

**The fate of sulphur during pyrolysis and steam gasification of
high-sulphur South Australian low-rank coals**

Samuel James Button

Thesis submitted for the degree of
Doctorate of Philosophy

School of Chemical Engineering
The University of Adelaide
February 2010

DECLARATION

This work contains no material which has been accepted for the award of any other degree or diploma in any university or any other tertiary institution, and to the best of my knowledge and belief, contains no material previously published or written by any other person, except where due reference has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being made available for photocopying and loan.

SIGNED :

DATE :

ABSTRACT

Australia's economy is underpinned by access to cheap electricity, and over 85% of the country's power generation capacity is based on pulverised coal combustion. South Australia has abundant resources of low-rank coal but its high sulphur content (typically 5% w/w db) raises both operational and environmental concerns in its utilisation. Depletion of current sub-bituminous coal reserves used for power generation means that competitive future coal-based energy supply may depend on efficient, cost-effective and environmentally-friendly utilisation of local lignite resources. Other unique properties such as high moisture, ash, sodium and chlorine content currently limit their utilisation and the study of their behaviour during fluidised-bed gasification (FBG) processes has been the focus of research by the Cooperative Research Centre (CRC) for Clean Power from Lignite.

Sulphur containing compounds in coal transform to sulphur dioxide (SO_2) in an oxidising atmosphere and hydrogen sulphide (H_2S) in a reducing atmosphere. The phenomenology of these transformations is detailed in the literature under a variety of conditions (pyrolysis, oxidation and reduction) but quantitative data for specific gasification processes is lacking. These gaseous sulphur compounds are precursors to acid rain on release to the atmosphere and cause corrosion in downstream processing units, requiring the need for effective desulphurisation strategies. Understanding the conversion of coal-bound sulphur to gas phase sulphur will enable the development of such strategies in order to comply with ever increasing emissions control.

The main objective of this study was to examine the extent of conversion and re-distribution of sulphur during the pyrolysis and gasification of two coals from South Australia: Lochiel and Bowmans. Both of these coals show similar proximate and ultimate analyses, and both contain significant quantities of sulphur, mainly in organic form. To this end, an experimental programme was designed to enable the accurate determination of the gas phase products of pyrolysis and gasification – on a continuous

basis as they formed throughout the processes – and determine the impact of varying key parameters such as final pyrolysis temperature, heating rate and gasification temperature.

Temperature Programmed Pyrolysis experiments (heating samples from ambient to 1200°C at 15 K.min⁻¹) employing Lochiel and Bowmans coal were employed with continuous gas phase measurement of product gases. This enabled the determination of carbon and sulphur mass balances, along with the correlation of temperature with the source of particular sulphur (and other) products, and hence original sulphur species in the coal. Over 85% of the gas phase sulphur species were detected as hydrogen sulphide (H₂S) with methyl mercaptan (CH₃SH) and carbonyl sulphide (COS) comprising the balance. For the acid-washed Lochiel and air-dried Bowmans samples, sulphur dioxide (SO₂) was also detected. The absolute sulphur conversion to the gas phase was, however, only 30-40% across the two coals and with acid-treatment. Sulphur conversion for small particle (less than 0.5mm particle diameter) acid-washed Lochiel coal was in excess of 41%, and the presence of calcium and sodium led to significant retention of sulphur in the ash phase post pyrolysis.

Fixed-bed, fast pyrolysis experiments were also undertaken to elucidate the effect of final temperature (700°C, 800°C, 900°C, 1000°C) on the extent of pyrolysis and the distribution of products. Final sulphur conversion did not increase with increasing final temperature with a complex re-attachment mechanism whereby evolved sulphur re-acts with the organic carbon matrix and inorganic species in the ash being the cause of this behaviour. Not only did the faster heating rates impact on the distribution of sulphur via an increase in conversion as H₂S and no SO₂ in the product gas, the effect on carbon conversion and distribution of carbon between CO and CO₂ was significant. In fluidised-bed pyrolysis experiments, the total sulphur and carbon conversion increased markedly relative to the fixed-bed heating rate processes, with a greater distribution of sulphur among CH₃SH and COS (at the expense of H₂S) and carbon among CO₂ and methane.

Steam gasification experiments were carried out on small quantities of char in the fixed-bed apparatus (25% v/v steam in nitrogen), enabling the determination of a relationship between sulphur and carbon conversion. Contrary to the assumption in the literature that sulphur and carbon convert in equal and direct proportion, sulphur conversion was found to lag carbon conversion by up to 60% for both coals and at gasification temperatures of 800°C and 850°C. At 750°C, however, Lochiel and Bowmans coal did not exhibit similar behaviour. Acid washing was found to have a dramatic effect on the char's reactivity, and in particular, on sulphur conversion up to around 20% carbon conversion.

Steam gasification experiments in the fluidised-bed, however, achieved a much slower gasification rate for the equivalent conditions of steam concentration and temperature. While the pyrolysis in the fluidised-bed was comparatively violent compared to the fixed-bed pyrolysis used to develop char for the experiments described above (Chapter 6), it was believed that such an environment led to a loss of both catalyst precursors from the char (largely sodium chloride, NaCl) and carboxyl groups to which those precursors organically bind in order to achieve their catalytic activity.

The implication of this work for industrial processes may be significant: it would appear that in order to achieve sufficient char reactivity during gasification, the creation of that char must be carried out at relatively mild conditions (of final temperature and heating rate).

The results from this suite of pyrolysis and gasification experiments provide a fundamental gas phase knowledge base on which further work can be carried out, and recommendations for the next steps along the commercialisation pathway for the effective utilisation of these coals is presented.

ACKNOWLEDGEMENTS

I gratefully acknowledge the financial and other support received for this research from the Cooperative Research Centre (CRC) for Clean Power from Lignite, which is established and supported under the Australian Government's Cooperative Research Centres program.

I am particularly grateful for the support and advice of my supervisor, Associate Professor Peter Ashman, especially these last few years in patiently seeing this thesis completed. Associate Professor Peter Mullinger, and the late Dr Peter Jackson, provided much appreciated advice during its early stages, and for that I am thankful.

I am indebted also to Dr Adam Kosminski for his support, on both a technical and personal level, and for our many creative and wide ranging discussions on matters PhD and other. Dr Davide Ross, and the staff of the Chemical Engineering workshop, Jason Peak, Peter Kay and Brian Mulcahy, provided help in all things experimental so to them I extend my greatest appreciation, along with Mary Barrow, Elaine Minerds, Terry Whitworth and Jennifer Critchley for their work in making my admin burden always light. To the other post-graduate students, especially those in A305 - David, Michael, Tim, and Dijan, and those in the Pillbox - Daniel and David Ey in particular – thank you for your advice, assistance and friendships over the years.

To my parents and siblings, you've always given unwavering support to me in all my endeavours, so it's from my heart that I say thank you. And to Emma: without you I wouldn't have begun what has turned out to be an excellent adventure. In you, and Ambrose, Veronica and Laurence who have joined us along the way, I've found a source of love, consolation and happiness which I can scarcely describe, let alone go anyway to fully appreciating with this acknowledgement.

Finally - most importantly - *Deo Gratias*.

TABLE OF CONTENTS

ABSTRACT.....	III
ACKNOWLEDGEMENTS	VII
TABLE OF CONTENTS	IX
LIST OF TABLES.....	XIII
LIST OF FIGURES	XV
1 INTRODUCTION.....	1
1.1 WHY SOUTH AUSTRALIAN BROWN COAL?.....	1
1.2 SCOPE AND STRUCTURE OF THIS WORK.....	3
2 LITERATURE REVIEW	5
2.1 INTRODUCTION AND AIMS	5
2.2 COAL RESOURCES AND POWER GENERATION TECHNOLOGY	7
2.2.1 <i>South Australian coal resources are significant</i>	7
2.2.2 <i>Gasification is the technology of choice</i>	8
2.2.3 <i>Low-rank coals presents unique challenges</i>	10
2.3 THE SOURCE AND CHEMISTRY OF COAL SULPHUR	12
2.3.1 <i>The origin of sulphur in coal</i>	12
2.3.2 <i>Behaviour of coal sulphur</i>	15
2.3.3 <i>Gas phase sulphur chemistry</i>	23
2.3.4 <i>Factors affecting sulphur redistribution</i>	27
2.4 ANALYTICAL AND EXPERIMENTAL METHODS.....	38
2.4.1 <i>Feedstock and product analysis</i>	39
2.4.2 <i>Determining experimental conditions</i>	43
2.5 PREVIOUS WORK ON SA LIGNITE.....	55
2.5.1 <i>Behaviour of sulphur</i>	55
2.5.2 <i>Ash agglomeration and deposition in fluidised-bed gasification</i>	66
2.5.3 <i>Kinetic modelling of sulphur and gasification</i>	69
2.6 LITERATURE EVALUATION	77
3 EXPERIMENTAL WORK	81
3.1 INTRODUCTION AND OBJECTIVES.....	81
3.2 COAL PREPARATION	82

3.3	ANALYTICAL METHODS FOR COAL AND CHAR	83
3.3.1	Wet Chemical Methods	83
3.3.2	X-Ray Diffraction (XRD) Analysis of Chars	83
3.4	EXPERIMENTAL EQUIPMENT	84
3.4.1	Fixed bed apparatus	84
3.4.2	Fixed-bed methodology.....	86
3.4.3	Fluidised-Bed.....	90
3.4.4	Gas analysis.....	94
3.4.5	Calibration.....	96
3.5	MASS BALANCE CALCULATION METHODOLOGY	99
4	TEMPERATURE PROGRAMMED PYROLYSIS.....	101
4.1	INTRODUCTION AND OBJECTIVES.....	101
4.2	CONCENTRATION PROFILES	102
4.3	CALCULATING EVOLVING RATE	103
4.4	EFFECT OF ACID-WASHING	107
4.4.1	Large particles (1-1.7mm)	107
4.4.1	Small particle (<0.5mm).....	112
4.5	COMPARING BOWMANS AND LOCHIEL.....	115
4.6	MINERAL MATTER CONSIDERATIONS	121
4.7	SUMMARY & CONCLUSIONS	123
5	FAST PYROLYSIS: FIXED BED.....	125
5.1	INTRODUCTION AND OBJECTIVES.....	125
5.2	CONCENTRATION DATA AND CONVERSION CALCULATION	126
5.3	SULPHUR CONVERSION WITH COAL TYPE AND TREATMENT.....	127
5.4	CARBON CONVERSION WITH COAL TYPE AND TREATMENT.....	133
5.5	THE PRESENCE OF SULPHUR DIOXIDE	137
5.6	TAR PHASE SULPHUR.....	140
5.7	RATIO OF SULPHUR TO CARBON CONVERSION	143
5.8	MINERAL MATTER CONSIDERATIONS	147
5.9	SUMMARY AND CONCLUSIONS	149
6	FIXED-BED STEAM GASIFICATION	151
6.1	INTRODUCTION AND OBJECTIVES.....	151
6.2	EXPERIMENTAL JUSTIFICATION	152
6.3	CONVERSION OF CARBON AND SULPHUR.....	153

6.3.1	<i>Calculation methodology</i>	154
6.3.2	<i>Conversion versus time calculation</i>	154
6.3.3	<i>Summary of results for conversion versus time</i>	161
6.4	CORRELATING SULPHUR TO CARBON CONVERSION	164
6.5	KINETIC MODELLING	170
6.5.1	<i>Background</i>	170
6.5.2	<i>Carbon kinetics</i>	172
6.5.3	<i>Comparison to literature</i>	176
6.6	SUMMARY & CONCLUSIONS	178
7	ATMOSPHERIC PRESSURE FLUIDISED-BED PYROLYSIS & GASIFICATION	181
7.1	INTRODUCTION AND OBJECTIVES.....	181
7.2	FLUIDISED-BED PYROLYSIS	182
7.2.1	<i>Air-dried Lochiel pyrolysis in nitrogen</i>	182
7.2.2	<i>Air-dried Bowmans pyrolysis in nitrogen</i>	189
7.2.3	<i>Comparing Lochiel and Bowmans</i>	194
7.2.4	<i>Effect of atmosphere during fluidised-bed pyrolysis</i>	196
7.3	FLUIDISED-BED STEAM GASIFICATION.....	199
7.4	SUMMARY & CONCLUSIONS	214
8	CONCLUSIONS & RECOMMENDATIONS.....	217
8.1	PYROLYSIS PRODUCTS.....	217
8.2	STEAM GASIFICATION	219
8.3	MINERAL MATTER CONSIDERATIONS	220
8.4	IMPLICATIONS AND RECOMMENDATIONS	221
9	REFERENCES	223
	APPENDIX A – UNCERTAINTY ANALYSIS	239
A1	GAS ANALYSIS	239
A2	CALCULATION OF CONVERSION	241
A3	TRAPEZOIDAL INTEGRATION METHOD.....	242
A4	TEMPERATURE PROGRAMMED PYROLYSIS (TPP)	243
A5	FAST PYROLYSIS	245
A6	STEAM GASIFICATION EXPERIMENTS.....	249
A7	SUMMARY AND CONCLUSIONS.....	249

LIST OF TABLES

Table 2-1	Analyses of raw Bowmans and Lochiel coal as per the work of Telfer (1999).....	14
Table 2-2	Comparison of thermal decomposition temperature and volatility of sulphate compounds (Medvedev and Petropolskaya, 1966).....	19
Table 2-3	Comparison of the sulphur retention for TPP of Bowmans lignite @ 900°C for various combinations of water/acid washing and ion exchange (Telfer, 1999).....	31
Table 2-4	Decomposition ranges for organic sulphur groups in coal.....	41
Table 2-5	Kinetic parameters for hydrodesulphurisation reactions (Yergey <i>et al.</i> 1974).....	72
Table 3-1	Analysis of Lochiel (LL) and Bowmans (BW) coal.....	84
Table 3-2	Micro-GC calibration data.....	97
Table 4-1	Elemental ash analysis of Lochiel, Bowmans and Acid-washed Lochiel coals (air-dried) used in TPP experiments.....	121
Table 4-2	XRD analysis of TPP residues for air-dried Lochiel (AD), acid-washed Lochiel (AW) and air-dried Bowmans (BW) coal.....	122
Table 5-1	Raw product concentration from fast pyrolysis of air-dried Lochiel coal at 800°C, along with normalised concentration.....	126
Table 5-2	Char properties for air-dried (AD) and acid washed (AW) Lochiel along with air-dried Bowmans (BW) chars created in the HTF at 800°C and with 5 minute holding time.....	140
Table 5-3	XRD analyses for air-dried (AD) and acid-washed (AW) Lochiel chars, along with air-dried Bowmans (BW) char, resulting from fixed bed pyrolysis under conditions of fast heating rate at 800°C final pyrolysis temperature.....	147
Table 6-1	Char properties for air-dried (AD) and acid-washed (AW) Lochiel along with air-dried Bowmans (BW) chars created in the HTF at 800°C and with 5 minute holding time.....	152
Table 6-2	XRD analysis of char for air-dried (AD) and acid-washed (AW) Lochiel along with air-dried Bowmans (BW) chars created in the HTF at 800°C and with 5 minute holding time.....	153

Table 6-3	Summary of results for conversion versus time relationships for steam gasification of chars created at 750°C from air-dried (AD) and acid-washed (AW) Lochiel, along with Bowmans (BW) coals.	161
Table 6-4	Summary of results for conversion versus time relationships for steam gasification of chars created at 800°C from air-dried (AD) and acid-washed (AW) Lochiel, along with Bowmans (BW) coals.	161
Table 6-5	Summary of results for conversion versus time relationships for steam gasification of chars created at 850°C from air-dried (AD) and acid-washed (AW) Lochiel, along with Bowmans (BW) coals.	161
Table 6-6	XRD analysis of 800°C steam gasification residue for Lochiel and Bowmans char.	162
Table 6-7	Homogeneous model comparison between reaction rate coefficient for carbon kinetics, k (min^{-1}), induction time t_0 and char type/reaction temperature.	175
Table 6-8	Comparison of activation energies (kJmol^{-1}) and pre-exponential factors (min^{-1}) for the homogeneous model.	176
Table 6-9	Activation energies (kJmol^{-1}) as evaluated by Kosminski (2001) for low mineral Lochiel coal impregnated with sodium, silica and kaolin.	177
Table 7-1	Absolute sulphur conversion to gas phase during fluidised-bed pyrolysis of air-dried Lochiel and Bowmans coals.	195
Table 7-2	Absolute carbon conversion to gas phase during fluidised-bed pyrolysis of air-dried Lochiel and Bowmans coals.	195
Table 7-3	Absolute carbon conversion to gas phase during fluidised-bed pyrolysis of air-dried Lochiel and Bowmans coals, as 'other' species.	195
Table 7-4	XRD analysis of bed material removed from the gasification of air-dried Lochiel and Bowmans coal at 800°C after 10 minutes of pyrolysis in either nitrogen (N_2 pyrolysis) or 25% v/v steam in nitrogen (N_2/Steam).	209
Table 7-5	Mass balance for each experimental method.	210
Table 7-6	Total % of original ash components removed from the reaction zone.	211
Table 7-7	Total % of original ash components removed as fines from the ash can.	211

LIST OF FIGURES

Figure 2-1	Map of South Australia showing coal deposits (PIRSA, 2009).....	8
Figure 2-2	Retention of various sulphur forms in the char during TPP of raw Bowmans and raw Lochiel coals (Telfer, 1999).	56
Figure 2-3	Comparison of the retention of total sulphur in the char during TPP of Bowmans coal after various treatments (Telfer, 1999).	58
Figure 2-4	Comparison of the sulphur forms remaining in the char during 5 minutes of fixed-bed pyrolysis at 700°C (i) and 900 °C (ii) for Bowmans and Lochiel lignite (Telfer, 1999).	61
Figure 2-5	Retention of various sulphur forms during two minutes of fluidised-bed pyrolysis at 800°C. Comparison between 6 mm, 8 mm and 10 mm pellets of Bowmans coal (Telfer, 1999).	62
Figure 2-6	Comparisons of the distribution of sulphur in (a) unpyrolysed and (b) pyrolysed raw Bowmans coal for concentrations ranges (i) 1.50 - 33.41 wt%, (ii) 4.0 - 33.41 wt% and (iii) 5.0 - 33.41 wt% (Telfer, 1999) Sulphur appears as dark grey in these images.	64
Figure 2-7	Coal desulphurisation scheme incorporating the H ₂ S uptake reaction (Sugawara <i>et al.</i> , 1994b)	73
Figure 3-1	Schematic diagram of the Horizontal Tube Furnace (HTF), configured for Temperature Programmed Pyrolysis (TPP).	86
Figure 3-2	Schematic diagram of the Horizontal Tube Furnace (HTF), configured for gasification in steam.....	87
Figure 3-3	Schematic diagram of the Perma Pure dryer gas conditioning system for steam gasification.....	90
Figure 3-4	Schematic diagram of the 50mm atmospheric-pressure fluidised-bed gasifier system.....	91
Figure 3-5	Schematic diagram of the reaction vessel, showing location of thermocouples.	92
Figure 3-6	Schematic diagram of the gas conditioning and sampling system.....	93
Figure 3-7	Micro-GC instrument method settings panel	95
Figure 3-8	Micro-GC instrument configuration panel.....	96

Figure 3-9	Chromatograms obtained for calibration data using hydrocarbon mix in nitrogen, for channel 1 (top) and channel 2 (bottom). Note the presence of nitrogen as the large peak at 0.282 minutes and the presence of moisture at 0.432 on channel 1.	98
Figure 3-10	Chromatogram obtained for calibration of H ₂ S (1% v/v) in nitrogen. Note the presence of nitrogen as the large peak at 0.282 minutes and the presence of moisture at 0.432.....	98
Figure 3-11	Chromatograms obtained for calibration of COS (1.5% v/v) in nitrogen. Note the presence of nitrogen as the large peak at 0.282 minutes, the presence of moisture at 0.432.....	99
Figure 4-1	Sulphur species concentration in the product gas (%v/v) of air-dried Lochiel coal TPP at 15Kmin ⁻¹	102
Figure 4-2	Sulphur gas phase evolving rate for individual sulphur species as a product of air-dried Lochiel TPP, along with cumulative coal sulphur conversion to the gas phase (secondary y-axis).	104
Figure 4-3	Evolving rate of sulphur species as a function of temperature for Lochiel and acid washed Lochiel coals.	108
Figure 4-4	Evolving rate of sulphur species as a function of temperature for acid washed Lochiel and acid washed Lochiel less than 0.5mm particles	114
Figure 4-5	Evolving rate of sulphur species as a function of temperature for Lochiel, acid washed Lochiel, acid washed Lochiel less than 0.5mm particles and Bowmans coals.....	116
Figure 4-6	Total conversion of sulphur to the gas phase for air dried (AD), acid washed (AW), AW particles less than 0.5mm (AW<0.5) TPP for Lochiel coal, compared to Bowmans (BW) coal.	120
Figure 4-7	Cumulative conversion of sulphur to the gas phase for air dried (AD), acid-washed (AW), AW particles less than 0.5mm (AW<0.5) TPP for Lochiel coal, compared to Bowmans (BW) coal.	120
Figure 5-1	Gas phase conversion of sulphur for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures ranging from 700-1000°C.	127
Figure 5-2	Gas phase conversion of sulphur as H ₂ S for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures ranging from 700-1000°C.	128
Figure 5-3	Gas phase conversion of sulphur as COS for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along	

	with air-dried Bowmans coal for pyrolysis at temperatures ranging from 700-1000°C.	129
Figure 5-4	Gas phase conversion of sulphur as CH ₃ SH for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures ranging from 700-1000°C.	130
Figure 5-5	Gas phase conversion of carbon for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures from 700-1000°C.	133
Figure 5-6	Gas phase conversion of carbon as CO ₂ for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures from 700-1000°C.	134
Figure 5-7	Gas phase conversion of carbon as CO for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures ranging from 700-1000°C.	135
Figure 5-8	Gas phase carbon conversion ratio – the ratio of carbon conversion as CO (%) to carbon conversion as CO ₂ (%) for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for fast pyrolysis at temperatures ranging from 700-1000°C (FAST) and TPP.	136
Figure 5-9	Sulphur distribution for air-dried (AD), acid-washed (AW) Lochiel coal and air-dried Bowmans coal fast heating rate pyrolysis at 800°C.	141
Figure 5-10	Carbon distribution for air-dried (AD), acid-washed (AW) Lochiel coal and air-dried Bowmans coal fast heating rate pyrolysis at 800°C.	142
Figure 5-11	Cumulative gas phase conversion ratio for sulphur to carbon conversion as a function of temperature, $(X_s/X_c)_{gas}$, for the TPP and Fast pyrolysis conditions, using air-dried (AD), acid-washed (AW) and air-dried Bowmans (BW) coal.	144
Figure 5-12	Ratio of cumulative gas phase conversion ratio for sulphur to carbon conversion as a function of temperature, $(X_s/X_c)_{gas}$, to the sulphur to carbon % mass content of the coal $(S/C)_{coal}$, for the TPP and Fast pyrolysis conditions, using air-dried (AD), acid-washed (AW), and air-dried Bowmans (BW) coal.	145
Figure 5-13	Ratio of cumulative sulphur conversion to volatiles per carbon conversion to volatiles $(X_s/X_c)_{vol}$ to the sulphur to carbon % mass content of the coal $(S/C)_{coal}$ for 800°C fast pyrolysis for air-dried Lochiel (AD), acid-washed Lochiel (AW) and air-dried Bowmans (BW) coals.	146

Figure 5-14	Relationship between sulphur to carbon conversion to volatiles ratio (X_s/X_c) _{vol} to inorganic species content (%db) for air-dried (AD) and acid-washed (AW) Lochiel coal, along with Bowmans coal.	149
Figure 6-1	%v/v (dry basis) concentration profile for product gas from steam (25% v/v) fixed-bed gasification of air-dried (AD) Lochiel char at 800°C.	154
Figure 6-2	Carbon conversion profile for air-dried (AD) Lochiel char, steam gasification (25% v/v) at 750°C, 800°C and 850°C temperature.	155
Figure 6-3	Sulphur conversion profile for air-dried (AD) Lochiel char, steam gasification (25% v/v) at 750°C, 800°C and 850°C temperature.	156
Figure 6-4	Carbon conversion profile for acid-washed (AW) Lochiel char, steam gasification (25% v/v) at 800°C and 850°C gasification temperature.	157
Figure 6-5	Sulphur conversion profile for acid-washed (AW) Lochiel char, steam gasification (25% v/v) at 800°C and 850°C gasification temperature.	157
Figure 6-6	Carbon conversion profile for air-dried Bowmans (BW) char, steam gasification (25% v/v) at 750°C, 800°C and 850°C temperature.	158
Figure 6-7	Sulphur conversion profile for air-dried Bowmans (BW) char, steam gasification (25% v/v) at 750°C, 800°C and 850°C gasification temperature.	159
Figure 6-8	Maximum sulphur conversion for steam (25% v/v) gasification for air-dried (AD) Lochiel, acid-washed (AW) Lochiel and air-dried Bowmans (BW), for 750°C (where available), 800°C and 850°C gasification temperature.	160
Figure 6-9	Cumulative sulphur conversion fraction as a function of carbon conversion fraction for air-dried (AD) Lochiel coal gasification in 25% steam at 750°C, 800°C and 850°C.	165
Figure 6-10	Cumulative sulphur conversion fraction as a function of carbon conversion fraction for acid-washed (AW) Lochiel coal gasification in 25% steam at 800°C and 850°C.	166
Figure 6-11	Cumulative sulphur conversion fraction as a function of carbon conversion fraction for air-dried Bowmans (BW) coal gasification in 25% steam at 750°C, 800°C and 850°C.	167
Figure 6-12	Cumulative sulphur conversion fraction as a function of carbon conversion fraction for air-dried Lochiel (AD) and Bowmans (BW) coal gasification in 25% steam at 750°C (BW only), 800°C and 850°C.	169
Figure 6-13	Comparison of homogeneous model predictions for carbon conversion with experimental data for air-dried (AD) Lochiel char gasification.	173

Figure 6-14	Comparison of homogeneous model predictions for carbon conversion with experimental data for acid-washed (AW) Lochiel char gasification (excluding data prior to 10 minutes at 850°C and 15 minutes at 800°C to calculate induction time).....	174
Figure 6-15	Comparison of homogeneous model predictions for carbon conversion with experimental data for air-dried Bowmans (BW) char gasification.	174
Figure 6-16	Arrhenius plot for carbon gasification of Lochiel (AD), Bowmans (BW) and acid-washed Lochiel (AW) char with 25% steam.	176
Figure 7-1	Species concentration for carbon (CO ₂ , CO and CH ₄), hydrogen (H ₂) and sulphur (H ₂ S and COS) for fluidised-bed pyrolysis (nitrogen atmosphere) of air-dried Lochiel coal at 800°C.....	183
Figure 7-2	Sulphur conversion to the gas phase for each pyrolysis mode for air-dried Lochiel coal. Volatile sulphur represents the predicted total gas and tar phase evolution at 800°C.	184
Figure 7-3	Normalised sulphur conversion to the gas phase for each pyrolysis mode for air-dried Lochiel coal.....	185
Figure 7-4	Carbon conversion to the gas phase for each pyrolysis mode for air-dried Lochiel coal. Other represents C1-C3 hydrocarbons and COS. Volatile carbon represents predicted total gas and tar evolution at 800°C.	186
Figure 7-5	Normalised carbon conversion to the gas phase for each pyrolysis mode for air-dried Lochiel coal. Other represents C1-C3 hydrocarbons and COS.	186
Figure 7-6	Carbon conversion (as hydrocarbons and COS/CH ₃ SH) to the gas phase for each pyrolysis mode for air-dried Lochiel coal.	187
Figure 7-7	Relative carbon conversion (as hydrocarbons and COS/CH ₃ SH) to the gas phase for each pyrolysis mode for air-dried Lochiel coal.	188
Figure 7-8	Sulphur conversion to the gas phase for each pyrolysis mode for air-dried Bowmans coal. Volatile sulphur represents the predicted total gas and tar phase evolution at 800°C.	190
Figure 7-9	Relative sulphur conversion to the gas phase for each pyrolysis mode for air-dried Bowmans coal. Volatile sulphur represents the predicted total gas and tar phase evolution at 800°C.....	191
Figure 7-10	Carbon conversion to the gas phase for each pyrolysis mode for air-dried Bowmans coal. Volatile carbon represents the predicted total gas and tar phase evolution at 800°C.	192
Figure 7-11	Relative carbon conversion to the gas phase for each pyrolysis mode for air-dried Bowmans coal. Volatile carbon represents the predicted total gas and tar phase evolution at 800°C.....	192

Figure 7-12 Carbon conversion (as hydrocarbons and COS) to the gas phase for each pyrolysis mode for air-dried Bowmans coal.	193
Figure 7-13 Relative carbon conversion (as hydrocarbons and COS) to the gas phase for each pyrolysis mode for air-dried Bowmans coal.	194
Figure 7-14 Species concentration for carbon (CO ₂ , CO and CH ₄) and hydrogen (H ₂) for fluidised-bed pyrolysis (25% v/v steam in nitrogen atmosphere) of air-dried Lochiel coal at 800°C.....	197
Figure 7-15 Carbon conversion to the gas phase during fluidised-bed pyrolysis of air-dried Lochiel (Loch) and Bowmans (BW) coals in nitrogen (N ₂) and nitrogen-steam (N ₂ /steam) atmospheres at 800°C.....	198
Figure 7-16 Fluidised-bed reactor temperature profiles for the fluidised bed pyrolysis (0-10minutes) and subsequent steam gasification (>10minutes) of air-dried Lochiel coal.....	200
Figure 7-17 Concentration of major product gases and nitrogen carrier gas for fluidised-bed pyrolysis and gasification of air-dried Lochiel coal at 800°C. Solid lines indicate that pyrolysis was conducted in the absence of steam whereas dashed lines represent N ₂ /steam pyrolysis results.....	201
Figure 7-18 % carbon conversion due to gasification for air-dried Lochiel coal at 800°C in 25% v/v steam and nitrogen.....	203
Figure 7-19 Concentration of major product gases and nitrogen carrier gas for fluidised-bed pyrolysis and gasification of air-dried Bowmans coal at 800°C. Solid lines indicate that pyrolysis was conducted in the absence of steam whereas dashed lines represent N ₂ /steam pyrolysis results.....	204
Figure 7-20 % carbon conversion due to gasification for air-dried Bowmans coal at 800°C in 25% v/v steam and nitrogen.....	206
Figure 7-21 Comparison of homogeneous model predictions for carbon conversion with experimental data for steam fluidised-bed gasification of air-dried (AD) Lochiel coal (up to 80% conversion).....	207
Figure 7-22 Comparison of the ratio of gas phase conversion of carbon as CO to the gas phase conversion of carbon as CO ₂ during 800°C pyrolysis of air-dried Lochiel (AD) and Bowmans coal (BW) for fixed-bed, fast pyrolysis in nitrogen (fixed N ₂) and fluidised-bed pyrolysis in nitrogen (fluid N ₂) and 25% v/v steam/nitrogen mixture (fluid H ₂ O)	213