Product evaluation and reaction modelling for the devolatilization of large coal particles

Burgert Hattingh
B.Eng (Chem. Eng) (NWU), M.Eng (Chem. Eng) (NWU)

Thesis submitted in fulfilment of the requirements for the degree
Philosophiae Doctor in Chemical Engineering
in the School of Chemical and Minerals Engineering at the Potchefstroom campus of the
North-West University, South Africa.

Supervisor:	Prof. R.C. Everson (North-West University)
Co-supervisors:	Prof. H.W.J.P. Neomagus (North-West University)
	Prof. J.R. Bunt (North-West University)
	Dr. D. Van Niekerk (Sasol Technology)

November 2012

"Science can only ascertain what is, but not what should be, and outside of its domain value judgements of all kinds remain necessary."

- Albert Einstein-

Declaration

I, Barend Burgert Hattingh, hereby declare that the thesis entitled: ***”Product evaluation and reaction modelling for the devolatilization of large coal particles”,*** submitted in fulfilment of the requirements for the degree Ph.D in chemical engineering is my own work, except where acknowledged in the text, and has not been submitted to any other tertiary institution in whole or in part.

Signed at Potchefstroom

Burgert Hattingh	Date

Acknowledgements

The success of this investigation has been mainly dependent on the involvement of a few important people/parties. The author hereby wishes to acknowledge and thank all the people/parties involved during the course of this project and would like to send out a special wish of gratitude to the following:

- Our heavenly Father for blessing and providing me with the opportunity to study. Furthermore for the guidance, courage and determination that was given to me through the course of this investigation and my entire life;
- My study coordinators Professors Ray Everson, Hein Neomagus, John Bunt and Dr. Daniel van Niekerk for their excellent guidance, assistance and willingness to help. Without their critical evaluation of this thesis and the priceless suggestions this investigation would not have been a success;
- Sasol for their financial support with respect to this investigation;
- Anglo coal and Exxaro for supplying the respective coals;
- Mr. Johan de Korte (CSIR) for his involvement in the arrangement of the coal samples;
- Mr. David Powell (Exxaro) for arranging and conducting the preliminary preparation (screening) of the TSH coal samples;
- Prof. Hein Neomagus for his friendship and the fruitful discussions regarding the design and development of the tar capturing apparatus;
- Mr. Jan Kroeze, Mr. Adrian Brock, Mr. Ted Paarlberg and Mr. Johan Broodryk for the construction of the tar capturing apparatus and the additional accessories for successfully capturing coal tars during devolatilization;
- Another word of appreciation to Dr. Daniel van Niekerk who assisted in the training, interpretation and analyses (SIMDIST, GC-MS, GC-FID and SEC) of the coal-derived tars;
- Sasol Infrachem® for performing SIMDIST, GC-MS and GC-FID on the generated tar samples.
- Dr. Alan Herod (Imperial College) for his thoughts and suggestions regarding tar production and -tar capturing strategies;
- Dr. Jonathan Mathews (Pennsylvania State University) for his valuable comments regarding advanced analyses on coals and chars as well as for his involvement in MALDI-TOF analyses of the four coals;

- Mr. Ben Ashton for his assistance with non-isothermal TGA measurements at Sasol;
- Prof. Nicola Wagner (University of Witwatersrand) for the morphological analyses conducted on the produced chars;
- Mr. Mokone Roberts for his assistance and valuable inputs during the development of the HRTEM image processing technique;
- Mr. Gregory Okolo for his involvement in establishing the XRD carbon crystallite method at the NWU;
- Dr. Johan Jordaan and Mr. Andre Joubert for their assistance and suggestions in developing analytical competency at the North West University in coal tar analyses via GC-MS and NMR;
- Dr. Jaco Brand from Stellenbosch University for assisting in the ^{1}H- and ^{13}C NMR analyses on the tar samples;
- Mr. Arno Hattingh (4th year student) for his assistance in evaluating the temperature profiles of the large coal particles;
- The coal group for their good nature and lively spirit during the past five years of my involvement with this astounding research entity;
- Mr. Francois Stander and Mr. Elmar Prinsloo for their friendship, assistance and suggestions during the course of my experimentation;
- My parents and my sister for their moral support, guidance and love;
- Last but definitely not the least, Monique Loock, my fiancée; for her love, moral support and assistance in dark times. Without you, hope would have been lost long before completion of this thesis!!!

Title page and chapter pictures:

Anon. 2012. Chemical plant-High resolution. http://www.onlyhdwallpapers.com/flower/chemical-plant-high-resolution-desktop-HD-wallpaper-340464.jpg Date of access: 30 September 2012.

Rast, R. 2012. Time to end the war on coal. http://www.netrightdaily.com/2012/03/Time-to-end-the-war-on-coal.jpg Date of access: 30 September 2012.

Abstract

A fundamental understanding of the process of devolatilization requires extensive knowledge of not only the intrinsic properties of the parent coal and its subsequent formed products (tars, gases and chars), but also its characteristic reaction rate behaviour. Devolatilization behaviour has been extensively addressed in literature with the use of powdered coal samples, which normally do not adhere to particle size constraints of coal conversion processes utilizing lump coal. The aim of this investigation was therefore to assess the devolatilization behaviour (with respect to product yield and -quality; and reaction rate modelling) of four typical South African coals (UMZ, INY, G#5 and TSH) confined to the large particle regime. All four coals were found to be bituminous in rank, with vitrinite contents ranging between 24.4 vol.% and 69.2 vol.% (mineral matter free basis). Two were inertinite-rich coals (UMZ and INY) and the other two were vitrinite-rich coals (G#5 and TSH). From thermoplasticity measurements it was evident that only coal TSH displayed extensive thermoplastic behaviour, while a comparison between molecular properties confirmed the higher abundance of poly-condensed aromatic structures (aromaticity of 81%) present in this coal.

Product evolution was evaluated under atmospheric conditions in a self-constructed, large particle, fixed-bed reactor, on two particle sizes (5 mm and 20 mm) at two isothermal reactor temperatures (450℃ and 750℃) using a combination of both GC and MS techniques for gas species measurement, while standard gravimetric methods were used to quantify tar- and char yield respectively. Elucidation of tar- and char structural features involved the use of both conventional- and advanced analytical techniques. From the results it could be concluded that temperature was the dominating factor controlling product yield- and quality, with significant increases in both volatile- and gas yield observed for an increase in temperature. Tar yields ranged between 3.6 wt.% and 10.1 wt.% and increased in the order UMZ < INY < TSH < G#5, with higher tar yields obtained for coal G#5, being ascribed to larger abundances of vitrinite and liptinite present in this coal. For coal TSH, lower tar yields could mainly be attributed to the higher aromaticity and extensive swelling nature of this coal. Evolved gases were found to be mainly composed of H_2, CH_4, CO and CO_2, low molecular weight olefins and paraffins; and some C_4 homologues. Advanced analytical techniques (NMR, SEC, GC-MS, XRD, etc.) revealed the progressive increase of the aromatic nature of both tars and chars with increasing temperature; as well as subsequent differences in tar composition between the different parent coals. In all cases, an increase in devolatilization temperature led to the evolution of larger amounts of aromatic compounds such as alkyl-naphthalenes and PAHs, while significant decreases in the amount of aliphatics and mixed compounds could be observed. From ^{13}C NMR, HRTEM and XRD carbon crystallite results it was clear that an increase in temperature led to the formation of progressively larger, more aromatic and structurally orientated poly-condensed carbon structures.

Reaction rate studies involved the use of non-isothermal (5-40 K/min) and isothermal (350-900°C) thermogravimetry of both powdered (-200 µm) and large particle samples (20 mm) in order to assess intrinsic kinetics and large particle rate behaviour, respectively. Evaluation of the intrinsic kinetic parameters of each coal involved the numerical regression of non-isothermal rate data in MATLAB® 7.1.1 according to a pseudo-component modelling philosophy. Modelling results indicated that the intrinsic devolatilization behaviour of each coal could be adequately described by using a total number of eight pseudo-components, while reported activation energies were found to range between 22.3 kJ/mol and 244.3 kJ/mol. Description of the rate of large particle devolatilization involved the evaluation of a novel, comprehensive rate model accounting for derived kinetics, heat and mass transport effects, as well as physical changes due to particle swelling/shrinkage. Evaluation of the proposed model with the aid of the COMSOL Multiphysics 4.3 simulation software provided a suitable fit to the experimental data of all four coals, while simulation studies highlighted the relevant importance of not only the effect of particle size, but also the importance of including terms affecting for heat losses due to particle swelling/shrinkage, transport of volatile products through the porous char structure, heat of reaction and heat of vaporization of water.

Keywords: South African coal, devolatilization, large particles, tar, char, reaction modelling.

Opsomming

’n Fundamentele begrip van die proses van termiese ontgassing (pirolise) vereis ekstensiewe kennis van nie net die intrinsieke eienskappe van die oorspronklike steenkool en sy daaropvolgende produkte (tere, gasse en sintels) nie, maar ook die karakteristieke tempo waarteen die betrokke steenkool reageer. Alhoewel pirolisegedrag van verpoeierde steenkoolmonsters reeds breedvoerig aangespreek is in beskikbare literatuur, is wynig egter bekend oor die pirolisegedrag van groot partikels, kenmerkend van groot-partikel steenkoolomsettingsprosesse. Die doel van hierdie ondersoek was dus om die pirolise gedrag (m.b.t. produkopbrengs en –gehalte, asook reaksie modellering) van vier tipies, Suid-Afrikaanse steenkole (UMZ, INY, G#5 en TSH), beperk tot groot partikel monsters, te assesseer. Al vier steenkole is geklassifiseer as bitumineuse rang steenkole met vitriniet inhoude tussen 24.4 vol.% en 69.2 vol.% (mineraal-vry basis). Twee hiervan was inertiniet-ryke steenkole (UMZ en INY) en die ander twee was vitriniet-ryke steenkole (G#5 en TSH). Vanuit termoplastiese analises is dit bevind dat slegs steenkool TSH drastiese termoplastiese gedrag vertoon, terwyl ’n vergelyking tussen molekulêre eienskappe bevestig het dat hierdie steenkool ook gekenmerk word aan ’n hoër konsentrasie van poli-gekondenseerde aromatiese strukture (aromatisiteit van 81%). Produkvorming is bestudeer onder atmosferiese kondisies in ’n self-vervaardigde, groot-partikel, vaste-bed reaktor deur gebruik te maak van twee partikel groottes (5 mm en 20 mm) en twee isotermiese reaksie temperature (450℃ en 750℃). Gasspesieontwikkeling is gemonitor deur gebruik te maak van ’n kombinasie van beide gaschromatografie (GC) en massaspektrometrie (MS) tegnieke, terwyl standaard gravimetriese metodes gebruik is om teer en sintel opbrengs onderskeidelik te kwantifiseer. Hiermee saam, is die gebruik van konvensionele- en gevorderde analitiese metodes ingespan om die strukturele eienskappe van beide die gevormde tere en sintels te evalueer. Vanuit die resultate was dit dus duidelik dat temperatuur die oorheersende faktor is wat die opbrengs en kwaliteit van die gevormde produkte beïnvloed. Gevolglik is ’n beduidende toename in beide vlugtige produk- en gasopbrengs waargeneem vir ’n toename in reaksietemperatuur, terwyl teeropbrengste gewissel het tussen 3.6 gewigs % en 10.1 gewigs %. Verder is dit bevind dat teeropbrengste verhoog het in die volgorde UMZ < INY < TSH < G#5, met die hoër opbrengs van steenkool G#5 toeskryfbaar aan die groter hoeveelhede vitriniet en liptiniet teenwoordig in hierdie steenkool. Die laer teer opbrengs verkry vir steenkool TSH kon egter toegeskryf word aan beide die hoër aromatisiteit en uitermatige swel eienskappe van hierdie steenkool. Vrygestelde gasse het hoofsaaklik bestaan uit H_2, CH_4, CO en CO_2, lae molekulêre gewig olefiene en parafiene; asook ’n paar C_4 homoloë. Gevorderde analitiese tegnieke soos kern magnetiese resonansspektroskopie (KMR), grootte-uitsluitings chromatografie (SEC), X-straal diffraksie (XRD), gaschromatografie-massaspektrometrie (GC-MS) ens. het nie net bewys gelewer van die progressiewe verhoging in die aromatiese karakter van beide die tere en sintels met ’n toename in temperatuur nie, maar het ook daaropvolgende verskille in teer samestelling tussen die verskillende steenkole uitgelig. ’n Toename in pirolisetemperatuur is dus gekenmerk deur die produksie van groter hoeveelhede aromatiese verbindings soos alkiel-naftalene en polisikliese aromatiese koolwaterstowwe (PAKs), terwyl aansienlike afnames in beide die hoeveelheid alifatiese- en vermengde verbindings egter waargeneem is. Vanuit ^{13}C KMR, HRTEM (hoë-resolusie transmissie-elektronmikroskopie) en XRD koolstof-kristallietanalises was dit verder duidelik dat ’n verhoging in temperatuur gelei het tot die vorming van groter en meer struktureel-georiënteerde, poli-gekondenseerde, aromatiese koolstofstrukture.

Pirolisereaktiwiteit is ondersoek op beide verpoeierde (-200 µm) en groot-partikel (20 mm) steenkoolmonsters deur onderskeidelik gebruik te maak van nie-isotermiese (5-40 K/min) en isotermiese (350-900℃) termogravimetriese (TG) metodes, ten einde beide intrinsieke kinetika en groot-partikel reaksiegedrag te bestudeer. Intrinsieke kinetiese parameters van elke steenkool is numeries bepaal vanuit die nie-isotermiese TG resultate deur gebruik te maak van ’n pseudo-komponent modellerings filosofie in MATLAB® 7.1.1. Modelleringsresultate het gevolglik daarop gedui dat die intrinsieke pirolise gedrag van elke steenkool voldoende beskryf kon word deur ’n totaal van agt pseudo-komponent reaksies waarvan aktiveringsenergieë wissel tussen 22.3 kJ/mol en 244.3 kJ/mol. Na aanleiding hiervan kon pirolise gedrag van die groot steenkoolpartikels dus beskryf word deur ’n omvattende model wat rekening hou met reaksiekinetika, hitte- en massaoordrageffekte, asook fisiese veranderinge weens partikel swelling/krimping. Modellering met behulp van die COMSOL Multiphysics® 4.3 simulasiepakket het daarop gedui dat die eksperimentele resultate bevredigend beskryf kon word deur die voorgestelde groot-partikel model, terwyl simulasie studies die belangrikheid van die effek van partikelgrootte en die effek van die insluiting van hitteverlies weens partikel termoplastisiteit, massaoordrag van vlugtige produkte deur die poreuse sintelstruktuur, reaksie-entalpie en die verdamping van water beklemtoon het.

Kernwoorde: Suid-Afrikaanse steenkool, pirolise, groot partikels, teer, sintels, reaksie modellering.

Table of Contents

Declaration iii
Acknowledgements iv
Abstract vi
Opsomming viii
Table of Contents x
List of Figures xv
List of Tables xxvi
List of Symbols xxx
Glossary xliv

1 GENERAL INTRODUCTION 1
1.1 Background and motivation 1
  1.1.1 Coal as an energy source 1
  1.1.2 Coal conversion technologies 3
  1.1.3 Non-fuel applications of coal 4
  1.1.4 Significance of devolatilization 5
1.2 Problem statement 6
1.3 Objectives of the investigation 7
1.4 Scope of the study 8
Bibliography 12

2 LITERATURE STUDY 16
2.1 Introduction 16
2.2 The nature of coal and coal utilization 17
  2.2.1 Coal as an important fossil fuel 17
  2.2.2 Assessing the fundamental structure of coal 19
2.3 Devolatilization as a coal conversion process 23
  2.3.1 Nature and scope of coal devolatilization 23
  2.3.2 Proposed mechanisms for coal devolatilization 25
  2.3.3 Classification of coal carbonization/devolatilization processes 28
  2.3.4 Valuable products obtainable from coal devolatilization 30
2.4 Current strategies available for assessing coal devolatilization behaviour 32
2.5 Factors affecting the efficiency of devolatilization 35
  2.5.1 Coal characteristic properties affecting the efficiency of devolatilization 35

2.5.2 Operational conditions affecting the efficiency of devolatilization 43
2.6 Modelling coal devolatilization behaviour 51
2.6.1 Modelling strategies 51
2.7 Summary of findings in the literature 56
Bibliography 56

3 MODELLING COAL DEVOLATILIZATION BEHAVIOUR 77
3.1 Introduction 77
3.2 Choice and description of an appropriate kinetic model 78
3.3 Model description and evaluation of intrinsic kinetics 79
3.3.1 Kinetic model description 79
3.3.2 Kinetic model evaluation 82
3.4 Inclusion of physical transport effects 85
3.4.1 Heat transfer considerations 87
3.4.2 Mass transfer considerations 90
3.5 Evaluation and validation procedure of the combined model 97
Bibliography 98

4 COAL CHARACTERISATION: CONVENTIONAL COAL ANALYSES 107
4.1 Introduction 107
4.2 Choice and origin of coal samples 107
4.3 Coal preparation 109
4.4 Overview of coal characterisation analyses 109
4.4.1 Conventional analyses 109
4.5 Characterisation techniques and apparatus 110
4.5.1 Conventional analyses 110
4.6 Results and discussion 114
4.6.1 Conventional analyses 114
4.7 Summary 142
Bibliography 144

5 COAL CHARACTERISATION: ADVANCED COAL ANALYSES 151
5.1 Introduction 151
5.2 Overview of coal characterisation analyses 151
5.2.1 Advanced analyses 151
5.3 Characterisation techniques and apparatus 152

5.3.1 *Advanced analyses* ... 152

5.4 Results and discussion ... 163

5.4.1 *Advanced analyses* ... 163

5.5 Summary ... 190

Bibliography ... 191

6 PRODUCT YIELD AND QUALITY ASSESSMENT FROM COAL DEVOLATILIZATION ... 196

6.1 Introduction ... 196

6.2 Materials used ... 196

6.2.1 *Coals* ... 196
6.2.2 *Gas* ... 197
6.2.3 *Solvents and analytical compounds* ... 197

6.3 Coal particle preparation and selection ... 198

6.3.1 *Sample preparation* ... 198
6.3.2 *Hand selection and grinding of larger particles* ... 199
6.3.3 *Mercury submersion tests* ... 199

6.4 Experimental equipment and -methodology ... 200

6.4.1 *Experimental equipment* ... 200
6.4.2 *Experimental plan and protocol* ... 204
6.4.3 *Product recovery and yield assessment* ... 206
6.4.4 *Product quality assessments* ... 207

6.5 Results and discussion ... 216

6.5.1 *Large particle selection via mercury submersion* ... 216
6.5.2 *Product yields* ... 217
6.5.3 *Product composition and quality* ... 223

6.6 Summary ... 310

Bibliography ... 312

7 REACTION RATE MODELLING OF COAL DEVOLATILIZATION ... 334

7.1 Introduction ... 334

7.2 Materials used ... 335

7.2.1 *Coals* ... 335
7.2.2 *Gas* ... 335

7.3 Experimental apparatus ... 335

7.3.1 *Overview* ... 335
7.3.2 *Small particle thermogravimetric analyser (Mettler-Toledo TGA/DSC 1 STAR^e)* ... 337
7.3.3 *Large particle thermogravimetric analyser (LPTGA)* ... 338

7.4 Experimental methodology ... 340

7.4.1 *Small particle thermogravimetric analyser (Mettler-Toledo TGA/DSC 1 STAR^e)* ... 340
7.4.2 *Large particle thermogravimetric analyser (LPTGA)* ... 342

7.5 Modelling strategies....344
7.5.1 Small particle modelling and determination of intrinsic kinetics....344
7.5.2 Large particle modelling....348
7.6 Results and discussion....356
7.6.1 Small particle devolatilization....356
7.6.2 Large particle devolatilization....362
7.7 Particle modelling and parameter estimation....369
7.7.1 Intrinsic kinetic parameter evaluation....369
7.7.2 Modelling the devolatilization behaviour of large coal particles....385
7.7.3 Simulation studies....397
7.8 Summary....405
Bibliography....407

8 CONCLUSIONS AND RECOMMENDATIONS....417
8.1 Introduction....417
8.2 Conclusions....417
8.2.1 Coal characteristic properties as determined by conventional methods....417
8.2.2 Coal characteristic properties as determined by advanced methods....418
8.2.3 Influence of operating conditions on the yield of devolatilization products....418
8.2.4 Product quality of generated gases, tars and chars....419
8.2.5 Reaction rate modelling of the devolatilization of large coal particles....420
8.3 Contribution to knowledge of coal science and technology....422
8.4 Recommendations....423

APPENDIX A....426
A.1 Description of standard methods used....426
A.2 XRD minerals-chemical structures and properties....427
A.3 Vitrinite reflectance and maceral scan analyses....428
A.4 Porosity calculations....429

APPENDIX B....431
B.1 ^{13}C NMR spectra obtained from CP-MAS DD analyses of all four coals....431
B.2 XRD: Deconvolution results for amorphous carbon calculation....433
B.3 XRD: Deconvolution results for aromaticity calculation....434
B.4 HRTEM processed images for coals UMZ, INY and G#5....435
B.5 HRTEM size-range selected images for coals UMZ, INY and G#5....436

APPENDIX C **438**
C.1 Influence of particle size on the yields of product obtained at 750℃ 438
C.2 Gas species evolution curves for 5 mm particles as determined from MS 438
C.3 Experimental reproducibility of gas evolution profiles determined by MS 443
C.4 Experimental reproducibility of gas evolution profiles determined by GC 452
C.5 Comparison between gas evolution profiles of 5 mm and 20 mm particles 457
C.6 GC/MS and GC/FID results of tars generated from the different coals 464
C.7 SEC results of tars generated from the different coals 479
C.8 Effect of coal type and temperature on the SEC molecular weight distribution of tars derived from 20 mm coal particles 480
C.9 Effect of particle size on the SEC molecular weight distribution of tars derived at the two different temperatures 483
C.10 Structural features of tars as determined from ^{1}H- and ^{13}C NMR 484
C.11 Chemical properties of chars derived from 5 mm coal particles 489
C.12 ^{13}C NMR spectra obtained from CP-MAS DD analyses of all chars 491
C.13 XRD: Deconvolution results for amorphous carbon calculation of chars 494
C.14 XRD: Deconvolution results for aromaticity calculation of chars 496
C.15 HRTEM and image analysis results 498

APPENDIX D **503**
D.1 MATLAB 7.1.1 algorithm for deriving intrinsic kinetic parameters 503
D.2 Scaling of the intrinsic rate equation for volatile release 520
D.3 Repeatability curves obtained from small particle TGA 522
D.4 Qualitative physical changes during large particle devolatilization 523
D.5 Repeatability curves obtained from large particle TGA 525
D.6 Comparison between modelled and experimental DTG and TG curves 532
D.7 Modelling comparison using two different thermal conductivity models 536
D.8 Experimental temperature profiles of 20 mm coal particles 537
Bibliography (Appendices) 539

CURRICULUM VITAE **543**

QUICK REFERENCE **545**

**A quick reference to the parent coal properties has been included for the reader's convenience.*

List of Figures

Figure 1.1 Total energy consumption a.) and coal production-and consumption rates b.) in South Africa (DOE, 2012; EIA, 2011). 2
Figure 1.2 Scope of study. 9
Figure 1.3 Simplistic research overview of chapters 4, 5, 6 and 7. 10

Figure 2.1 Representative structure of bituminous coal (taken from Levine *et al*., 1982).....22
Figure 2.2 Three-dimensional molecular representation of inertinite-rich South African coal (taken from Van Niekerk, 2008; and Van Niekerk and Mathews, 2008).....23
Figure 2.3 Hypothetical coal molecules during different stages of devolatilization (adapted from Solomon *et al*., 1988).....25
Figure 2.4 Mechanistic model of primary- and secondary devolatilization reactions.....26

Figure 3.1 Hypothetical DTG curve of coal devolatilization (adapted from Alonso *et al*. (2001)).....83
Figure 3.2 Transport and reaction processes during large particle coal devolatilization. 86

Figure 4.1 Vitrinite reflectance histograms of coals INY, UMZ, G#5 and TSH. 120
Figure 4.2 Total maceral reflectance scan histograms for the four coals. 123
Figure 4.3 Comparison of volatile matter content with a.) liptinite content and b.) rank......126
Figure 4.4 Parity plot of predicted VM against experimental VM.....129
Figure 4.5 Comparison between Maceral Index and Fischer tar yield.....131
Figure 4.6 Comparison between Reactive maceral index and Fischer tar yield. 131
Figure 4.7 CO_2 adsorption isotherms for the four coals. 137
Figure 4.8 Nitrogen adsorption- and desorption isotherms for the four coals. 138
Figure 4.9 Graphical representations of results obtained from a.) Gieseler fluidity and b.) dilatometry tests performed on all four coals. 142

Figure 5.1 HRTEM image processing methodology. 161
Figure 5.2 CP-MAS acquired spectra for coal INY. 165
Figure 5.3 CP-MAS acquired spectra for coal G#5. 165

Figure 5.4 CP-MAS acquired spectra for coal UMZ. 166
Figure 5.5 CP-MAS acquired spectra for coal TSH. 166
Figure 5.6 Annotated CP-MAS spectra of coal G#5 (According to Suggate & Dickinson (2004)). 167
Figure 5.7 Correlation between fraction aromatics and atomic O/C ratio. 169
Figure 5.8 Correlation between fraction aromatics and vitrinite reflectance. 170
Figure 5.9 Average cluster size and attachments for the four coals. 171
Figure 5.10 Raw diffractograms of the four coals. 172
Figure 5.11 Corrected and smoothened diffractograms of the four coals. 173
Figure 5.12 Determination of the fraction of amorphous carbon of coal G#5. 175
Figure 5.13 Determination of the aromaticity of coal G#5. 176
Figure 5.14 Dependency of aromaticity on atomic H/C ratio. 177
Figure 5.15 Influence of X_A and *DOI* on coal volatile matter. 178
Figure 5.16 Influence of fraction of aliphatics on order of coal structure. 178
Figure 5.17 MALDI-TOF spectra of coals UMZ and INY. 179
Figure 5.18 MALDI-TOF spectra of coals G#5 and TSH. 180
Figure 5.19 HRTEM micrographs for coals UMZ, INY, G#5 and TSH. 182
Figure 5.20 Overview of some of the processing steps during the lattice fringe-extraction of coal TSH. 183
Figure 5.21 Colored-by-length value distribution of coal TSH. 183
Figure 5.22 Selected fringes of coal TSH in different size-ranges. 184
Figure 5.23 Example of a 6x6 fringe with maximum (MaxL) and minimum (MinL) length. 185
Figure 5.24 Aromatic raft size distribution w.r.t to fringe length for coals G#5 and TSH. 187
Figure 5.25 Aromatic raft size distribution w.r.t to fringe length for coals UMZ and INY. 187
Figure 5.26 Molecular weight distribution from HRTEM for coals G#5 and TSH. 188
Figure 5.27 Molecular weight distribution from HRTEM for coals UMZ and INY. 189

Figure 6.1 Mercury submersion test-rig. 199
Figure 6.2 Schematic overview of TCR facility. 202
Figure 6.3 Schematic representation of the a.) primary solvent trap and b.) secondary dry traps. 204
Figure 6.4 Density distribution of coal particles. 216
Figure 6.5 Comparison between tar yield and Maceral Index (MI) 219
Figure 6.6 Effect of temperature on product yield for both particle sizes. 220

Figure 6.7 Effect of particle size on product yield. 222
Figure 6.8 Evolution curves of selected ion species obtained from 20 mm particles at 450°C. 225
Figure 6.9 Evolution curves of selected ion species obtained from 20 mm particles at 750°C. 227
Figure 6.10 Gas evolution profiles determined at 450°C for 20 mm coal particles. 231
Figure 6.11 Gas evolution profiles determined at 750°C for 20 mm coal particles. 232
Figure 6.12 Gas evolution profiles determined at 450°C for both particle sizes of coal UMZ. 238
Figure 6.13 Gas evolution profiles determined at 750°C for both particle sizes of coal UMZ. 239
Figure 6.14 Distillation curves of the generated tars as determined from SIMDIST analysis for 450°C (a.) & (c.) and 750°C (b.) & (d.). 242
Figure 6.15 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal UMZ at 450°C. 247
Figure 6.16 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal UMZ at 750°C. 247
Figure 6.17 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal G#5 at 450°C. 248
Figure 6.18 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal G#5 at 750°C. 248
Figure 6.19 Correlation of aliphatic- and phenolic content in tars with coal liptinite content, *DOI* and elemental oxygen content.. 252
Figure 6.20 Comparison of GC results between particle sizes. 256
Figure 6.21 SEC chromatogram of the 10 calibration standards used a.) and b.) calibration curve determined from the elution times of the different calibration standards. 257
Figure 6.22 SEC chromatogram (370 nm) for tar generated from coal UMZ at 450°C and 5 mm shown as a function of a.) elution time and b.) molecular mass (Da) estimate. 258
Figure 6.23 SEC chromatograms (370 nm) for tars generated at 450°C and 750°C from 5 mm particles of coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH. 259
Figure 6.24 Comparison between SEC results (370 nm) obtained on tars generated from the different coals at a.) 450°C and b.) 750°C. 262

Figure 6.25 Comparison between SEC results (370 nm) obtained on tars generated from coals UMZ (a.) and (b.) and G#5 (c.) and (d.) for the different particle sizes. ...264

Figure 6.26 NMR spectral assignments as adapted from Diaz *et al*. (2003), Guillen *et al*. (1998), Morgan *et al*. (2008) and Wang *et al*. (2010)......................................265

Figure 6.27 ^{1}H NMR spectra of tars generated at the two different temperatures from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH (5 mm particles). 266

Figure 6.28 Comparison of the relative abundance of aliphatic proton with a.) *DOI* and b.) total liptinite content (m.m.f.b). 270

Figure 6.29 Comparison of the relative abundance of aliphatic proton confined to 0.5 to 3.0 ppm with a.) DOI and b.) total liptinite content (m.m.f.b)..................................270

Figure 6.30 Comparison of mean random vitrinite reflectance (coal rank) with the relative abundance of a.) total aliphatic protons and b.) aliphatic protons confined to 0.5 to 3.0 ppm. 271

Figure 6.31 ^{13}C NMR spectra of tars generated at the two different temperatures from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH (5 mm particles). 273

Figure 6.32 Comparison of the relative abundance of aliphatic carbon with a.) *DOI* and b.) total liptinite content (m.m.f.b). 277

Figure 6.33 Comparison of the relative abundance of methyl carbon with a.) *DOI* and b.) total liptinite content (m.m.f.b). 277

Figure 6.34 Comparison of mean random vitrinite reflectance (coal rank) with the relative abundance of a.) total aliphatic carbons and b.) methyl carbons. 278

Figure 6.35 Comparison of proximate results for the transition from raw coal to char for a.) the inertinite-rich coals and b.) the vitrinite-rich coals. 279

Figure 6.36 Comparison of ultimate results for the transition from raw coal to char for a.) the inertinite-rich coals and b.) the vitrinite-rich coals. 281

Figure 6.37 Specimens of char structures: a.) devolatilized coal, b.) partial coke massive (TSH), c.) partial coke devolatilized (TSH), d.) honeycomb (tenuinetwork) structures, e.) dense char, f.) fusinoid, g.) mixed dense structures, h.) mixed porous structures and i.) pyrite mineral. 284

Figure 6.38 Comparison between the a.) original image obtained under reflected light and the occurrence of b.) isotropic/anisotropic structures within the chars using a retarder plate under crossed polars. 285

Figure 6.39 Correlation of number of honeycomb structures with maceral index (MI). 287

Figure 6.40 Comparison between the relative amounts of isotropic or 288

Figure 6.41 Comparison of CP-MAS acquired spectra for chars generated from coal a.) UMZ, b.) INY, c.) G#5 and d.) TSH respectively. 290
Figure 6.42 Smoothened and background corrected diffractograms of the parent coals and their respective chars. 295
Figure 6.43 Estimation of the fraction of amorphous carbon for chars generated at a.) 450℃ and b.) 750℃ from coal G#5. 299
Figure 6.44 Estimation of the fraction aromatics for chars generated at a.) 450℃ and b.) 750℃ from coal G#5. 299
Figure 6.45 Correlation of a.) aromaticity and d.) DOI with crystallite stacking diameter. 301
Figure 6.46 Comparison of aromaticity and *DOI* with volatile matter (a.) and, b.)) and atomic H/C ratio (c.) and d.)). 302
Figure 6.47 Overview of some of the processing steps during the lattice fringe-extraction of chars generated from coal TSH. 303
Figure 6.48 Selected fringes in different size-ranges for chars derived from coal UMZ at 450℃ and 750℃. 305
Figure 6.49 Selected fringes in different size-ranges for chars derived from coal TSH at 450℃ and 750℃. 306
Figure 6.50 Onion-like structures observed for chars derived from coal G#5. 307
Figure 6.51 Molecular weight distributions from HRTEM for the parent coals and their respective chars. 309

Figure 7.1 Schematic overview of the Mettler-Toledo TGA/DSC 1 STAR^{e} system. 337
Figure 7.2 Large particle thermogravimetric analyser. 339
Figure 7.3 MATLAB algorithm used for solving kinetic parameters. 347
Figure 7.4 Couplings between the different descriptive equations. 355
Figure 7.5 Normalised mass versus temperature (TGA) results from the devolatilization of the four coals at a.) 5 K/min, b.) 10 K/min, c.) 25 K/min and d.) 40 K/min, respectively 356
Figure 7.6 DTG profile comparison for coal devolatilization at the four different heating rates. 358
Figure 7.7 Effect of heating rate on the devolatilization rate of the different coals: a.) UMZ, b.) INY, c.) G#5 and d.) TSH. 361
Figure 7.8 Coal particles before and after devolatilization at 450℃. 362
Figure 7.9 Coal particles before and after devolatilization at 900℃. 363

Figure 7.10 Experimental result as obtained for coal G#5 at 600℃. 364
Figure 7.11 Normalised devolatilization results for coal G#5 at 600℃. 364
Figure 7.12 Effect of temperature on the devolatilization rate of coals a) UMZ, b) INY, c) G#5 and d) TSH for total reaction time. 366
Figure 7.13 Effect of temperature on the initial devolatilization rate of coals a) UMZ, b) INY, c) G#5 and d) TSH for the first 30 minutes. 367
Figure 7.14 Simulated reaction rate curves for coal UMZ based on the first order model of a.) 3, b.) 4, c.) 5 and d.) 8 pseudo-components. 370
Figure 7.15 Simulated reaction rate curves for coal G#5 based on the first order model of a.) 3, b.) 4, c.) 5 and d.) 8 pseudo-components. 371
Figure 7.16 Comparison between experimental and modelled TG curves for coal INY assuming a-d.) 3 reactions and e-h.) 8 reactions...372
Figure 7.17 Comparison between experimental and modelled TG curves for coal TSH assuming a-d.) 3 reactions and e-h.) 8 reactions...373
Figure 7.18 Comparison between a.) proximate moisture content and fractional contribution of peak 1 to the volatile matter and b.) tar yield and the fractional contribution of the main DTG peak to the volatile matter. 382
Figure 7.19 Comparison of $Tm_{1,exp}$ to a.) $Tm_{1,calc}$ and b.) parent coal aromaticity. 384
Figure 7.20 Empirical model fitting to the dilatometry results of coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH. 386
Figure 7.21 Comparison between model predictions for coals INY and G#5 using a.) thermal conductivity model (1) and b.) thermal conductivity model (2). 390
Figure 7.22 Comparison of experimental, fractional volatile release from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH with model predictions (full reaction time). 391
Figure 7.23 Comparison of experimental, fractional volatile release from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH with model predictions (half the reaction time). 392
Figure 7.24 Comparison of experimental temperature profiles with model predictions at 450℃ for coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH. 394
Figure 7.25 Comparison of experimental temperature profiles with model predictions at 750℃ for coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH. 395
Figure 7.26 Model-predicted radial volatile loss- and temperature profiles at different time instances for the devolatilization of coal UMZ at a.) 450C and b.) 750C respectively. 398

Figure 7.27 Profiles simulating the effect of particle size on total volatile loss and core temperature for the devolatilization of coal INY at a.) 450°C and b.) 750°C, respectively. 400
Figure 7.28 Effect of heat losses due to the internal transport of volatiles as depicted for the temperature profiles of coal G#5 at a.) 450°C and b.) 750°C. 402
Figure 7.29 Effect of heat losses due to heat of reaction and heat of vaporization as depicted for the temperature profiles of coal G#5 at a.) 450°C and b.) 750°C. 403
Figure 7.30 Effect of swelling/shrinkage on the temperature profile of a typical inertinite-rich coal (a.) and (b.) and a typical vitrinite-rich coal (c.) and (d.) for devolatilization at 450°C and 750°C. 404

Figure B.1 CP-MAS DD spectra obtained for coal INY 431
Figure B.2 CP-MAS DD spectra obtained for coal UMZ. 431
Figure B.3 CP-MAS DD spectra obtained for coal G#5. 432
Figure B.4 CP-MAS DD spectra obtained for coal TSH. 432
Figure B.5 Amorphous carbon deconvolution results for coal a.) INY and b.) UMZ. 433
Figure B.6 Amorphous carbon deconvolution results for coal a.) G#5 and b.) TSH. 433
Figure B.7 Aromaticity deconvolution results for coal a.) INY and b.) UMZ. 434
Figure B.8 Aromaticity deconvolution results for coal a.) G#5 and b.) TSH. 434
Figure B.9 Processed HRTEM images of coal INY (FFT threshold as well as skeletonised). 435
Figure B.10 Processed HRTEM images of coal UMZ (FFT threshold as well as skeletonised). 435
Figure B.11 Processed HRTEM images of coal G#5 (FFT threshold as well as skeletonised). 436
Figure B.12 Size range selected, skeletonised images of coal INY. 436
Figure B.13 Size range selected, skeletonised images of coal UMZ. 437
Figure B.14 Size range selected, skeletonised images of coal G#5. 437

Figure C.1 Evolution curves of selected ion species obtained from 5 mm particles at 450°C. 439
Figure C.2 Evolution curves of selected ion species obtained from 5 mm particles at 750°C. 441

Figure C.3 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm UMZ coal at 450℃. 444
Figure C.4 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm INY coal at 450℃. 446
Figure C.5 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm G#5 coal at 450℃. 448
Figure C.6 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm TSH coal at 450℃. 450
Figure C.7 Reproducibility curves for the different gas species observed by GC during the devolatilization of 20 mm UMZ coal at 450℃. 453
Figure C.8 Reproducibility curves for the different gas species observed by GC during the devolatilization of 20 mm INY coal at 450℃. 454
Figure C.9 Reproducibility curves for the different gas species observed by GC during the devolatilization of 20 mm G#5 coal at 450℃. 455
Figure C.10 Reproducibility curves for the different gas species observed by GC during the devolatilization of 20 mm TSH coal at 450℃. 456
Figure C.11 Gas evolution profiles determined at 450℃ for both particle sizes of coal INY. 458
Figure C.12 Gas evolution profiles determined at 450℃ for both particle sizes of coal G#5. 459
Figure C.13 Gas evolution profiles determined at 450℃ for both particle sizes of coal TSH. 460
Figure C.14 Gas evolution profiles determined at 750℃ for both particle sizes of coal INY. 461
Figure C.15 Gas evolution profiles determined at 750℃ for both particle sizes of coal G#5. 462
Figure C.16 Gas evolution profiles determined at 750℃ for both particle sizes of coal TSH. 463
Figure C.17 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal INY at 450℃. 465
Figure C.18 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal INY at 750℃. 465
Figure C.19 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal TSH at 450℃. 466
Figure C.20 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal TSH at 750℃. 466

Figure C.21 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal UMZ at 450℃. 467
Figure C.22 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal UMZ at 450℃. 467
Figure C.23 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal INY at 450℃. 468
Figure C.24 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal INY at 750℃. 468
Figure C.25 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal G#5 at 450℃. 469
Figure C.26 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal G#5 at 750℃. 469
Figure C.27 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal TSH at 450℃. 470
Figure C.28 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal TSH at 750℃. 470
Figure C.29 Raw SEC chromatograms (370 nm) for tar generated from 5 mm particles of coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH at 450℃ and 750℃, shown as a function of elution time. 479
Figure C.30 Raw SEC chromatograms (370 nm) for tar generated from 20 mm particles of coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH at 450℃ and 750℃, shown as a function of elution time. 480
Figure C.31 SEC chromatograms (370 nm) for tars generated at 450℃ and 750℃ from 20 mm particles of coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH. 481
Figure C.32 Comparison between SEC results (370 nm) obtained on tars generated from coals INY (a.) and (b.) and TSH (c.) and (d.) for the different particle sizes. 483
Figure C.33 ^{1}H NMR spectra of tars generated at the two different temperatures from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH (20 mm particles). 485
Figure C.34 ^{13}C NMR spectra of tars generated at the two different temperatures from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH (20 mm particles). 487
Figure C.35 CP-MAS DD spectra obtained for chars produced from coal UMZ at a.) 450℃ and b.) 750℃. 491
Figure C.36 CP-MAS DD spectra obtained for chars produced from coal INY at a.) 450℃ and b.) 750℃. 492

Figure C.37 CP-MAS DD spectra obtained for chars produced from coal G#5 at a.) 450℃ and b.) 750℃. 493
Figure C.38 CP-MAS DD spectra obtained for chars produced from coal TSH at a.) 450℃ and b.) 750℃. 494
Figure C.39 Estimation of the fraction of amorphous carbon for chars generated at a.) 450℃ and b.) 750℃ from coal UMZ. 495
Figure C.40 Estimation of the fraction of amorphous carbon for chars generated at a.) 450℃ and b.) 750℃ from coal INY. 495
Figure C.41 Estimation of the fraction of amorphous carbon for chars generated at a.) 450℃ and b.) 750℃ from coal TSH. 495
Figure C.42 Estimation of the fraction aromatics for chars generated at a.) 450℃ and b.) 750℃ from coal UMZ. 496
Figure C.43 Estimation of the fraction aromatics for chars generated at a.) 450℃ and b.) 750℃ from coal INY 496
Figure C.44 Estimation of the fraction aromatics for chars generated at a.) 450℃ and b.) 750℃ from coal TSH. 497
Figure C.45 Overview of some of the processing steps during the lattice fringe-extraction of chars generated from coal UMZ. 498
Figure C.46 Overview of some of the processing steps during the lattice fringe-extraction of chars generated from coal INY. 499
Figure C.47 Overview of some of the processing steps during the lattice fringe-extraction of chars generated from coal G#5. 500
Figure C.48 Selected fringes in different size-ranges for chars derived at 450℃ and 750℃ from coal INY. 501
Figure C.49 Selected fringes in different size-ranges for chars derived at 450℃ and 750℃ from coal G#5 502

Figure D.1 Isothermal small particle simulation studies using derived kinetic parameters. .521
Figure D.2 Repeatability curves obtained for coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH at 5 K/min. 522
Figure D.3 Particles from inertinite-rich coal before and after devolatilization at 350, 550, 600, 650 and 750℃. 523
Figure D.4 Particles from vitrinite-rich coal before and after devolatilization at 350, 550, 600, 650 and 750℃. 524

Figure D.5 Normalised devolatilization results for all four coals at 350℃. 525

Figure D.6 Normalised devolatilization results for all four coals at 450℃. 526

Figure D.7 Normalised devolatilization results for all four coals at 550℃. 527

Figure D.8 Normalised devolatilization results for all four coals at 600℃. 528

Figure D.9 Normalised devolatilization results for all four coals at 650℃. 529

Figure D.10 Normalised devolatilization results for all four coals at 750℃. 530

Figure D.11 Normalised devolatilization results for all four coals at 900℃. 531

Figure D.12 Simulated reaction rate curves for coal INY based on the first order model of a.) 3, b.) 4, c.) 5 and d.) 8 pseudo-components. 532

Figure D.13 Simulated reaction rate curves for coal TSH based on the first order model of a.) 3, b.) 4, c.) 5 and d.) 8 pseudo-components. 533

Figure D.14 Comparison between experimental and modelled TG curves for coal UMZ, assuming a-d.) 3 reactions and e-h.) 8 reactions. 534

Figure D.15 Comparison between experimental and modelled TG curves for coal G#5 assuming, a-d.) 3 reactions and e-h.) 8 reactions. 535

Figure D.16 Comparison between model predictions for coals UMZ and TSH using a.) thermal conductivity model (1) and b.) thermal conductivity model (2). 536

Figure D.17 Reproducibility profiles for a.) surface temperature and b.) core temperature determined from the devolatilization of all four coals at 450℃. 537

Figure D.18 Reproducibility profiles for a.) surface temperature and b.) core temperature determined from the devolatilization of all four coals at 750℃. 538

List of Tables

Table 2.1 Summary of some known industrial processes including devolatilization (Lee, 1996). 29
Table 2.2 Relative yields of condensable products (Macrae, 1943). 39
Table 2.3 Temperature regions in coal devolatilization (Adapted from Ladner, 1988). 44
Table 2.4 Product yields for low- and high temperature devolatilization. 44
Table 2.5 Compositional difference between products (Adapted from Ladner (1988)). 45

Table 3.1 Summary of methods for determining the kinetic parameters of the first order model. 80
Table 3.2 Summary of important correlations for thermophysical properties. 89
Table 3.3 Thermophysical constants used for the heat equation. 90
Table 3.4 Characteristic constants used for the mass transfer equation. 94
Table 3.5 Auxiliary equations used in the conservation of mass. 95

Table 4.1 Conventional characterisation analyses performed on the four coal samples. 110
Table 4.2 Methods used for chemical-and mineralogical analyses of the four coal samples. 111
Table 4.3 Chemical analyses of the four coals. 115
Table 4.4 Fischer tar results for the four coals. 117
Table 4.5 XRD (mineral analyses) results of all four coals. 118
Table 4.6 XRF (ash analyses-L.O.I. free basis) results on the ash of all four coals. 118
Table 4.7 Vitrinite reflectance distributions for each coal. 121
Table 4.8 Summary of maceral scan analyses. 124
Table 4.9 Summary from point count analyses. 124
Table 4.10 Organic (Maceral) composition of the four coals. 125
Table 4.11 Estimation of VM from maceral content (Borrego *et al.*, 2000). 127
Table 4.12 Volatile prediction parameters for the coals. 128
Table 4.13 Microlithotype composition of the four coals. 133
Table 4.14 Carbominerite- and minerite species as a % of total carbominerite and minerite. 134

Table 4.15 Mercury porosimetry results of the four coals. 136
Table 4.16 CO_2 adsorption results of the four coals. 137
Table 4.17 Nitrogen adsorption analysis results. 139
Table 4.18 Comparison between porosities determined from different techniques. 140
Table 4.19 FSI, Gieseler fluidity and dilatation results obtained for all four coals. 141

Table 5.1 Advanced characterisation analyses performed on the four coal samples. 152
Table 5.2 Summary of apparatus settings and parameters for carbon crystallite analyses. 157
Table 5.3 Proximate analysis comparison between raw- and demineralised coal samples. 164
Table 5.4 Summary of sub-sections of main spectral areas. 167
Table 5.5 Structural parameters from ^{13}C NMR for all four coals. 168
Table 5.6 NMR derived lattice parameters for the four coals. 170
Table 5.7 Summary of crystallite parameters of the four coals. 174
Table 5.8 Summary of additional crystallite parameters. 176
Table 5.9 Assignment of parallelogram sizes to HRTEM fringes (Roberts, 2012) 186
Table 5.10 Comparison between average molecular weight from different analytical methods. 189
Table 5.11 Summary of advanced characterisation results. 190

Table 6.1 Solvents and analytical compounds used. 198
Table 6.2 TCR experimental conditions. 205
Table 6.3 Analyses conducted on obtained devolatilization products. 208
Table 6.4 Experimental conditions used for gas chromatography. 209
Table 6.5 Experimental parameters for NMR analyses. 213
Table 6.6 Comparison between mercury intrusion and -submersion results. 217
Table 6.7 Effect of coal type on the product distribution during devolatilization at 450℃. 218
Table 6.8 Effect of temperature on the product distribution during devolatilization. 219
Table 6.9 Effect of particle size on the product distribution during devolatilization at 450℃. 221
Table 6.10 Molecular formulas for selected ion masses (Silverstein *et al.*, 2005) 223
Table 6.11 Mass composition of gas species evolved at both temperatures for 20 mm particles. 233

Table 6.12 Molar composition of gas species evolved at both temperatures for 20 mm particles. 233
Table 6.13 Summary of amount of gas species evolved at 450°C for both particle sizes. ..240
Table 6.14 Summary of amount of gas species evolved at 750°C for both particle sizes. ..240
Table 6.15 Boiling point distributions for the different tars based on crude oil fractions......244
Table 6.16 Boiling range distributions for commercial petrochemical products (adapted from Lee (2012a & b) and Villalanti *et al*. (2000)). 245
Table 6.17 GC-MS/FID results obtained for tars generated from 5 mm coal particles. 249
Table 6.18 GC-MS/FID results obtained for tars generated from 20 mm coal particles. 250
Table 6.19 Summary of SEC results obtained on different tars generated from 5 mm particles. 261
Table 6.20 ^{1}H NMR distribution of tars derived at two different temperatures from 5 mm coal particles. 267
Table 6.21 ^{13}C NMR distribution of tars derived at two different temperatures from 5 mm coal particles. 274
Table 6.22 Chemical properties of chars produced at 450°C and 750°C. 280
Table 6.23 Summary of char morphological results as obtained for the different chars......283
Table 6.24 Structural parameters from 13C NMR for chars generated from all four coals..292
Table 6.25 Summary of crystallite parameters for the different chars as derived from the XRD. 297
Table 6.26 Summary of additional crystallite parameters. 300
Table 6.27 Average structural properties as derived from HRTEM. 308

Table 7.1 Summary of Mettler-Toledo TGA/DSC STAR^e constraints and limitations. 338
Table 7.2 Overview of experimental conditions used for kinetic rate measurements. 341
Table 7.3 Experimental conditions. 342
Table 7.4 Summary of characteristic parameters derived from DTG results. 359
Table 7.5 Effect of experimental temperature on the ultimate volatile yield. 365
Table 7.6 Quality of fit or percentage deviation for the simulated rate curves^a. 369
Table 7.7 Kinetic parameters for coal INY obtained from 1st order model fitting on multiple heating rate data (5-40 K/min). 375
Table 7.8 Kinetic parameters for coal UMZ obtained from 1st order model fitting on multiple heating rate data (5-40 K/min). 376

Table 7.9 Kinetic parameters for coal G#5 obtained from 1st order model fitting on multiple heating rate data (5-40 K/min). 377
Table 7.10 Kinetic parameters for coal TSH obtained from 1st order model fitting on multiple heating rate data (5-40 K/min). 378
Table 7.11 Comparison of evaluated kinetic parameters with those reported in literature. .380
Table 7.12 Parametric equations used to relate $Tm_{1,calc}$ to coal rank and maceral content. 383
Table 7.13 Values determined according to Alonso *et al*. (2001) and Borrego *et al*. (2000). 384
Table 7.14 Summary of adjusted R^2 values obtained from the empirical model fitting analyses. 386
Table 7.15 Quality of fit or percentage deviation for the simulated rate curves 389
Table 7.16 Relative mean error for the simulated temperature profiles. 397

Table A.1 Chemical formulas and properties of XRD minerals. 427
Table A.2 Results obtained from vitrinite random reflectance conducted on all four coals. 428
Table A.3 Results obtained from maceral scan analyses conducted on all four coals. 428

Table C.1 Effect of particle size on the product distribution during devolatilization at 750℃. 438
Table C.2 Chemical compound distribution (wt.%) as measured by GC-MS and GC-FID on tars generated from the 5 mm particles. 471
Table C.3 Chemical compound distribution (wt.%) as measured by GC-MS and GC-FID on tars generated from the 20 mm particles. 475
Table C.4 Summary of SEC results obtained on different tars generated from 20 mm particles. 481
Table C.5 ^1H NMR distribution of tars derived at two different temperatures from 20 mm coal particles. 486
Table C.6 ^{13}C NMR distribution of tars derived at two different temperatures from 20 mm coal particles. 488
Table C.7 Chemical properties of chars produced at 450℃ and 750℃. 490

Table Q.1 Quick reference of coal properties. 545

List of Symbols

ROMAN SYMBOLS

Symbol	Description	Units
a	*Kinetic compensation constant*	-
b	*Kinetic compensation constant*	K^{-1}
B.L.	*Number of bridges and loops*	-
C	*Number of aromatic carbons per cluster*	-
C_A	*Acenaphthene type aliphatic carbons*	%
C_{Al}	*Aliphatic carbons*	%
C_{Ar}	*Aromatic carbons*	%
C_{Ar1}	*Aromatic carbons (C_{ar}-H ortho to C_{ar}-OH)*	%
C_{Ar2}	*Aromatic carbons (C_{ar}-H para to C_{ar}-OH, etc.)*	%
C_{Ar3}	*Aromatic carbons (C_{ar}-CH_3 para to C_{ar}-OH)*	%
C_{Ar4}	*Quaternary aromatic carbons; C_{ar}-H meta to C_{ar}-OH*	%
C_{Ar5}	*Aromatic carbons (C_{ar}-CH_3; CH_2 or CH para to C_{ar}-OH)*	%
C_{Ar6}	*Aromatic carbons (CH_2 or CH meta to C_{ar}-OH)*	%
C_{Ar7}	*Aromatic carbons (C_{ar}-OH)*	%
C_{ArP}	*Pericondensed aromatic- or protonated aromatic carbons*	%
C_{ArC}	*Catacondensed aromatic carbons*	%
C_{ave}	*Average number of carbon atoms*	-
C_F	*Fluorene type aliphatic carbons*	%
CH2	*Methylene (CH_2) and methine (CH) carbons α*	%
CH3	*Methyl carbons*	%
C_{max}	*Maximum number of carbon atoms*	-
C_{min}	*Minimum number of carbon atoms*	-
$C_{\alpha 2}$	*Methylene and methine carbons α to two aromatic rings*	%
$c_{p,a}$	*Mass specific heat capacity for water*	$J.kg^{-1}.K^{-1}$
$c_{p,s}$	*Mass specific heat capacity for coal*	$J.kg^{-1}.K^{-1}$
$c_{p,v}$	*Mass specific heat capacity for volatiles*	$J.kg^{-1}.K^{-1}$
d_{002}	*Interlayer spacing*	Å

ROMAN SYMBOLS (CONTINUED)

Symbol	Description	Units
d_p	*Diameter of coal particle*	m
d_{pore}	*Pore diameter*	Å
$D_{a\text{-}air}$	*Binary diffusion coefficient for water vapour and air*	$m^2.s^{-1}$
D_{ik}	*Knudsen diffusion of species i (a or v)*	$m^2.s^{-1}$
D_{eff}	*Effective diffusion coefficient*	$m^2.s^{-1}$
$D'_{eff,i}$	*Effective diffusion coefficient of i (a or v)*	$m^2.s^{-1}$
$D_{eff,i}$	*Effective diffusion coefficient of species i (a or v)*	$m^2.s^{-1}$
$D_{v\text{-}air}$	*Binary diffusion coefficient for volatiles and air*	$m^2.s^{-1}$
$D_{t\text{-}gv}$	*Binary diffusion coefficient for tar and volatile gas*	$m^2.s^{-1}$
DOI	*Degree of disorder index*	-
E_0	*Mean activation energy for DAEM*	$kJ.mol^{-1}$
E_a	*Activation energy*	$kJ.mol^{-1}$
$E_{a,a}$	*Activation energy of moisture evolution*	$kJ.mol^{-1}$
$E_{a,i}$	*Activation energy of component i*	$kJ.mol^{-1}$
E_I	*Exponential integral*	-
f_a	*Aromaticity/Fraction of aromatic carbon*	-
f_a'	*Corrected fraction of aromatics (excluding CO)*	-
f_a^B	*Fraction of bridgehead carbons*	-
f_a^{CO}	*Fraction of carbonyl/carboxyl functionalities*	-
f_a^H	*Fraction of protonated aromatic carbons*	-
f_a^N	*Fraction of non-protonated aromatic carbons*	-
f_a^P	*Fraction of phenolic functionalities*	-
f_a^S	*Fraction of alkylated aromatic carbons*	-
f_{al}	*Fraction of aliphatic carbons*	-
$f_{al}*$	*Fraction of non-protonated aliphatic carbons*	-
f_{al}^H	*Fraction of protonated aliphatic carbons*	-
f_{al}^O	*Fraction of oxygenated aliphatic carbons*	-
FC	*Fixed carbon*	wt.%
$F_{VM,i}$	*Amount of component i, w.r.t. ultimate volatile yield*	wt.%
h_{conv}	*External/convective heat transfer coefficient*	$W.m^{-2}.K^{-1}$
H_{Al}	*Aliphatic protons*	%

ROMAN SYMBOLS (CONTINUED)

Symbol	Description	Dimension
H_{Ar}	*Aromatic protons*	%
H_{ArUC}	*Aromatic hydrogen*	%
H_{ArC}	*Sterically hindered aromatic hydrogen*	%
$H_{A,F}$	*Acenaphthene and fluorine type protons*	%
H_D	*Diphenylmethane type protons*	%
H_O	*Olefinic protons*	%
$H_{\alpha 1}$	*Aliphatic protons methyl or methylene in α position*	%
$H_{\beta 1}$	*Aliphatic protons methyl or methylene in β position*	%
$H_{\beta 2}$	*Alicyclic protons methyl or methylene in γ position*	%
H_{γ}	*Aliphatic protons to two aromatics in β position*	%
ΔH_r	*Enthalpy/heat of reaction*	kJ.kg^{-1}
$\Delta H_{vap,a}$	*Enthalpy/heat of evaporation of water*	J.kg^{-1}
HV	*Heating value / Gross Calorific Value*	MJ/kg
HVF	*Heating Value Factor*	-
$I_{main\ peak}$	*Fractional amount of main peak associated to inertinite*	-
INR	*Non-reactive inertinite macerals (mineral matter free basis)*	vol.%
INT	*Inertinite content (mineral matter free basis)*	vol.%
k	*Rate constant*	s^{-1} or min^{-1}
K	*Constant depending on X-ray reflection plane*	-
$K_{\alpha 1}$	*X-ray radiation from cobalt due to* $K_{\alpha 1}$	counts
$K_{\alpha 2}$	*X-ray radiation from cobalt due to* $K_{\alpha 2}$	counts
k_0	*Pre-exponential constant*	s^{-1} or min^{-1}
$k_{0,a}$	*Pre-exponential constant of moisture evolution*	s^{-1}
$k_{0,i}$	*Pre-exponential constant of the* i^{th} *pseudo-component*	s^{-1}
k_g	*Heat/thermal conductivity of heating medium* (N_2)	W.m^{-1}.K^{-1}
K_p	*Permeability of coal*	m^2
k_s	*Solid effective heat/thermal conductivity*	W.m^{-1}.K^{-1}
L_a	*Crystallite diameter*	Å
L_c	*Crystallite height*	Å
$L_{main\ peak}$	*Fractional amount of main peak associated to liptinite*	-
LIP	*Liptinite content (mineral matter free basis)*	vol.%

ROMAN SYMBOLS (CONTINUED)

Symbol	Description	Dimension
m_0	*Initial sample mass*	mg
m_{ash}	*Ash mass*	mg
$m_{ash,raw}$	*Original ash mass value*	mg
$m_{ash,demin}$	*Demineralised coal ash mass value*	mg
m_f	*Final sample mass*	mg
m_t	*Logged mass at a certain time t*	mg
M_a	*Molecular weight of water*	g.mol^{-1}
M_{air}	*Molecular weight of air*	g.mol^{-1}
$MaxL$	*Maximum fringe length*	Å
m_{coal}	*Mass of coal*	mg or g
M_G	*Fraction of aromatic carbons with attached proton*	-
MR_i	*Maximum weight loss rate of peak i, in DTG curve*	min^{-1}
$MinL$	*Minimum fringe length*	Å
M_{gv}	*Molecular weight of devolatilization gas*	g.mol^{-1}
MI	*Maceral index*	-
M_n	*Number average molecular weight*	g.mol^{-1} or Da
m_p	*Mass of particle*	mg
M_p	*Molecular weight estimate from SEC*	g.mol^{-1} or Da
m_{pl}	*Mass of submerged plunger*	mg
m_{sb}	*Mass of submerged particle*	mg
M_t	*Molecular weight of tars*	g.mol^{-1}
M_v	*Average molecular weight of volatiles*	g.mol^{-1}
$M_{r,i}$	*Molecular weight of species, i*	g.mol^{-1}
$M_{w,p}$	*Weight average molecular weight*	g.mol^{-1}
Mw	*Molecular weight of fringe*	g.mol^{-1}
MW	*Average molecular weight of cluster*	g.mol^{-1}
M_δ	*Average molecular weight of side chain or half of bridge*	g.mol^{-1}
n	*Reaction order*	-
$\acute{n}_i$	*Mass flux of species, i*	kg.m^{-3}.s^{-1}
N_{ave}	*Average number of layers per carbon crystallite*	-
N_k	*Number of heating rates*	-

ROMAN SYMBOLS (CONTINUED)

Symbol	Description	Dimension
N_m	*Number of DTG experimental points*	
n_T	*Total molar flow of N_2 gas*	$mol.min^{-1}$
OBF	*Objective function*	-
p	*Pressure*	Pa
p_0	*Initial ambient pressure*	Pa
P_0	*Number of all possible bridges intact*	-
p_i	*Partial pressure of species i (a or v)*	Pa
$p_{v,t}$	*Total pressure of gas product mixture*	Pa
P_i	*Peak i, in DTG curve*	-
Pr	*Prandtl number*	-
QOF	*Quality of fit*	%
r	*Radial coordinate of coal particle*	m
R	*Molar gas constant*	$J.K^{-1}.mol^{-1}$
R_a	*Intrinsic rate of moisture evaporation*	$kg.m^{-3}.s^{-1}$
R_i	*Intrinsic rate of the evolution of species, i*	$kg.m^{-3}.s^{-1}$
Re	*Reynolds number*	-
RF	*Reactivity Factor*	-
RMI	*Reactive maceral index*	-
R_p	*Radius of coal particle*	m
R_r	*Mean random vitrinite reflectance*	%
R_v	*Intrinsic rate of volatile evolution*	$kg.m^{-3}.s^{-1}$
S_{002}	*Area under the d_{002} peak*	Intensity. Å
S_A	*Area under the amorphous peak*	Intensity. Å
S_G	*Area under the graphitic peak*	Intensity. Å
S_γ	*Area under the γ-band*	Intensity. Å
S.C.	*Number of side chains per cluster*	-
t	*Time*	s or min
t_∞	*Infinite time*	s or min
t_E	*Elution time during SEC analyses*	min
T	*Temperature*	℃ or K
T_f	*External temperature*	℃ or K

ROMAN SYMBOLS (CONTINUED)

Symbol	**Description**	**Dimension**
T_s	*Coal particle temperature*	°C or K
$T_{p,i}$	*Temperature of local maxima of peak i, in DTG curve*	°C or K
T_0	*Initial temperature*	°C or K
$T_{10\ wt.\%}$	*SIMDIST temperature at 10 wt.% mass recovery*	°C or K
$T_{30\ wt.\%}$	*SIMDIST temperature at 30 wt.% mass recovery*	°C or K
$T_{50\ wt.\%}$	*SIMDIST temperature at 50 wt.% mass recovery*	°C or K
$T_{70\ wt.\%}$	*SIMDIST temperature at 70 wt.% mass recovery*	°C or K
$T_{90\ wt.\%}$	*SIMDIST temperature at 90 wt.% mass recovery*	°C or K
$Tm_{1,calc}$	*Calculated temperature of maximum global reactivity*	°C or K
$Tm_{1,exp}$	*Experimental temperature of maximum global reactivity*	°C or K
$\Delta Tm_1 (I_{rmain\ peak})$	*Parametric term of temperature prediction*	°C or K
$\Delta Tm_1 (L_{rmain\ peak})$	*Parametric term of temperature prediction*	°C or K
$\Delta Tm_1(R_r)$	*Parametric term of temperature prediction*	°C or K
$\Delta Tm_1(R_r)$	*Parametric term of temperature prediction*	°C or K
u	*Darcy velocity field of gas mixture (volatiles, air and vapour)*	$m.s^{-1}$
v_0	*Initial particle volume*	m^3
v	*Coal particle volume*	m^3
v_g	*Superficial gas velocity of heating medium (N_2)*	$m.s^{-1}$
VIT	*Vitrinite content (mineral matter free basis)*	vol.%
VM	*Volatile matter*	wt.%
VM_j	*Volatile matter contribution of maceral, j*	wt.%
VM_{TGA}	*Ultimate volatile yield from TGA results*	wt.%
V_a^*	*Ultimate amount of moisture evolved*	- or %
V_i	*Volatile yield of pseudo-component, i at time t*	- or %
V_i^*	*Ultimate volatile yield of pseudo-component, i*	- or %
V_t^*	*Ultimate volatile yield*	- or %
V_t	*Volatile yield at time, t*	- or %
$V_{t,T}$	*Total product yield (moisture and volatiles) at time t and temperature T*	- or %

ROMAN SYMBOLS (CONTINUED)

Symbol	Description	Dimension
$V^*_{t,T}$	*Ultimate product yield (moisture and volatiles) at time t and temperature T*	- or %
$V_{t,v}^*$	*Ultimate total volatile yield*	- or %
WABP	*Weight average boiling point*	°C or K
X	*Fractional conversion*	-
X_a	*Fractional conversion of moisture evolution*	-
X_A	*Fraction amorphous carbon*	-
X_b	*Fractional conversion of peak b*	-
$X_{f,v}^*$	*Scaling factor/Final isothermal total conversion*	-
X_g	*Fractional conversion of the molecular phase*	-
X_i	*Fractional conversion of the* i^{th} *pseudo-component*	-
X_t	*Overall fractional conversion of volatiles*	-
X_v	*Fractional conversion of volatiles*	-
$X_{v,t}$	*Fractional conversion of volatiles at time, t*	-
$X'_{v,t}$	*Re-scaled/normalised fractional conversion of volatiles at time, t*	-
Y_j	*Content of maceral, j in the coal*	vol.%
Y_m	*Content of residual macerals in the coal*	vol.%

GREEK SYMBOLS

Symbol	Description	Units
α	*Kinetic compensation constant*	mol.kJ^{-1}
α_{iI}	*Rank dependent fractional contribution of inertinite*	-
α_{iL}	*Rank dependent fractional contribution of liptinite*	-
α_{iV}	*Rank dependent fractional contribution of vitrinite*	-
β	*Heating rate*	°C.min^{-1}/K.min^{-1}
β_{002}	*Full width at half maximum of the* d_{002} *peak*	degrees (°)
β_{100}	*Full width at half maximum of the (10) peak*	degrees (°)

GREEK SYMBOLS (CONTINUED)

Symbol	Description	Units
χ_b	*Mole fraction of aromatic bridgehead carbons*	-
δ	*Kinetic compensation constant*	-
ε	*Coal porosity at time, t*	- or %
$\varepsilon_{L,gv}$	*Characteristic energy of interaction of gas molecules*	ergs
$\varepsilon_{L,t}$	*Characteristic energy of interaction of tar molecules*	ergs
$\varepsilon_{L,air}$	*Characteristic energy of interaction of air molecules*	ergs
$\varepsilon_{L,gt}$	*Characteristic energy of interaction of gas-tar mixture*	ergs
$\varepsilon_{L,v-air}$	*Characteristic energy of interaction of volatile-air mixture*	ergs
ε_{rad}	*Effective emissivity*	-
$\varepsilon_{rad,s}$	*Emissivity of coal particle*	-
$\varepsilon_{rad,t}$	*Emissivity of TGA tube*	-
ϕ_j	*Fractional volatile matter content of maceral, j*	-
ϕ_m	*Fractional volatile matter content of residual macerals*	-
γ	*Gamma band*	-
$\eta_{dem.}$	*Effectiveness of demineralization*	%
κ	*Boltzmann constant*	ergs.K^{-1}
λ	*Wavelength of incident X-ray*	Å
μ_a	*Viscosity of water vapour*	Pa.s
μ_g	*Viscosity of heating medium (N_2)*	Pa.s
μ_v	*Viscosity of volatiles*	Pa.s
μ_m	*Viscosity of gas product mixture (volatiles, vapour and air)*	Pa.s
π	*Pi*	-
θ	*Peak position/XRD angle of scan*	degrees (°)
θ_{002}	*Peak position of d_{002} peak*	degrees (°)
θ_{10}	*Peak position of (10) peak*	degrees (°)
θ_{11}	*Peak position of (11) peak*	degrees (°)
ρ_a	*Density of water*	kg.m^{-3}
ρ_{air}	*Density of air*	kg.m^{-3}
ρ_{avg}	*Average particle density from mercury submersion*	kg.m^{-3}

GREEK SYMBOLS (CONTINUED)

Symbol	Description	Units
$\rho_{f,Hg}$	*Density of mercury*	$kg.m^{-3}$
ρ_{coal}	*Distribution of coal particle density*	$kg.m^{-3}$
ρ_i	*Density for species, i*	$kg.m^{-3}$
$\rho_{i,0}$	*Initial density of species, i*	$kg.m^{-3}$
ρ_p	*Particle density from mercury submersion*	$kg.m^{-3}$
$\rho_{s,0}$	*Initial coal particle density*	$kg.m^{-3}$
ρ_s	*Coal particle density at time, t*	$kg.m^{-3}$
$\rho_{s,k}$	*Skeletal density*	$kg.m^{-3}$
ρ_g	*Density of heating medium (N_2)*	$kg.m^{-3}$
ρ_v	*Density of released volatiles*	$kg.m^{-3}$
$\rho_{v,t}$	*Density of total gas product mixture*	$kg.m^{-3}$
σ	*Standard deviation of DAEM distribution*	$kJ.mol^{-1}$
$\sigma+1$	*Number of attachments per cluster*	-
σ_{air}	*Collision diameter of air*	Å
σ_b	*Stefan-Boltzmann constant*	$W.m^{-2}.K^{-4}$
σ_{gv}	*Collision diameter of gaseous volatiles*	Å
σ_{gt}	*Collision diameter of gas-tar mixture*	Å
σ_t	*Collision diameter of tar*	Å
σ_v	*Collision diameter of volatiles*	Å
σ_{vair}	*Collision diameter of volatile-air mixture*	Å
τ	*Tortuosity*	-
ξ_a	*Fractional contribution of moisture to the total volatiles*	-
ξ_b	*Fractional contribution of peak b to the total volatiles*	-
ξ_g	*Fractional contribution of peak g to the total volatiles*	-
ξ_i	*Fractional contribution of component i, to the total volatiles*	-
ξ_i^*	*Moisture fraction free, fractional contribution of component i, to the total volatiles*	-
ζ_j	*Percentage contribution of maceral, j*	%
$\Omega_{D,i}$	*Mass transfer collision integral for species, i*	-

GREEK SYMBOLS (CONTINUED)

Symbol	Description	Units
$\Omega_{D,j}$	*Mass transfer collision integral for species, j*	-
$\Omega_{D,i,j}$	*Mass transfer collision integral for specie mixture, i-j*	-
$\Omega_{D,gt}$	*Mass transfer collision integral for tar-gas mixture*	-
$\Omega_{D,vair}$	*Mass transfer collision integral for volatile-air mixture*	-
Ω_v	*Collision integral*	-
$\Omega_{v,i}$	*Collision integral for species, i*	-
$\Omega_{v,g}$	*Collision integral for devolatilization gas*	-
$\Omega_{v,t}$	*Collision integral for tars*	-

ABBREVIATIONS:

ACT : Advanced coal technology
a.d.b : Air dry basis
a.f.b : Ash free basis
AFROX : African Oxygen
ALG : Alginite
ASTM : American Society for Testing Materials
BD : Block decay
BET : Brunauer-Emmett-Teller
BJH : Barret-Joyner-Halenda
BTX : Benzene, toluene and xylene
calc : Calculated
CCSEM : Computer controlled scanning electron microscopy
CM1 : Conductivity model 1
CM2 : Conductivity model 2
CPD : Chemical percolation devolatilization model
CP-MAS : Cross-polarization with magic-angle-spinning
CRMP : CO_2 reforming methane process conditions
CSA : Chemical shielding anisotropy

ABBREVIATIONS (CONTINUED):

C.V. : Calorific value
d.a.f. : Dry, ash free basis
d.b : Dry basis
DAEM : Distributed activation energy model
DAN : Dialkyl substituted naphthalene
DSC : Differential Scanning Calorimetry
DD : Dipolar dephasing
DEPT : Distortionless enhancement by polarization
DOE : Department of Energy
D-R : Dubinin-Radushkevich
DTG : Differential thermogravimetric/thermogravimetry
DTI : Department of trade and industry
EIA : Energy Information Administration
exp : Experimental
FFT : Fast Fourier Transform
FG-DVC : Functional Group-Depolymerisation Vaporization Cross linking
FID : Flame ionization detection/detector (for GC work)
FID : Free induction decay (for NMR work)
FIMS : Field ionization mass spectrometry
F/SEC : Fusinite/Secretinite
FSI : Free swelling index
FTIR : Fourier transform infrared spectroscopy
FWHM : Full width at half maximum
G#5 : Abbreviation used for coal obtained from Witbank seam 5
GC : Gas chromatography
HMB : Hexamethylbenzene
HPLC : High performance liquid chromatography
HRTEM : High resolution transmission electron microscopy
I INT : Inert Inertodetrinite
INY : Abbreviation used for coal obtained from Witbank seam 2
ISF : Inert semifusinite
ISO : International Standards Organization

ABBREVIATIONS (CONTINUED):

LCPs	:	Liquid crystalline polymers
LOIF	:	Loss of ignition free basis
LPTGA	:	Large Particle Thermogravimetric Analysis/Analyzer
MALDI-TOF	:	Matrix assisted laser-desorption ionization, time-of flight
MI	:	Maceral Index
MIC	:	Micrinite
MS	:	Mass spectrometry
MSCs	:	Molecular sieving carbons
MSD	:	Mass selective detector
MPRM	:	Multiple, parallel reaction model
MSRM	:	Multiple, stage reaction model
m.m.b.	:	Mineral matter basis
m.m.f.b	:	Mineral matter free basis
MUMPS	:	Multifrontal Massively Parallel Sparse
NMP	:	N-methyl-2-pyrrolidinone
NMR	:	Nuclear magnetic resonance spectroscopy
ODE	:	Ordinary differential equation
PAHs	:	Polycyclic aromatic hydrocarbons
PBN	:	Poly(butylene terephtalate)
PDE	:	Partial differential equation
PEN	:	Poly(ethylene naphthalate)
PONA	:	Paraffins, olefins, napththenes and aromatics
Prox	:	Proximate
PTFE	:	Polytetrafluorethylene
PV	:	Pseudo-vitrinite
Py-GC-MS	:	Pyrolysis- gas chromatography-mass spectrometry
Py-MS	:	Pyrolysis- mass spectrometry
R&D	:	Research and Development
RID	:	Refractive index detection/detector
R INT	:	Reactive Inertodetrinite
ROM	:	Run of mine
RSF	:	Reactive semifusinite

ABBREVIATIONS (CONTINUED):

SABS	:	South African Bureau of Standards
SANS	:	South African National Standard
SEC	:	Size exclusion chromatography
S.e.c.s.	:	Sequential elution solvent chromatography
SIMDIST	:	Simulated distillation
SPE	:	Single pulse excitation
S/R/C	:	Sporinite/Resinite/Cutinite
SRM	:	Single reaction model
SSB	:	Spinning sideband
sym-OHAn	:	*sym*-octahydroanthracene
sym-OHP	:	*sym*-octahydrophenanthrene
TBE	:	Tetrabromo-ethane
TCD	:	Thermal conductivity detection/detector
TCR	:	Tar capturing reactor
TG	:	Thermogravimetric/thermogravimetry
TGA	:	Thermogravimetric Analyzer
THF	:	Tetrahydrofuran
TI	:	Total inertinite
TIC	:	Total ion chromatogram
TKS	:	Tetrakis(trimethylsilyl)silane
TL	:	Total liptinite
TMS	:	Tetramethylsilane
TSH	:	Abbreviation used for coal obtained from the Venda-Pafuri district
TV	:	Total vitrinite
UHP	:	Ultra high purity
Ult	:	Ultimate
UMZ	:	Abbreviation used for coal obtained from Witbank seam 4
USB	:	Universal serial bus
UV	:	Ultra violet
VIS	:	Visible light detector
VIT	:	Vitrinite
vol.%	:	Volume percentage

ABBREVIATIONS (CONTINUED):

WCI	:	World Coal Institute
wt.%	:	Weight percentage
XRD	:	X-Ray Diffraction
XRF	:	X-Ray Fluorescence
XPS	:	X-ray photoelectron spectroscopy

Glossary

"Advanced analyses" refers to more advanced analytical strategies applied for assessing the molecular properties of coal and coal-derived products and includes analyses such as: GC-FID, GC-MS, NMR, HRTEM, XRD, MALDI-TOF MS, SEC, etc.

"Conventional analyses" refers to standard analytical techniques applied in the coal research domain and includes methods such as: proximate-, ultimate-, calorific value-, petrographic-, mercury porosimetry analyses, etc.

"Core temperature" refers to the temperature measured at the centre of the coal particle.

"Devolatilization" refers to the process of tar, water and gas evolution, including char production, via the thermal degradation of coal under an inert atmosphere. This process is also more commonly referred to as pyrolysis.

"G#5" refers to the abbreviation used for the vitrinite-rich coal sample obtained from seam 5 of the Witbank coalfields.

"INY" refers to the abbreviation used for the inertinite-rich coal sample obtained from seam 2 of the Witbank coalfields.

"Loss free basis" refers to the normalisation of product yields by taking into account any loss in product material that could have occurred during product separation, removal and/or measurement.

"Molecular properties" refers to characteristic properties describing the molecular structure of coal and includes properties such as aromaticity, molecular mass distribution, fraction of amorphous carbon.

“Non-fuel use of coal” refers to the exclusive usage of coal for other applications than electricity generation and the production of fuels. This includes application of coal for the production of aromatic chemicals and/or higher value carbons such as graphites.

“Pseudo-component” refers to a group of chemical entities displaying similar reaction behaviour and can be described by a lumped average of kinetic parameters.

“Pseudo-isothermal conditions” refers to devolatilization of coal particles under isothermal reactor conditions i.e.: introduction of coal particles into the reactor or TG which is controlled at an isothermal set point.

“Thermophysical properties” refers to coal specific properties related to heat transfer parameters such as the thermal conduction and heat capacity of a coal.

“Thermoplasticity or thermoplastic nature” refers to the swelling and/or -shrinkage behaviour of coal.

“TSH” refers to the abbreviation used for the vitrinite-rich coal sample obtained from seam 1and 2 of the Venda-Pafuri coalfields.

“UMZ” refers to the abbreviation used for the inertinite-rich coal sample obtained from seam 4 of the Witbank coalfields.