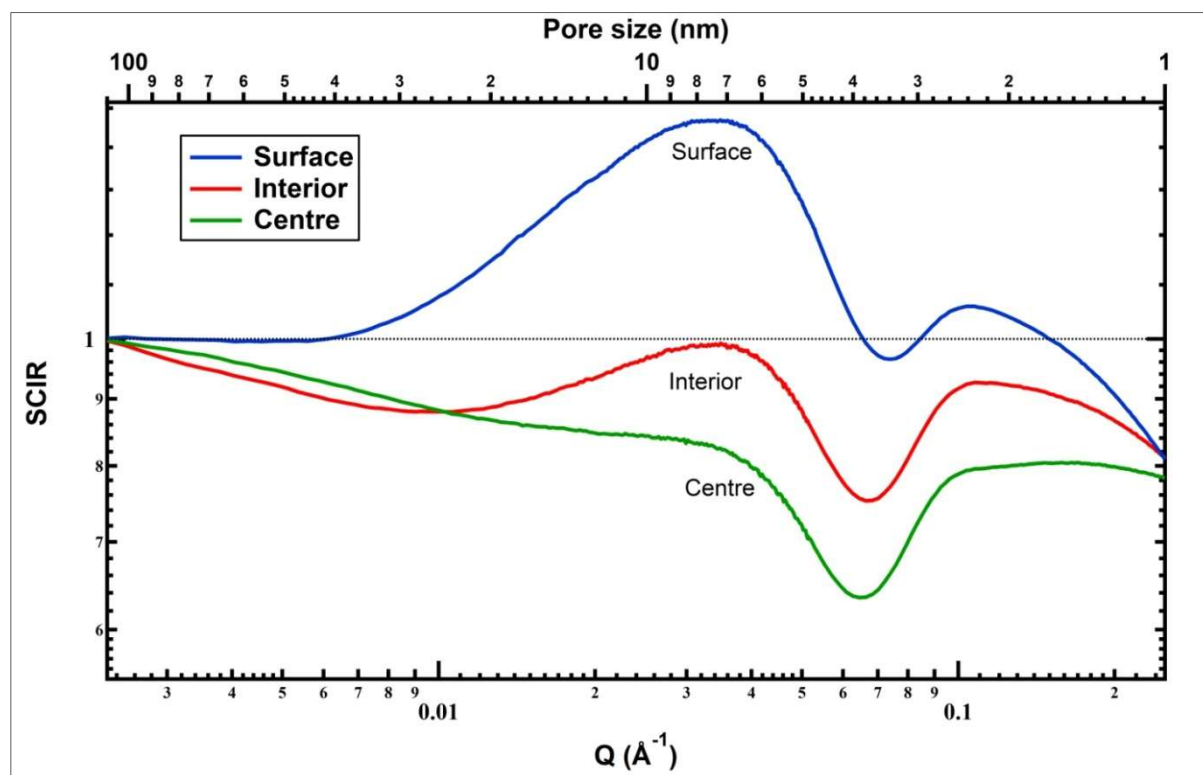


Figure 5.7: Steam gasified SCIR at 25% conversion.

For the curves in Figure 5.7, the conversion of 25% was used due to increased influence of mineral matter scattering on the SCIR plot for the surface sample at greater conversions. A systematic decrease in SCIR is observed over the entire Q-range in the order of surface, interior and centre samples, comparable to CO₂. The radial SCIR shape change also shows radially changing individual pore growth rates, which was also observed for CO₂ gasification.

Table 5.7: Micro-, meso-, and macropore pore volume and surface area for steam gasification chars of all particle sizes.

X (%)	Pore volume (mL/g _c)						Surface area (m ² /g _c)					
	Micropore		Mesopore		Macropore		Micropore		Mesopore		Macropore	
	800°C	950°C	800°C	950°C	800°C	950°C	800°C	950°C	800°C	950°C	800°C	950°C
	75 µm											
0	0.075		0.007		0.006		161		1.58		0.06	
10	0.322	0.199	0.074	0.022	0.031	0.012	538	405	18.9	5.13	0.27	0.11
25	0.542	0.521	0.102	0.124	0.044	0.037	891	837	23.9	29.2	0.36	0.31
35	0.582	0.693	0.081	0.193	0.055	0.053	984	1019	17.0	42.3	0.44	0.41
50	0.855	0.705	0.239	0.206	0.077	0.061	1256	1084	54.3	45.5	0.59	0.47
	2 mm											
0	0.092	0.008	0.006	181	1.56	0.05	181		1.6		0.05	
10	0.242	0.223	0.032	0.032	0.025	0.018	448	421	7.46	7.03	0.22	0.15
25	0.539	0.449	0.103	0.095	0.057	0.035	854	707	24.9	22.2	0.49	0.28
35	0.550	0.582	0.095	0.129	0.040	0.044	899	904	23.3	29.9	0.33	0.33
50	1.235	0.930	0.370	0.263	0.112	0.098	1604	1408	84.3	62.6	0.79	0.78
	20 mm											
0	0.140		0.010		0.006		218		1.80		0.04	
10	0.278		0.057		0.034		532		13.1		0.29	
25	0.526		0.086		0.042		898		23.0		0.40	
35	0.610		0.107		0.045		978		28.0		0.37	
50	1.245		0.276		0.079		1710		72.9		0.65	

5.4. Conclusions

The influence of char particle size as gasification progresses, using chars prepared from 75 μm , 2 and 20 mm inertinite rich South African coal particles, was evaluated. Previously, the authors showed that for 75 μm particles, the pore growth rate observed for different sized pores are influenced by gasification reagents, and here the pore growth rate is further detailed as a function of temperature, gasification reagent, and particle size. A novel application of radial SAXS measurement was developed to obtain pore development profiles for the 20 mm gasified chars, using SAXS to investigate the pore development (0.3 to 147 nm) as gasification progresses. It was shown for these samples generated under the conditions discussed earlier that:

- Particle size influences the growth rate of individual pore sizes, with particle size influencing the growth rates of CO_2 gasification over the entire pore range probed. Specifically, development of micro-, and macropores prevailed over the intermediate sized pores for these samples.
- For the steam gasified samples studied here, particle size only influenced the growth rate in the macropore range.
- For both the steam and the CO_2 gasified chars, larger particle sizes resulted in a decrease in growth rate for < 0.6 nm pores.
- The 20 mm pore development study found radial changes in the growth rates of individual pore sizes, and is proposed to be due to intra-particle mass transfer limitations. The surface sample for both the CO_2 and the steam chars, had the greatest pore development over the entire pore range, followed by the interior and center. Evaluation of the growth rates show more pores > 25 nm at the surface, than for samples taken from the interior and centre.
- Here, initial char porosity and surface area increases with an increase in particle size, with a systematic increase in smaller pore fraction (for pores < 10 nm) as char particle size increases.

The influence of particle size on the pore growth rate seen here shows an additional complexity that needs to be addressed in reaction rate models of gasification of carbons and production of activated carbon. These complexities need to be incorporated into single particle models to better understand gasification rate and pore development, specifically with regards to surface area and pore volume. It is recommended to extend this study to other chars, prepared at different conditions and originating from different coals, to confirm the general validity of the conclusions as presented in this study.

5.5. Nomenclature

Symbols:

$f_{NPPV}(X)$ - Fraction of non-probed pore volume

I - Intensity

Q - Scattering vector ($\text{\AA}^{-1}$)

$SAR_i(X)$ - Surface area ratio of bin i

$S_i(X)$ - Surface area of bin i (m^2/g_C)

$S_{i,0}$ - Char surface area of bin i (m^2/g_C)

$V_P^{id}(X)$ - Ideal total pore volume (mL/g_C)

$V_{SAXS}(X)$ - Total pore volume as determined by SAXS (mL/g_C)

X - Conversion

ρ_C - Density of carbon ($\text{kg}.\text{m}^{-3}$)

5.6. Chapter References

- [1] Smith RM. Chemical Process: Design and Integration. West Sussex: John Wiley & Sons Ltd; 2005, p. 97-120.
- [2] Yagi S, Kunii D. Studies on combustion of carbon particles in flames and fluidized beds. *Symp Int Combust* 1955;5(1):231-44. [http://dx.doi.org/10.1016/S0082-0784\(55\)80033-1](http://dx.doi.org/10.1016/S0082-0784(55)80033-1)
- [3] Fogler HS. Elements of Chemical Reaction Engineering. 4th ed. New York: Prentice Hall PTR; 2006, p. 815-26
- [4] Foster MD, Jensen KF. Small angle X-ray scattering investigations of pore structure changes during coal gasification. *Fuel* 1990;69(1):88-96. [http://dx.doi.org/10.1016/0016-2361\(90\)90263-P](http://dx.doi.org/10.1016/0016-2361(90)90263-P)
- [5] Foster MD, Jensen KF. SAXS investigation of model carbon pore structure and its change with gasification. *Carbon* 1991;29(2):271-82. [http://dx.doi.org/10.1016/0008-6223\(91\)90077-V](http://dx.doi.org/10.1016/0008-6223(91)90077-V)
- [6] Rodríguez-Reinoso F, Molina-Sabio M, González MT. The use of steam and CO₂ as activating agents in the preparation of activated carbons. *Carbon* 1995;33(1):15-23. [http://dx.doi.org/10.1016/0008-6223\(94\)00100-E](http://dx.doi.org/10.1016/0008-6223(94)00100-E)
- [7] Linares-Solano A, Salinas-Martínez de Lecea C, Cazorla-Amorós D, Martín-Gullón I. Porosity development during CO₂ and steam activation in a fluidized bed reactor. *Energy Fuels* 2000;14(1):142-9. <http://dx.doi.org/10.1021/ef9900637>
- [8] Calo JM, Hall PJ, Antxustegi M. Carbon porosity characterization via small angle neutron scattering. *Colloids Surf Physicochem Eng Aspects* 2001;187–188:219-32. [http://dx.doi.org/10.1016/S0927-7757\(01\)00635-5](http://dx.doi.org/10.1016/S0927-7757(01)00635-5)
- [9] Arenas E, Chejne F. The effect of the activating agent and temperature on the porosity development of physically activated coal chars. *Carbon* 2004;42(12):2451-5. <http://dx.doi.org/10.1016/j.carbon.2004.04.041>
- [10] Jasieńko-Hałat M, Kędzior K. Comparison of molecular sieve properties in microporous chars from low-rank bituminous coal activated by steam and carbon dioxide. *Carbon* 2005;43(5):944-53. <http://dx.doi.org/10.1016/j.carbon.2004.11.024>
- [11] Feroso J, Gil MV, Borrego AG, Pevida C, Pis JJ, Rubiera F. Effect of the pressure and temperature of devolatilization on the morphology and steam gasification reactivity of coal chars. *Energy Fuels* 2010;24(10):5586-95. <http://dx.doi.org/10.1021/ef100877t>

-
- [12] Louw E, Mitchell GD, Winans RE, Mathews JP, Constitution of drop-tube generated coal chars from vitrinite-rich and inertinite-rich South African coals. *Energy Fuels* 2016; 30(1):112-20. <http://dx.doi.org/10.1021/acs.energyfuels.5b01517>
- [13] Szekely J, Evans JW. A structural model for gas-solid reactions with a moving boundary. *Chem Eng Sci* 1970;25(6):1091-107. [http://dx.doi.org/10.1016/0009-2509\(70\)85053-9](http://dx.doi.org/10.1016/0009-2509(70)85053-9)
- [14] Gavalas GR. A random capillary model with application to char gasification at chemically controlled rates. *AIChE J* 1980;26(4):577-85. <http://dx.doi.org/10.1002/aic.690260408>
- [15] Bhatia SK, Perlmutter DD. A random pore model for fluid-solid reactions: I. Isothermal, kinetic control. *AIChE J* 1980;26(3):379-86. <http://dx.doi.org/10.1002/aic.690260308>
- [16] Gavalas GR, Wilks KA. Intraparticle mass transfer in coal pyrolysis. *AIChE J* 1980;26(2):201-12. <http://dx.doi.org/10.1002/aic.690260203>
- [17] Biggs MJ, Agarwal PK. The CO/CO₂ product ratio for a porous char particle within an incipiently fluidized bed: a numerical study. *Chem Eng Sci* 1997;52(6):941-52. [http://dx.doi.org/10.1016/S0009-2509\(96\)00489-7](http://dx.doi.org/10.1016/S0009-2509(96)00489-7)
- [18] Liu G, Niksa S. Coal conversion submodels for design applications at elevated pressures. Part II. Char gasification. *Prog Energ Combust* 2004;30(6):679-717. <http://dx.doi.org/10.1016/j.pecs.2004.08.001>
- [19] von Zedtwitz P, Lipiński W, Steinfeld A. Numerical and experimental study of gas-particle radiative heat exchange in a fluidized-bed reactor for steam-gasification of coal. *Chem Eng Sci* 2007;62(1-2):599-607. <http://dx.doi.org/10.1016/j.ces.2006.09.027>
- [20] Wang FY, Bhatia SK. A generalised dynamic model for char particle gasification with structure evolution and peripheral fragmentation. *Chem Eng Sci* 2001;56(12):3683-97. [http://dx.doi.org/10.1016/S0009-2509\(01\)00060-4](http://dx.doi.org/10.1016/S0009-2509(01)00060-4)
- [21] Singer SL, Ghoniem AF. Comprehensive gasification modeling of char particles with multimodal pore structures. *Combust Flame* 2013;160(1):120-37. <http://dx.doi.org/10.1016/j.combustflame.2012.09.007>
- [22] Gavalas GR. Analysis of char combustion including the effect of pore enlargement. *Combustion Sci Technol* 1980;24(5-6):197-210. <http://dx.doi.org/10.1080/00102208008952438>
- [23] Bhatia SK, Perlmutter DD. A random pore model for fluid-solid reactions: II. Diffusion and transport effects. *AIChE J* 1981;27(2):247-54. <http://dx.doi.org/10.1002/aic.690270211>

-
- [24] Kajitani S, Suzuki N, Ashizawa M, Hara S. CO₂ gasification rate analysis of coal char in entrained flow coal gasifier. *Fuel* 2006;85(2):163-9. <http://dx.doi.org/10.1016/j.fuel.2005.07.024>
- [25] Kim YT, Seo DK, Hwang J. Study of the effect of coal type and particle size on Char-CO₂ gasification via gas analysis. *Energy Fuels* 2011;25(11):5044-54. <http://dx.doi.org/10.1021/ef200745x>
- [26] Huo W, Zhou Z, Wang F, Yu G. Mechanism analysis and experimental verification of pore diffusion on coke and coal char gasification with CO₂. *Chem Eng J* 2014;244:227-33. <http://dx.doi.org/10.1016/j.fuel.2014.04.058>
- [27] Veca E, Adrover A. Isothermal kinetics of char-coal gasification with pure CO₂. *Fuel* 2014;123:151-7. <http://dx.doi.org/10.1016/j.fuel.2014.01.066>
- [28] Agrawal RK, Gandhi F, McCluskey RJ. Low-pressure pyrolysis of newsprint. *J Anal Appl Pyrolysis* 1984;6(3):325-38. [http://dx.doi.org/10.1016/0165-2370\(84\)80026-1](http://dx.doi.org/10.1016/0165-2370(84)80026-1)
- [29] Stubington JF, Sumaryono. Release of volatiles from large coal particles in a hot fluidized bed. *Fuel* 1984;63(7):1013-9. [http://dx.doi.org/10.1016/0016-2361\(84\)90327-2](http://dx.doi.org/10.1016/0016-2361(84)90327-2)
- [30] Solomon P.R HDG. Pyrolysis. In: Schlosberg RH, editor. *Chemistry of Coal Conversion*, New York: New York: Humana Press; 1985, p. 121-95.
- [31] Devanathan N, Saxena SC. Transport model for devolatilization of large nonplastic coal particles: the effect of secondary reactions. *Ind Eng Chem Res* 1987;26(3):539-48. <http://dx.doi.org/10.1021/ie00063a021>
- [32] Stubington JF, Linjewile TM. The effects of fragmentation on devolatilization of large coal particles. *Fuel* 1989;68(2):155-60. [http://dx.doi.org/10.1016/0016-2361\(89\)90316-5](http://dx.doi.org/10.1016/0016-2361(89)90316-5)
- [33] Stubington JF, Huang G, Scaroni AW. Devolatilization times of mm-size coal particles. *Fuel* 1991;70(9):1105-8. [http://dx.doi.org/10.1016/0016-2361\(91\)90268-F](http://dx.doi.org/10.1016/0016-2361(91)90268-F)
- [34] Kawahata M, Walker PL. Mode of porosity development in activated anthracite. In: Mrozowski S, editor. *Proceedings of the Fifth Conference on Carbon*. Pennsylvania State University (University Park, Pennsylvania, USA): Elsevier Science; 1963, p. 251-264.
- [35] Satya Sai PM, Ahmed J, Krishnaiah K. Production of activated carbon from coconut shell char in a fluidized bed reactor. *Ind Eng Chem Res* 1997;36(9):3625-30. <http://dx.doi.org/10.1021/ie970190v>

-
- [36] Satya Sai PM, Krishnaiah K. Development of the pore-size distribution in activated carbon produced from coconut shell char in a fluidized-bed reactor. *Ind Eng Chem Res* 2005;44(1):51-60. <http://dx.doi.org/10.1021/ie0400090>
- [37] Coetzee GH, Sakurovs R, Neomagus HWJP, Morpeth L, Everson RC, Mathews JP *et al.* Pore development during gasification of South African inertinite-rich chars evaluated using small angle X-ray scattering. *Carbon* 2015;95:250-60. <http://dx.doi.org.nwulib.nwu.ac.za/10.1016/j.carbon.2015.08.030>
- [38] Strydom CA, Bunt JR, Schobert HH, Raghoo M. Changes to the organic functional groups of an inertinite rich medium rank bituminous coal during acid treatment processes. *Fuel Process Technol* 2011;92(4):764-70. <http://dx.doi.org/10.1016/j.fuproc.2010.09.008>
- [39] Lozano-Castelló D, Raymundo-Piñero E, Cazorla-Amorós D, Linares-Solano A, Müller M, Riekkel C. Characterization of pore distribution in activated carbon fibers by microbeam small angle X-ray scattering. *Carbon* 2002;40(14):2727–35. [http://dx.doi.org/10.1016/S0008-6223\(02\)00186-0](http://dx.doi.org/10.1016/S0008-6223(02)00186-0)
- [40] Okolo GN, Everson RC, Neomagus HWJP, Roberts MJ, Sakurovs R. Comparing the porosity and surface areas of coal as measured by gas adsorption, mercury intrusion and SAXS techniques. *Fuel* 2015;141:293-304. <http://dx.doi.org/10.1016/j.fuel.2014.10.046>
- [41] Radlinski AP, Mastalerz M, Hinde AL, Hainbuchner M, Rauch H, Baron M *et al.* Application of SAXS and SANS in evaluation of porosity, pore size distribution and surface area of coal. *Int J Coal Geol* 2004;59(3-4):245-71. <http://dx.doi.org/10.1016/j.coal.2004.03.002>
- [42] Ilavsky J, Jemian PR. Irena: tool suite for modeling and analysis of small-angle scattering. *J Appl Crystallogr* 2009;42(2):347-53. <http://dx.doi.org/10.1107/S0021889809002222>
- [43] Roberts MJ, Everson RC, Neomagus HWJP, Van Niekerk D, Mathews JP, Branken DJ. Influence of maceral composition on the structure, properties and behaviour of chars derived from South African coals. *Fuel* 2015;142:9-20. <http://dx.doi.org/10.1016/j.fuel.2014.10.033>
- [44] Bale HD, Carlson ML, Schobert HH. Thermal modification of the pore structure of a North Dakota lignite. *Fuel* 1986;65(9):1185-9. [http://dx.doi.org/10.1016/0016-2361\(86\)90227-9](http://dx.doi.org/10.1016/0016-2361(86)90227-9)
- [45] Foster MD, Jensen KF. Small angle X-ray scattering investigations of pore structure changes during coal gasification. *Fuel* 1990;69(1):88-96. [http://dx.doi.org/10.1016/0016-2361\(90\)90263-P](http://dx.doi.org/10.1016/0016-2361(90)90263-P)

-
- [46] Pfeifer, P., Ehrburger-Doller, F., Rieker, T., Schmidt, P. W., Voss, D.J., Rodriguez-Reinoso, F., Molina-Sabio, M and Gonzalez, M.T. Fractal networks of carbon nanopores. Extended abstracts, 23rd Biennial conference on carbon. University Park (Pennsylvania, USA): American Carbon Society, 1997; p. 350-1.
- [47] Liu G, Benyon P, Benfell KE, Bryant GW, Tate AG, Boyd RK *et al.* The porous structure of bituminous coal chars and its influence on combustion and gasification under chemically controlled conditions. *Fuel* 2000;79(6):617-26. [http://dx.doi.org/10.1016/S0016-2361\(99\)00185-4](http://dx.doi.org/10.1016/S0016-2361(99)00185-4)
- [48] Pikunic J, Clinard C, Cohaut N, Gubbins KE, Guet J, Pellenq RJ *et al.* Structural modeling of porous carbons: Constrained reverse Monte Carlo method. *Langmuir* 2003;19(2):8565-82. <http://dx.doi.org/10.1021/la034595y>
- [49] Cabiellles M, Rouzaud J, Garcia AB. High-resolution transmission electron microscopy studies of graphite materials prepared by high-temperature treatment of unburned carbon concentrates from combustion fly ashes. *Energy Fuels* 2009;23(2):942-50. <http://dx.doi.org/10.1021/ef800763s>
- [50] Coetzee S, Neomagus HWJP, Bunt JR, Strydom CA, Schobert HH. The transient swelling behaviour of large ($-20 + 16$ mm) South African coal particles during low-temperature devolatilisation. *Fuel* 2014;136:79-88. <http://dx.doi.org/10.1016/j.fuel.2014.07.021>

Chapter 6.

Concluding summary

The conclusions drawn throughout this investigation are summarised in this Chapter.

6.1. Concluding Remarks

A typical South African coal with low ash content was identified, with the selected parent coal sample being a density separated ($< 1500 \text{ kg/m}^3$) Witbank Seam 4 lump coal (particle size $> 30 \text{ mm}$). The bulk sample was prepared to obtain representative samples used for parent coal characterisation, and preparation of the $75 \text{ }\mu\text{m}$ and 2 mm chars. The 20 mm particle samples were handpicked and mechanically reshaped to form near spherical particles. Chemical and mineralogy characterisation of chars produced, showed that the chemical composition of the three particle sizes does not differ significantly. In contrast, pore structural parameters evaluated using low pressure CO_2 gas adsorption measurements showed an increase in micropore volume and surface area with an increase in particle size.

For the gasification experiments, the charred samples were partially converted using a TGA, with time required to produce specific converted chars experimentally determined. Further it was also experimentally established that gasification is chemical reaction controlled at the lowest gasification temperature and that external mass transfer limitation has negligible effect on reactivity of $75 \text{ }\mu\text{m}$ and 2 mm chars at the chosen gasification temperatures.

SAXS measurements of partially converted chars were conducted at the Australian Synchrotron in Melbourne. A novel ratio analysis technique was developed during this investigation, which used three separate ratios, calculated from the SAXS measurement data, to compare results of different scans: intensity conversion ratio (ICR), scaled intensity (SI) and scaled conversion intensity ratio (SCIR). The ratio analysis was used to qualitatively compare the relative extent to which the number of pores at different sizes is affected for different samples, without modelling pore volume and/or pore surface area using non-fractal pore modelling.

For CO_2 and steam gasification of powder char, it was found that different sized pores exhibited different growth rates, with pore sizes between 1 and 40 nm having the highest pore growth rates. The increased selectivity of $1 - 40 \text{ nm}$ pores cannot be explained by gas accessibility alone. Compared to CO_2 , steam created a more porous char at specific conversion, and also showed increased selectivity of the $0.6 - 40 \text{ nm}$ pores. For pore sizes below 1 nm , the pore generation rate was slower compared to larger pore sizes, with steam showing increased pore development compared to CO_2 . The slower rate observed below 1 nm resulted in the critical cross over pore size classification, where the critical cross over pore size indicates at what size the pore generation rate is observed to be below the largest pore

size. Comparing the critical cross over pore size results for steam to CO₂ gasification showed that a smaller cross over pore size is observed (0.6 nm for steam, compared to 1 nm for CO₂). The smaller cross over pore size and greater selective increase of the 1 - 40 nm pore sizes further clarifies the observation of steam showing greater accessibility to micropore surface area observed for low pressure CO₂ gas adsorption results. The increased accessibility seems to be extended from the micropore range (< 2 nm), as seen for low pressure CO₂ gas adsorption results, to 40 nm due to increased resolution and pore size range probed using SAXS.

Particle size influenced the growth rates of CO₂ gasification over the entire pore range probed, with particle size only influencing the growth rate of macropores for steam gasified chars. A decrease in growth rate for < 0.6 nm pores was observed with an increase in particle size for both CO₂ and steam gasified chars. For both gasification reagents, a decreasing growth rate of smaller pores was observed with an increase in particle size. Also, an increased growth rate for larger pore sizes is observed as particle size increases, with a more pronounced change seen for the largest particle size studied here.

Evaluation of pore development for 20 mm particles showed radial changes in the growth rates of individual pore sizes, which is proposed to be due to intra-particle mass transfer limitations. The surface sample for partially converted chars, had the greatest pore development over the entire pore range, followed by the interior and center. Evaluation of the radial pore structure show increased selectivity of pores > 25 nm at the surface, than for samples taken from the interior and centre

6.2. Contribution to science

The evaluation of pore development during gasification shows different sized pores grow at different rates, with differences observed when comparing the influence of steam to CO₂ gasification. The results for micropore surface area development suggesting that reported trends (increased surface area development for steam compared to CO₂) are mainly due to differences in pore growth for pores smaller than 7 nm and could be a direct implication of the smaller kinetic diameter of water, compared to CO₂. The observation of local pore structure dependent on particle depth for 20 mm samples also highlights the additional complexities that needs to be addressed in advanced dynamic single particle reaction modelling. The following additions are considered valuable to the current knowledge in coal science:

- Development of a novel ratio analysis technique allowing semi-quantitative evaluation of pore growth (on pore scale) using SAXS measurements without modelling.
- A novel application of radial SAXS measurement allowing the evaluation of radial pore development for large char particles.
- Further demonstrating the advantages of utilising SAXS for the evaluation of pore structure and the development thereof.
- A semi-quantitative evaluation and comparison on the pore growth rate of individual sized pores, using SAXS data.
- A quantitative evaluation and comparison on the pore growth rate using different pore bins, using scaled SAXS data.
- A novel classification system was defined to characterise critical cross over pore size.

6.3. Future prospects and recommendations

The results obtained during this investigation, and the consequent conclusions drawn, provide new insights in the field of single coal char particle conversion, and an overall better understanding of pore development during the progress of gasification. In order to further this research, it is proposed that the following research topics be investigated in future:

- The influence of inert diluent gas on pore development during charring and gasification can be evaluated. Pore development is observed even at the smallest scale measured here ($\sim 3 \text{ \AA}$), and it is proposed that the diluent gas can influence the mass transfer properties of the reagent gas due to different molecular properties of the diluent gas (e.g. kinetic diameter), which can inherently influence the pore development of the smaller pores.
- Further extend the experimental procedure to evaluate the influence of different char preparation procedures (e.g. first char single particle size, followed by size preparation) on the influence of particle size on initial char structure.
- Combine the insight into growth rate of individual pore sizes with advanced molecular characterisation and (molecular) modelling to further evaluate the pore development mechanism. This could possibly further explain the reason for individual sized pores to grow at different rates.
- Further extend the experimental procedure to include chars from different regions and prepared at different conditions to confirm the general validity of the conclusions as presented in this study.
- Elucidate the effect of temperature on a wider set of parameters for powder char.

- Extend this study to predict the pore development results using single particle models. The results obtained here can be used to validate, extend or correct advanced dynamic reaction models developed by authors such as Singer *et al.* [Combust Flame 2013;160(1):120-37].

Appendix A

Additional results

This Appendix provides additional experimental results which have not been included in preceding chapters.

A.1 Temperature profile of furnace

The temperature profile along the holding tube length was measured using a 1 mm, K-type thermocouple. The furnace was set to control at 1050°C with argon gas flow rate set at 1.0 L/min. Once temperature was stable, an additional 1 hour was allowed for temperature stabilisation before measurements were taken. Figure A.1 shows the temperature profile of the furnace.

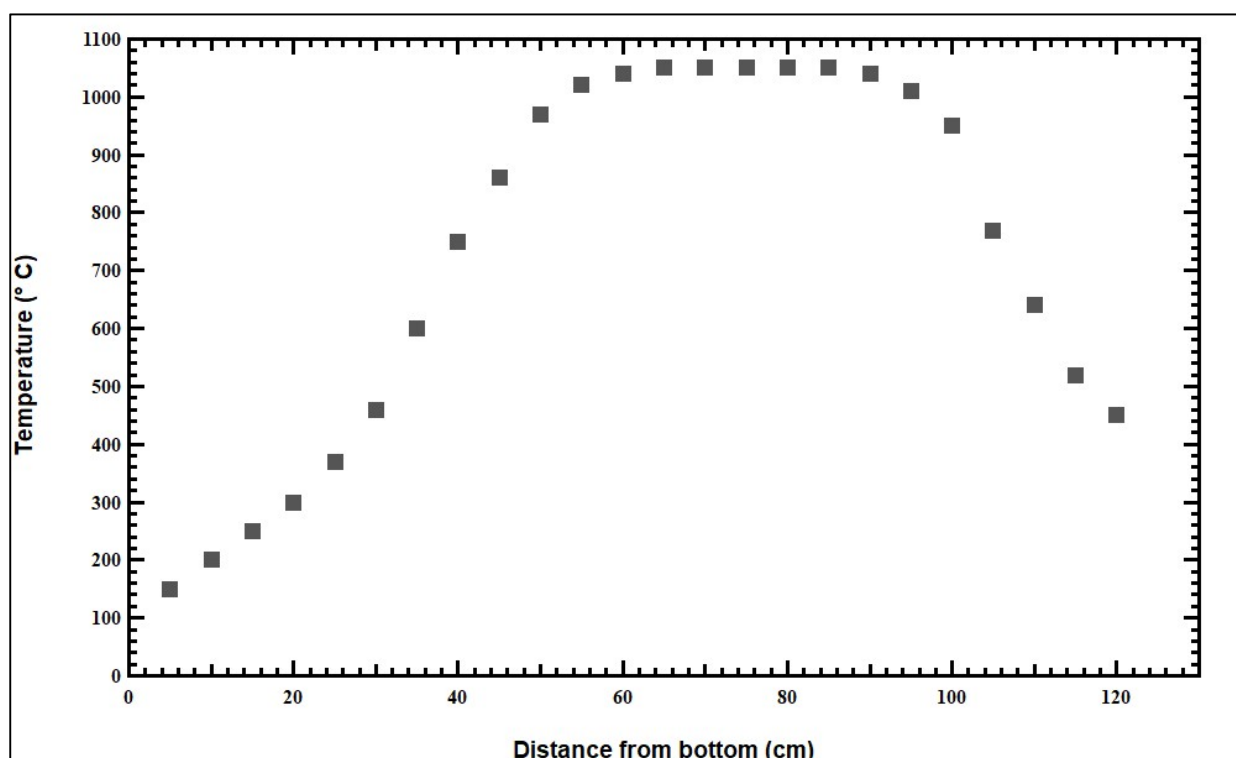


Figure A.1: Temperature profile of furnace.

The temperature profile shown in Figure A.1 remain constant in the presence (and absence) of argon gas flow and reagent gas flow, due to the low flow rates used for this evaluation. For cooling of partially converted chars, the sample will be positioned at approximately 5 cm from the bottom of the tube.

A.2 Total gas flow influence

The influence of total gas flow was experimentally evaluated for 75 μm and 2 mm char samples. Samples were converted at the highest gasification temperature (950°C for steam and 1000°C for CO_2) using two total gas flows, with the first set of total gas flow parameters selected as shown in Table 3.2. The second set of parameters doubles the total gas flow

while keeping the reagent concentration constant. Figure A.2 shows the experimental results for total gas flow evaluation for steam and CO₂ gasification, at 950 and 1000°C respectively.

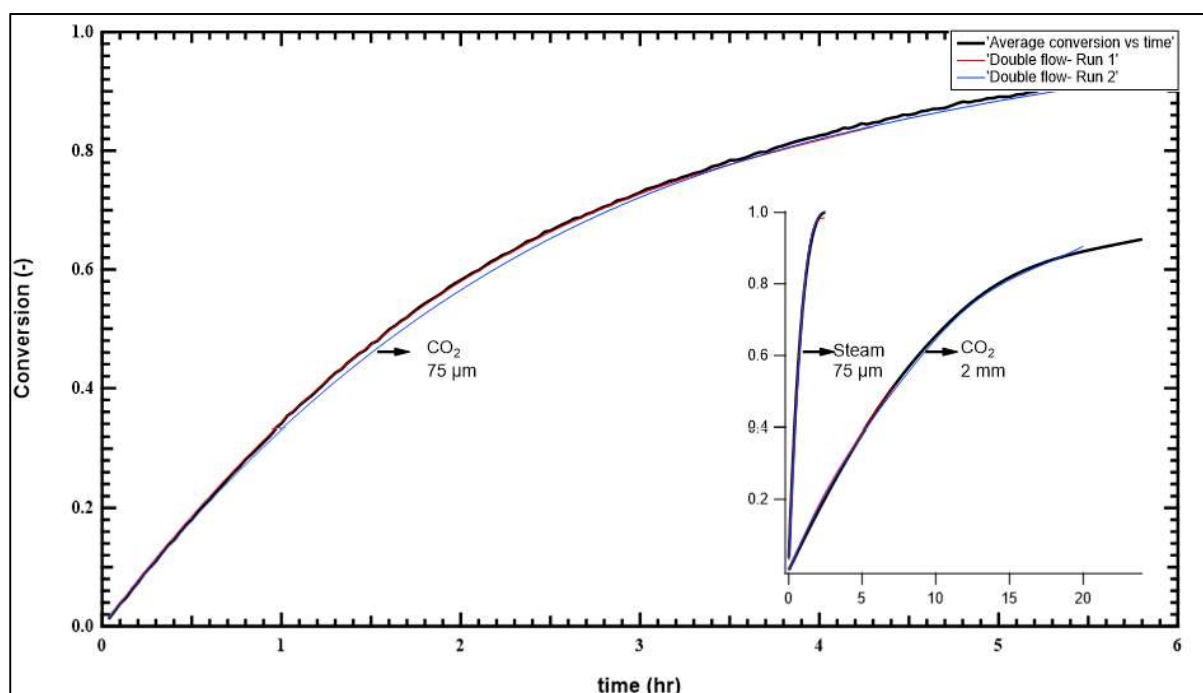


Figure A.2: Conversion versus time graphs for total gas flow experimental results.

The main plot in Figure A.2 shows negligible influence of total gas flow for CO₂ gasification of 75 μm particles at 1000°C, with the subplot further illustrating negligible influence of total gas flow for CO₂ gasification of 2 mm particles at 1000°C. The same trend is observed for steam gasification of 75 μm (subplot in Figure A.2) and 2 mm particles at 950°C, with 2 mm results not shown to improve readability of Figure A.2. The influence of total gas flow was experimentally proven to not influence reactivity at the highest gasification temperature for both CO₂ and steam gasification of 75 μm and 2 mm particles.

A.3 Sample size influence

The influence of initial char sample weight was experimentally evaluated for 75 μm and 2 mm char samples. Samples were converted at the highest gasification temperature (950°C for steam and 1000°C for CO₂) using three different initial char weights ranging from 0.7 to 1.5 g. Figure A.3 shows the experimental results for steam and CO₂ gasification of 75 μm, at 950 and 1000°C respectively.

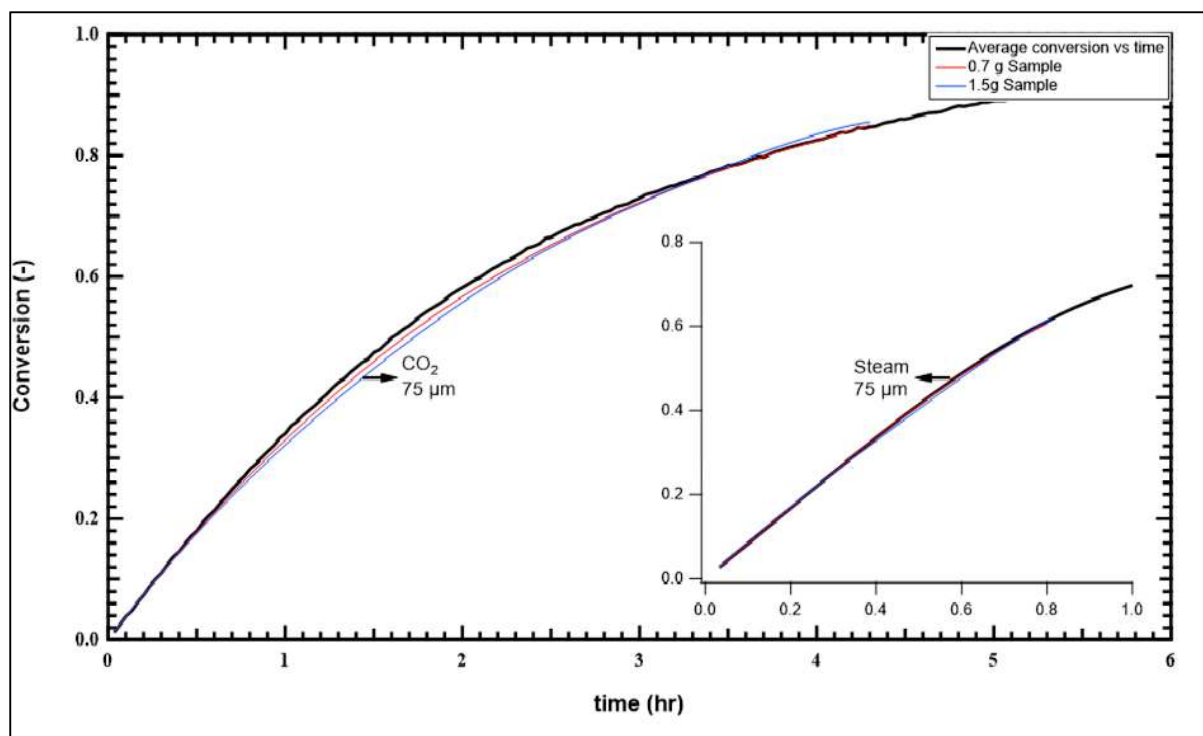


Figure A.3: Conversion versus time graphs for initial char weight experimental results.

The main plot in Figure A.3 shows negligible influence of initial char weight for CO₂ gasification of 75 μm particles at 1000°C, with the subplot further illustrating negligible influence for steam gasification of 75 μm at 950°C. Negligible influence is also observed for 2 mm particles, with trends not shown here. The results of total gas flow and initial char sample weight experimentally proves negligible external mass transfer limitations for char gasification at the highest temperature for both 75 μm and 2 mm particles.

A.4 Observed reaction regime for 75 μm

The reactivity of 75 μm particles was experimentally tested for chemical controlled reactivity at the lowest gasification temperature using two particle size ranges, with a second powder char particle size selected. The second size range was selected as 212 μm and was prepared using a narrow size range (+ 150 μm, - 212 μm) during char preparation of 75 μm and 2 mm particles. Figure A.4 shows the experimental results for steam and CO₂ gasification of 75 μm, at 800 and 850°C respectively.

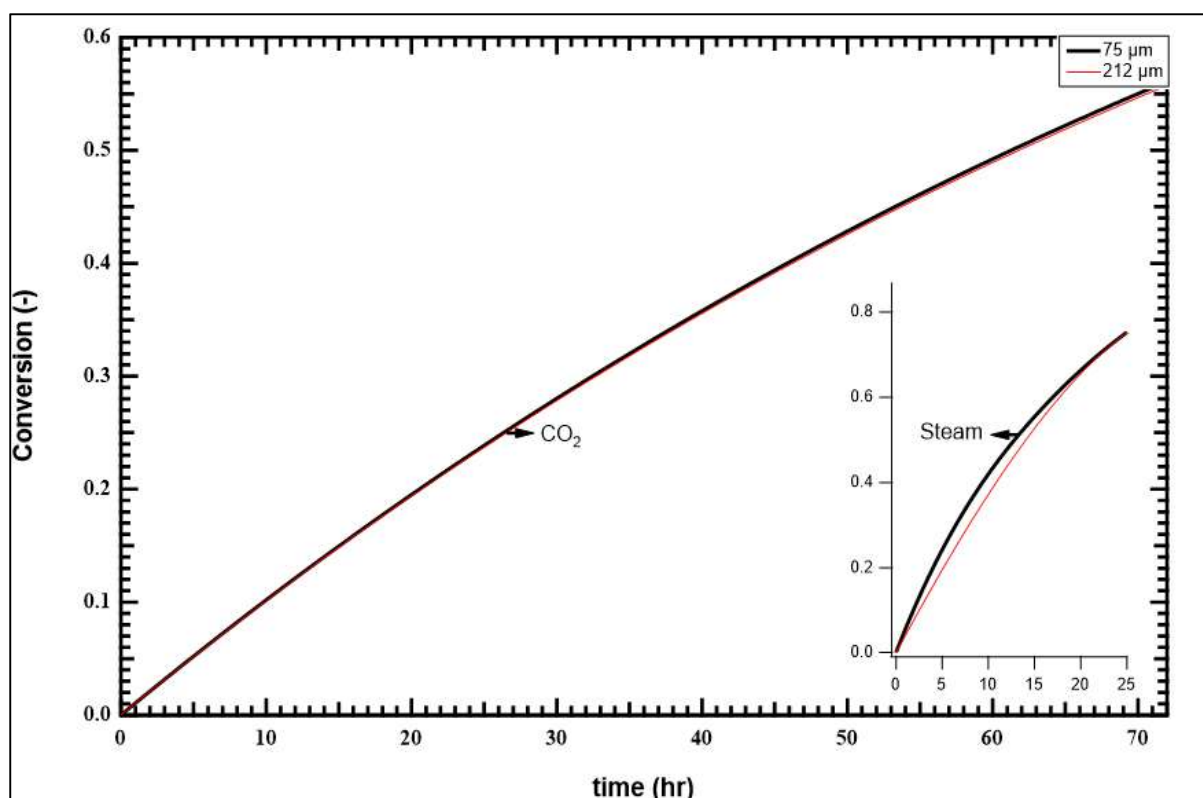


Figure A.4: Conversion versus time graphs for particle size experimental results.

The main plot in Figure A.4 shows negligible influence of particles size on CO₂ gasification at 850°C, with 212 μm conversion being negligibly slower compared to 75 μm. Comparing the results for steam gasification at 800°C in the subplot, it is observed that 212 μm conversion is slower compared to 75 μm for conversion < 60%. The slower conversion is observed to be less than 10% and is therefore deemed negligible when experimental variance is taken into consideration. The results shown in Figure A.4. show particle independent conversion plots for steam and CO₂ gasification at the lowest gasification temperatures, which experimentally indicates chemical controlled reactivity for observed reaction rates.