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 (H_2S) with methyl mercaptan (CH_3SH) and carbonyl sulphide (COS) comprising the balance. For the acid-washed Lochiel and air-dried Bowmans samples, sulphur dioxide (SO_2) 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-reacts 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 H_2S and no SO_2 in the product gas, the effect on carbon conversion and distribution of carbon between CO and CO_2 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 CH_3SH and COS (at the expense of H_2S) and carbon among CO_2 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 – thankyou 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 thankyou. 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 South Australian coal resources are significant *7*

2.2.2 Gasification is the technology of choice *8*

2.2.3 Low-rank coals presents unique challenges *10*

2.3 THE SOURCE AND CHEMISTRY OF COAL SULPHUR 12

2.3.1 The origin of sulphur in coal *12*

2.3.2 Behaviour of coal sulphur *15*

2.3.3 Gas phase sulphur chemistry *23*

2.3.4 Factors affecting sulphur redistribution *27*

2.4 ANALYTICAL AND EXPERIMENTAL METHODS 38

2.4.1 Feedstock and product analysis *39*

2.4.2 Determining experimental conditions *43*

2.5 PREVIOUS WORK ON SA LIGNITE 55

2.5.1 Behaviour of sulphur *55*

2.5.2 Ash agglomeration and deposition in fluidised-bed gasification *66*

2.5.3 Kinetic modelling of sulphur and gasification *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 Calculation methodology ... 154
6.3.2 Conversion versus time calculation ... 154
6.3.3 Summary of results for conversion versus time ... 161
6.4 CORRELATING SULPHUR TO CARBON CONVERSION ... 164
6.5 KINETIC MODELLING ... 170
6.5.1 Background ... 170
6.5.2 Carbon kinetics ... 172
6.5.3 Comparison to literature ... 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 Air-dried Lochiel pyrolysis in nitrogen ... 182
7.2.2 Air-dried Bowmans pyrolysis in nitrogen ... 189
7.2.3 Comparing Lochiel and Bowmans ... 194
7.2.4 Effect of atmosphere during fluidised-bed pyrolysis ... 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 *et al.* 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_2S uptake reaction (Sugawara *et al.*, 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_2S (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_2S 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_3SH 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 dataprior 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_2S 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_3SH) 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_3SH) 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_2O 213

1 INTRODUCTION

1.1 Why South Australian Brown Coal?

"Energy security", that is, the reliability, availability and affordability of fuel for power generation and transport, is acknowledged today by oil majors, power producers and politicians alike, as something fundamental to economic development. In the US, it is a call to reduce reliance on middle-eastern oil for the transport sector while in Western Europe, it refers to the reliability and availability (less so affordability) of natural gas imports from Russia. In Australia, energy security means something very different, given that the reliability and availability of natural resources for power generation and transport fuels (with the exception of our declining indigenous oil production) are not in question. Energy security in Australia relates to energy *affordability*.

Australia has the cheapest power of any industrialised nation and the bulk of this power, over 85%, is produced by the combustion of coal. While NSW and QLD are blessed with an abundance of high rank coals, whose export alone fuelled almost $25 Billion in export earnings during financial year 2007-2008, the South Eastern states of Australia, Victoria and South Australia, have an abundance of cheap low rank coal that is used solely for power generation (ABARE, 2009). While the Victorian operations are mine-to-mouth, whereby large scale sub-critical boilers (for example Loy Yang A&B at 6 x 500MW boilers) are situated in the coal fields of the Latrobe Valley, with the coal transported less than 1km to the boilers, the South Australian power generation facilities of Port Augusta burn coal mined some 225 km away near Leigh Creek in the state's north east. A sloping coal seam means that, in using cheap open cut mining methods, the coal becomes more expensive with each year that mining operations increase in depth, thereby increasing the short run marginal cost of power and diminishing the Port Augusta power station's competitive advantage over its natural gas fired competitors in the electricity wholesale market.

Maintaining coal-based power generation's competitive advantage in the National Electricity Market (NEM), and place in South Australia's supply mix, may depend on the utilisation of vast resources of brown coal located, amongst other sites, in the state's mid-north, at Lochiel and Bowmans. Unlike the Leigh Creek coal fields, this coal is located close to the surface and could have an as mined cost comparable to Victorian brown coals at less than A\$0.1/GJ (ACIL Tasman, 2009). However, the high ash content of the coal, along with the high sulphur content, render it unsuitable for use in conventional pulverised fuel (pf) boilers. While fluidised-bed combustion received considerable attention in the 1990's under the then Electricity Trust of South Australia's (ETSA) research activities, gasification technologies may also be a suitable route to generating electricity from these coals at high conversion efficiency.

Gasification is the conversion of organic matter into gaseous form (Smoot and Smith, 1985) whereby feedstock is added to a reactor in which it is contacted with a reducing atmosphere at high temperature and pressure, variables that depend on whether the gasifier is a fixed, fluidised or entrained bed reactor type. The main products of coal gasification – referred to as synthesis gas or syngas - are carbon monoxide and hydrogen along with carbon dioxide and methane (Williams *et al.*, 2000). Levels of impurities and pollutants such as hydrogen sulphide (H_2S) depend on feedstock type and operating parameters.

There is currently no commercially proven air-blown gasification technology for low-rank coals (CRC for Clean Power from Lignite, 2005). The High Temperature Winkler (HTW) fluidised-bed gasifier and the Halliburton/KBR Transport Reactor Integrated Gasifier (TRIG), are the most promising reactor types. The Cooperative Research Centre (CRC) for Clean Power from Lignite is aiming to develop cost-effective, efficient and clean power generation processes based on the HTW fluidised bed gasification process.

While the capital costs of these technologies are at present much higher than equivalent conventional processes, it is expected that they will become cheaper over time as those currently under construction prove both efficiency and reliability. Gasification is also proposed as a source of poly-generation, that is, syngas can be used as a source of hydrogen, a feed stock for chemicals production, or combusted in a gas turbine to generate electricity. The ability to produce a multiple use product is very attractive, in addition to the ability of gasification to produce a high purity CO_2 stream suitable for underground storage, and has the potential to see gasification as a Zero Emission Technology (ZET) of choice in developed economies which value carbon as they move to an international emission trading scheme.

1.2 Scope and Structure of this Work

Accurate process modelling is an essential tool during the design of these processes, in order to provide the fundamental basis of gasifier and downstream processing equipment design, thus providing the necessary confidence investors need to back a novel technology. It is essential, in establishing the environmental credentials of any advanced technology, to accurately predict the fate of system pollutants. To this end, this thesis aims to examine the behaviour of the sulphur species found in South Australia's coal deposits during the fluidised-bed gasification process, and provide a way forward in developing strategies that will diminish their negative impact during the utilisation of these vast resources.

Chapter 2 provides a historical basis for embarking on this work, showing the present gaps in the literature that are addressed in later chapters. Chapter 3 provides detailed descriptions of the experimental equipment and procedures that were employed in this research.

Chapter 4 examines the behaviour of the coal sulphur under fixed-bed pyrolysis conditions as a basis for gaining a better understanding as to how the coal sulphur is found and bound. This is appropriate given that any gasification process features pyrolysis as its primary step. While this work is characterised by the use of low heating rates to elucidate sulphur species, Chapter 5 looks at the pyrolytic transformations of sulphur under conditions of higher heating rate, conditions that better approximate those found in a fluidised-bed gasifier.

Chapter 6 examines the fixed-bed steam gasification of sulphur, with a simple reaction system selected as the first step to gaining a fundamental understanding of the process in the absence of the complex phenomena found in fluidised-beds, while Chapter 7 looks at the results of laboratory scale fluidised-bed gasification experiments, the final stage of this work's experimental programme.

Chapter 8 presents an evaluation of the current work and its implication for industrial systems, recommending an action pathway for future investigations into the behaviour of sulphur during pyrolysis and gasification.

2 LITERATURE REVIEW

2.1 Introduction and aims

The evolution of sulphur during gasification (FBG) has not previously received much attention. Despite most fuel sulphur being released during the pyrolysis stage of coal conversion processes (~50%) (Furimsky *et al.*, 1991), primarily as hydrogen sulphide (H_2S), there is still a significant amount of sulphur to react during subsequent gasification. The reaction pathways, however, depend on a number of complex factors. These include the pyrolysis step itself, reactions of sulphur gas species with mineral matter, the organic matrix and reactions with other gas phase species. The resultant mix of sulphur gases, believed to consist mainly of hydrogen sulphide (H_2), but also including carbon disulphide (CS_2), carbonyl sulphide (COS), mercaptans and thiophenes (Garcia-Labiano *et al.*, 1995), all lead to the formation of SO_2 when combusted in a gas turbine which, when released to the atmosphere, contributes to acid rain. Being able to predict the rate of formation of sulphur species and understand their evolution in a commercial-scale fluidised-bed gasifier is needed in order to optimise operating conditions and to successfully design sulphur removal systems to minimise this environmental impact (Sugawara *et al.*, 2003).

It is difficult at this stage to construct a fundamental model of sulphur transformations during coal gasification due firstly to incomplete knowledge of the transforming reactions, and secondly to limited availability of kinetic data for those reactions that are known (Garcia-Labiano *et al.*, 1996). In the absence of reliable kinetic data, it has been suggested that the rate of sulphur conversion during gasification could be assumed to be proportional to the rate of carbon conversion (Ma *et al.* 1989) although there is no concrete evidence in the literature to support this assumption, particularly as sulphur is found in both organic and inorganic structures in coal.

The CRC for Clean Power from Lignite has previously developed a mathematical model of a bubbling fluidised-bed gasifier (Yan *et al.*, 1999), however, this model assumes that all coal-sulphur (that is, bonded to the carbon matrix) is instantaneously converted to H_2S during pyrolysis. In addition, during subsequent steam gasification, the only reaction pathway included is the reaction of pyrite with hydrogen – which is not relevant to the South Australian coals in question as their main inorganic form of sulphur is sulphate. While these are useful approximations for relatively low sulphur coals, more detailed predictions of the sulphur redistribution among the various phases and an understanding of gas-phase sulphur partitioning and gasification reactivity are required for South Australian coals, given their high sulphur content (Ashman and Mullinger, 2003).

For the South Australian coals in question, Telfer (1999) conducted a number of experiments in order to examine the behaviour of the solid phase sulphur groups during pyrolysis only. Temperature Programmed Pyrolysis (TPP) experiments monitored the sulphur forms in the resultant char, detailing their behaviour with temperature. Fixed-bed experiments in a horizontal tube furnace and fluidised-bed experiments under inert conditions examined the effect of heating rate and particle size on the solid phase sulphur transformations. This provided a detailed quantitative and qualitative understanding of the behaviour of the coal sulphur under a variety of conditions.

The present study aims at developing this understanding in the corresponding gas-phase sulphur chemistry for pyrolysis, at both slow and fast heating rate, and to develop an understanding of the relationship between sulphur and coal gasification rates during fluidised-bed steam gasification.

The aim of the following literature review is to provide an assessment of the body of knowledge surrounding the conversion of sulphur during fluidised-bed gasification of coal. Section 2.2 examines the location, extent and properties of South Australian low-rank coals, in particular issues with their utilisation for power generation. Section 2.3 looks at the chemistry of sulphur during pyrolysis and gasification processes and its sensitivity to parent coal and treatment processes. Section 2.4 looks at the most appropriate analytical/experimental methods to characterise coal sulphur forms, and analyse the various products of pyrolysis and gasification. Section 2.5 details the substantial body of work that has previously been completed to examine the behaviour of sulphur in SA coals under pyrolysis conditions. This work forms the basis for determining the experimental programme of this thesis, as outlined in Chapter 3.

2.2 Coal resources and power generation technology

Coal is the fuel of choice for the world's power generation fleet, and its dominance is predicted to increase as the world enters an era of expensive gas and concerns about nuclear power (BP, 2008). An impending value on the equivalent carbon dioxide emissions from coal fired power stations, however, and the depletion of existing reserves of high quality coals, mean that cheaper fuels, often of poorer quality in terms of non-carbon emissions such as sulphur, are likely to be employed to a greater extent, particularly in the growing economies of Asia such as India and China. This section looks at chemistry of coal sulphur, putting the question about the future role of coal in Australia in context by examining the size and quality of South Australia's significant resources of low rank coal.

2.2.1 South Australian coal resources are significant

South Australia has several locations where large resources of low rank coal have been delineated, however, they have similar coal properties which render them unsuitable for re-fuelling the existing coal-fired power stations that provide about 40% of the state's power (ESIPC, 2007). The proximity of the Lochiel and Bowmans deposits to areas of high electricity demand and a large workforce (as shown in **Figure 2-1**) and the overall size of their resource base, makes them attractive deposits for future exploitation. Understanding the impact of coal properties on the technology of choice for generating power from them is crucial in selecting the appropriate fuel around which a power station can be designed.

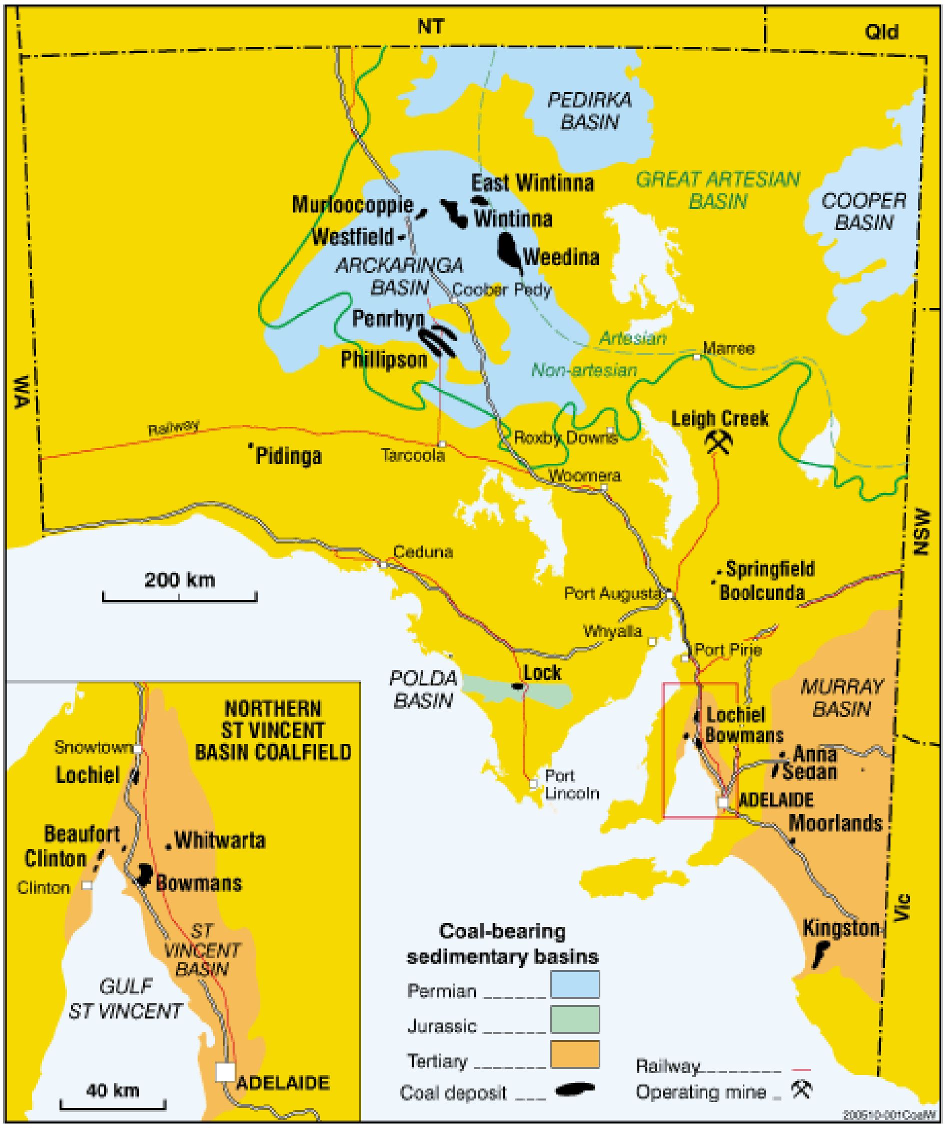


Figure 2-1 Map of South Australia showing coal deposits (PIRSA, 2009)

2.2.2 Gasification is the technology of choice

It is widely believed that a technology shift in generation plant is required to achieve deep cuts in emissions from power stations, and several studies have estimated the costs of such a change.

Gasification of coal, that is, the conversion of the coal into a synthetic or syngas for combustion in gas turbines, has been singled out as the technology of choice for shifting to a high efficiency, low emission power generation future and to this end, the

CRC for Clean Power from Lignite has been investigating its applicability to the suite of low rank coals that are found in Victoria and South Australia.

Fluidised-bed gasification involves adding millimetre size particles of coal to a reactor where they are held in a fluidised state by an appropriate flow rate of reducing atmosphere at high temperature (800-1000°C) and pressure (0.1-7 MPa). The reducing atmosphere is oxygen limiting and is referred to as the gasifying medium or agent. The high reactivity of low-rank coals enables the use of air as the gasifying agent, which results in lower up-front capital costs and higher efficiency than oxygen blown processes (the parasitic load of the Air Separation Unit (ASU) is significant). Oxygen-blown gasification is necessary for black coals, which require higher reaction temperatures due to their lower reactivity.

The main products of coal gasification are carbon monoxide and hydrogen along with carbon dioxide and methane (Williams *et al.*, 2000), with levels of impurities and pollutants present depending on the feedstock and operating atmosphere. There are two main stages of gas production during gasification. The first is pyrolysis or devolatilisation. During pyrolysis the coal matrix undergoes irreversible internal transformations where chemical bonds degrade with increasing temperature, releasing low molecular weight gas species (Smoot and Smith, 1985; Ross, 2000; Williams *et al.*, 2000). These low molecular weight gas species include CO, CO_2, H_2, CH_4 and water vapour along with high molecular weight condensable organics that are referred to as tar. The remaining mass, enriched with carbon and depleted in oxygen and hydrogen is called char. Pyrolysis results in up to 50% weight loss incurred by low-rank coals during conversion processes (Ross, 2000). The volatiles formed may undergo a number of reactions with other gases, and the solid phase, depending on the type of atmosphere present. Changing the operating conditions can change the gas composition, an effect that is most desirable when a gas of particular heating value is required (Williams *et al.*, 2000).

Gasification of the resulting char with carbon dioxide is usually the main stage in the process along with partial oxidation in the oxygen rich zones of the fluidised-bed. This is usually termed complete gasification, whereas pyrolysis is often referred to as partial gasification (Williams *et al.*, 2000).

Coal gasification processes, coupled with combined cycle utilisation of the syngas, are much more efficient relative to conventional processes. Due to the excellent mass transfer and mixing of volatiles with solid particles in fluidised-beds, gasification achieves a greater overall conversion of the chemical energy in coal to product gas. The ability to operate in an isothermal temperature environment facilitates rapid heat and mass transfer and high chemical reactions rates that are favourable from a process control perspective.

2.2.3 Low-rank coals presents unique challenges

The problems that occur during low-rank coal utilisation are primarily due to a combination of unfavourable coal properties and utilisation conditions. Moisture and ash content, along with the emission of fuel nitrogen and sulphur pose significant operational and environmental concerns.

Low-rank coals have high moisture content.

To accommodate the high flow rate of water vapour and in order to provide sufficient heat transfer area, brown coal reactors are much larger than their black coal counterparts. This size increase is accompanied by increased capital and maintenance costs along with longer plant down-time during shutdown (Allardice and Newell, 1991).

South Australian low-rank coals have significant quantities of ash.

Leigh Creek coal contains approximately 9 wt% ash while Bowmans and Lochiel contain approximately 5 wt% as received. In conventional pulverised fuel furnaces, the effect of high ash content such as slagging, fouling and ash deposition cause problematic operation and high maintenance costs, with sodium a key contributor to fouling. Knowledge of the agglomeration and defluidisation behaviour of ash during fluidised-bed gasification (and combustion) is critical and this has been a major focus of the CRC's experimental programme since its inception in 1993.

South Australian low-rank coals contain relatively little nitrogen.

During combustion, the chemistry of fuel nitrogen transformations is complicated and can lead to NO and N_2, in proportions related to the fuel nitrogen content and volatility along with the combustion conditions. During gasification conditions, the presence of steam enhances the yields of HCN and NH_3, which can impact on the performance and integrity of gas turbines when combusted. Both the behaviour of coal nitrogen during gasification and the fate of that nitrogen when combusted in a gas turbine have been the object of extensive study at the CRC.

South Australian low-rank coals have high sulphur content.

In gasification systems, H_2S is the major source of gaseous sulphur, with traces of carbonyl sulphide (COS) and carbon disulphide (CS_2), which, once released to the atmosphere, form acid rain (Khan, 1989). As low sulphur content resources are depleted and utilities move to higher sulphur coals as their fuel source, and as emissions legislation becomes more stringent with respect to the release of sulphur, innovative ways of utilising high sulphur coals, whilst realising high levels of efficiency and environmental responsibility, are being sought.

For advanced technologies, the problem of utilising high sulphur fuels also relates to operation. Gasification products, to be combusted in a gas turbine or converted for fuel cell use, must meet rigid specifications with emission limits for sulphur of 20ppmv (Bhattacharya, 2003). This implies that gasification of high sulphur coals, where the product gas may be 1 vol% H_2S or more, requires a heavy investment in desulphurisation, either through coal pre-treatment, in-situ removal or pre-combustion scrubbing. Ash-phase sulphur compounds have also been found to form low melting point compounds that contribute to slagging, fouling and agglomeration in combustion and gasification applications (Kolodney *et al.*, 1976; Manzoori, 1990; Marinov *et al.*, 1992; Mason, 1992; Kosminski, 2001; McCullough, 2007).

The behaviour of the high sulphur content of these deposits requires detailed investigation in order to develop strategies that will minimise its impact in fluidised-bed gasification processes.

2.3 The source and chemistry of coal sulphur

The form of sulphur in coal and its concentration greatly affects the inter-conversion of sulphur compounds during the devolatilisation, oxidation and reduction stages of gasification (Khan, 1989). It is necessary then to have a comprehensive knowledge of these sulphur groups in order to understand their chemistry and redistribution during coal utilisation.

Sulphur is found in coal in both inorganic and organic forms, and while the behaviour of inorganic sulphur forms is well understood, the reactions of the organic portion are poorly known. Inter-conversion between inorganic and organic sulphur forms, and the reaction of sulphur in the gas phase with the coal matrix to reform complex sulphur species, are phenomena observed by a number of workers, affecting the sulphur content of product char from heat treatment.

2.3.1 The origin of sulphur in coal

Coal is a complex structure comprised of inorganic and organic matter made up primarily of large arrays of benzene-like rings linked together (McMurray, 1996). The heterogeneous nature of the macroscopic coal structure means that the term “coal” is broadly defined and that “the solids to which it is applied are often more dissimilar than alike” (Berkowitz, 1979). The organic portion of coal is derived from the decomposition and subsequent ‘coalification’ of plant matter that has formed peat swamps. Coalification is the process which changes plant matter to peat then low rank coals followed by anthracite. Its extent is related to the temperatures, depth of burial and residence time that the matter undergoes (George and Mackay, 1991). The degree of coalification determines a coal's *rank*, while a coal's *type* refers to its petrographic composition (Ting, 1982), and is related to the historical environment at the time of deposition. This implies that similar material, under similar climatic and tectonic conditions would lead to the formation of similar peat and coal types.

Sulphur is found in coal in both inorganic and organic forms. Iron disulphide, FeS_2, is typically the main form of inorganic sulphur and is found in two structures: pyrite and marcasite. These compounds have similar reactivity and density but differ in crystal geometry – pyrite is cubic in form and marcasite orthorhombic. For this reason they are often considered solely as pyrite (Attar, 1978). Inorganic sulphur is also found in the form of sulphates, particularly iron, barium and calcium. Normally found in negligible amounts (Attar and Hendrickson, 1982), sulphate concentration increases with exposure to ambient air as a result of oxidation reactions (Attar, 1978; Khan, 1989). These inorganic sulphur forms are found in vein-like structures discretely dispersed in organic coal measures.

Organic sulphur refers to sulphur that is bound to the coal's carbon matrix. It is found evenly dispersed throughout the coal structure in a wide variety of forms. The exact organic sulphur functional groups present in coal are unknown but 'model' compounds have been used to describe their chemistry (Attar, 1978). It has been established that these groups differ in their reactivity on heat treatment – their reactivity is closely related to their sulphur bonding complexity (Attar, 1978; Khan, 1989).

A coal's type and rank give an indication of how its sulphur is bound. While the total sulphur concentration is dependent on the physical matter at the time of deposition and subsurface conditions, the form of sulphur (organic or inorganic) is related to coal rank and the chemical reactions that occurred during the coalification process. While some of the organic sulphur in coal might originate from the coal-forming plant and animal remains in the initial peat-bog, these origins are not considered concentrated enough to lead to the development of high-sulphur coals (Attar and Hendrickson, 1982).

Sources of inorganic sulphur such as sulphates are the main contributor to the high sulphur content of many of today's coals. Anaerobic sulphate-reducing bacteria may produce H_2S and even elemental sulphur from the reduction of sulphates to disulphides and then H_2S, and these may react with the organic constituents present in the peat to become organically bound sulphur (Attar and Hendrickson, 1982). Elemental sulphur, however, is not found in significant quantities (Attar, 1978).

Bowmans and Lochiel lignite have high organic sulphur content, with inorganic sulphur found mostly as sulphates. **Table 2-1** shows the proximate and ultimate analysis of these lignites along with their sulphur form distribution. Investigations to define the nature of organic sulphur forms in South Australian lignite have been undertaken by Telfer (1999) but only indirect quantification of these forms has been carried out.

Table 2-1 Analyses of raw Bowmans and Lochiel coal as per the work of Telfer (1999)

Proximate (%db)	***Bowmans***	***Lochiel***
Moisture (a.r.)	56.0	31.4
Ash	11.9	10.0
Volatile Matter	49.3	49.6
Fixed Carbon	38.8	40.4
Ultimate (%db)		
Carbon	69.4	43.5
Hydrogen	4.6	3.5
Oxygen	20.9	49.4
Nitrogen	0.8	0.3
Sulphur	4.8	3.3
Sulphur forms (%S_T)		
Pyrite	0.9	0.3
Sulphate	19.1	14.5
Organic	80.0	85.2
Sulphide	-	-

%db: percent dry basis
%daf: percent dry ash free basis
%S_T: percent Total Sulphur

Knowledge of the sulphur forms in coal enables the clarification of their chemistry and sensitivity to certain operating parameters. The fact that South Australian low-rank coals contain significant amounts of organic sulphur will greatly influence their behaviour during pyrolysis and gasification.

2.3.2 Behaviour of coal sulphur

Most sulphur is released during the pyrolysis stage of coal conversion processes, including gasification (Morris and Keairns, 1979; Khan, 1989; Furimsky *et al.*, 1991). For coals of high organic sulphur content, however, the retention of sulphur is of vital importance to its gasification behaviour.

Sulphides

Pyrite or iron disulphide, FeS_2, is usually the main form of inorganic sulphur found in coal (Attar and Hendrickson, 1982), however, Lochiel and Bowmans coal contain only small amounts of it. During pyrolysis, pure pyrite decomposes according to the following reaction:

$$FeS_2 \rightarrow FeS + \frac{1}{n} S_n \qquad \text{Eq 2-1}$$

The rate of this reaction is large between 550°C and 600°C (Attar, 1978) and conversion is kinetically limited (Khan, 1989). Commencing around 450°C, it is complete at 850°C for sufficiently low heating rate (Khan, 1989). Hydrogen and carbon monoxide may also react with pyrite producing iron sulphide (Attar, 1978; Khan, 1989). Reaction with hydrogen becomes important above 500°C but the reaction with carbon monoxide is very slow, even below 800°C.

$$FeS_2 + H_2 \rightarrow FeS + H_2S \qquad \text{Eq 2-2}$$

$$FeS_2 + CO \rightarrow FeS + COS \qquad \text{Eq 2-3}$$

Pyrite can also react with methane in the following reaction (Khan, 1989; Garcia-Labiano *et al.*, 1995):

$$4FeS_2 + CH_4 \xrightarrow[500°C]{} CS_2 + 4FeS + 2H_2S \qquad \text{Eq 2-4}$$

Khan (1989) proposed that at lower temperatures, pyrite reacts with hydrogen donated by decomposing coal according to the following reactions:

$$2FeS_2 \xrightarrow[230°C]{H_2} Fe_2S_3 + H_2S$$ Eq 2-5

$$Fe_2S_3 + H_2S \xrightarrow[280°C]{H_2} 2FeS + 5H_2S$$ Eq 2-6

$$2FeS + 5H_2S \xrightarrow[370°C]{2H_2} 2FeS + 2H_2S$$ Eq 2-7

While Attar (1978) proposed that pyrite may also react with oxygen, proceeding with dependence on the size of pyrite inclusions in the coal structure and oxygen partial pressure:

$$FeS_2 + O_2 \longrightarrow FeS + FeSO_4 + Fe_2(SO_4)_3 + SO_2 + Fe_2O_3$$ Eq 2-8

$$FeS + O_2 \longrightarrow FeSO_4 + Fe_2(SO_4)_3 + SO_2 + Fe_2O_3$$ Eq 2-9

Solid phase reactions also play an important role in the decomposition of pyrite. At high temperature (1000°C) carbon can reduce it to iron sulphide and subsequently to metallic iron (Attar, 1978; Khan, 1989):

$$2FeS_2 + C \rightarrow 2FeS + CS_2$$ Eq 2-10

Pyrite also reacts with hydrocarbons such as ethylene (C_2H_2) to produce carbon disulphide and these hydrocarbons react with 'free sulphur' formed from the decomposition of pyrite, before it has the chance to polymerise (Attar, 1978). In fact, in the presence of many organic compounds, pyrite has been reduced to sulphide at temperatures as low as 250-300°C (Attar, 1978; Robinson, 1978; Gryglewicz and Jasienko, 1992). These observations indicate that it can be the organic hydrocarbon material in the coal matrix that is the reactive species leading to reduction, rather than the hydrogen or hydrogen radicals produced by thermal degradation or devolatilisation. Most researchers, however, consider the reaction of hydrogen to dominate and modelling efforts in this area refer only to the hydropyrolysis of pyrite.

Attar (1978) noted that mass transfer of the reactive gas species was not the rate-limiting step in pyrite decomposition. It was proposed that diffusion in the solid limited pyrite decomposition, and that pyrite decomposition in any environment is controlled by the availability of sulphide (S^{2-}) ions on the surface of the pyrite crystal with the rate of diffusion from the bulk of the crystal that determines this availability. Hence an active gasifying agent will readily ‘consume’ the available sulphur resulting in a concentration gradient that drives the diffusion. This control relates well to conditions where gas-solid contact is calm, but in situations such as fluidised-bed gasification, where the contacting method is sufficiently ‘violent’, factors such as agglomeration, particle fracture and inter-particle interactions play an important role.

Telfer (1999) observed an increase in pyrite concentration during Temperature Programmed Pyrolysis (TPP) of South Australian lignites from 400 – 500°C. Pyrite was believed to act as an intermediate in solid-state transformations of sulphate sulphur to organic sulphur. Between 500°C and 700°C, pyrite concentration was then found to decrease to negligible amounts, in agreement with Attar (1978).

Sulphide compounds, other than pyrite and organic sulphides, are not normally found in raw coal in appreciable quantities. Sulphides are, however, formed during coal conversion, mainly due to the decomposition of sulphate and pyrite to iron sulphide and reactions of H_2S with basic minerals to form metal sulphides (Kucukbayrak and Kadioglu, 1988; Ibarra *et al.*, 1989; Gryglewicz and Jasienko, 1992).

Gryglewicz and Jasienko (1992) monitored the transformation of sulphides during non-isothermal pyrolysis, finding that the concentration increased over 400-600°C and 700-1000°C, corresponding with the decomposition of pyrite and the interactions between H_2S and basic minerals respectively.

Reactions of basic minerals in coal with H_2S are one of the primary mechanisms for sulphur retention in char post heat treatment (Attar, 1978; Gryglewicz and Jasienko, 1992). Calcium and magnesium, along with iron oxides and/or carbonates convert to their corresponding sulphides when reacted with H_2S and are retained as a solid. These reactions occur as follows, where M signifies Ca^{2+}, Mg^{2+} or Fe^{2+}:

$$MO + H_2S \rightarrow MS + H_2O \qquad \text{Eq 2-11}$$

$$MCO_3 + H_2S \rightarrow MS + H_2O + CO_2 \qquad \text{Eq 2-12}$$

Attar (1978) proposed that iron sulphide reacts during pyrolysis and gasification as follows:

$$FeS + H_2 \rightarrow Fe + H_2S \qquad \text{Eq 2-13}$$

$$FeS + O_2 \rightarrow FeSO_4 + Fe_2(SO_4)_3 + Fe_2O_3 + SO_2 \qquad \text{Eq 2-14}$$

$$2FeS + C \rightarrow 2Fe + CS_2 \qquad \text{Eq 2-15}$$

Reaction with hydrogen is slow, even at 800°C, while reaction with oxygen occurs as low as 350 – 400°C (Attar, 1978). Reduction with carbon occurs at temperatures above 1000°C. However, investigations by a number of researchers (Attar, 1978; Gryglewicz and Jasienko, 1992; Patrick, 1993) have shown that FeS is only completely decomposed to Fe by 1700°C, well beyond the practical operating temperature of advanced processes. This suggests that the retention of sulphides as FeS in advanced processes may be important if they are formed in appreciable quantities.

Sulphates

Iron and calcium sulphates are the most abundant forms of sulphate found in coal. Sulphates can also exist as barium, sodium and magnesium sulphates. The decomposition and transformation of sulphates begins above 350°C, and they are believed to be the main source of SO_2 during gasification (Furimsky *et al.*, 1991).

Ibarra *et al* (1994) observed sulphur dioxide evolution during coal pyrolysis at temperatures as low as 300°C, corresponding to the decomposition of iron sulphate. The remaining sulphate was accounted for as calcium sulphate reacting with pyrite to produce sulphur dioxide (Khan, 1989):

$$CaSO_4 + FeS_2 + H_2O \rightarrow CaO + FeS + 2SO_2 + H_2 \qquad \text{Eq 2-16}$$

Medvedev and Petropolskaya (1966) studied what they termed the 'volatility' of sulphate compounds in coal during carbonisation. The volatility of $CaSO_4$, $FeSO_4$ and

$FeSO_4.Na_2SO_4$ additives in coal were compared by isotopic tracing of sulphur species. The mechanism of transformation of these salts was concluded to involve either:

- volatile sulphur in the gas and tar products;
- organic sulphur in the char or
- corresponding sulphides in the coal char.

Their results showed that the thermal decomposition temperature of sulphates was lower when surrounded by a carbon/coal environment compared to the decomposition of the pure substances (Table 2-2). It was suggested that the free radicals formed during the decomposition of the surrounding carbon/coal environment were responsible for the drop in decomposition temperature. The solid phase reaction of sulphates with the carbon structure was believed to proceeds as follows, where M denotes a metal cation.

$$MSO_4 + 2C \rightarrow MS + 2CO_2 \qquad \text{Eq 2-17}$$

Medvedev and Petropolskaya (1966), along with Ibarra *et al.* (1994b), identified the transformation of sulphates to organic sulphur as a likely decomposition pathway. The following mechanism was proposed, where M is a divalent cation, for example, Ca^{2+}, Fe^{2+}, etc:

$$MSO_4 + coal \rightarrow MS - coal\ complex \rightarrow coal - S\ complex + M^{++} \qquad \text{Eq 2-18}$$

Table 2-2 Comparison of thermal decomposition temperature and volatility of sulphate compounds (Medvedev and Petropolskaya, 1966)

Sulphate Additive	T (°C) Pure Additive	T (°C) Additive in Coal
$CaSO_4$	>1000°C	300-350°C
$FeSO_4$	450-480°C	300°C
$FeSO_4.Na_2SO_4$	450-480°C	250°C

From their work it was calculated that 87.5% of sulphates transformed to organic sulphur, while the remainder of the initial sulphate transformed to sulphides. The sulphides were formed at elevated temperature where they were believed to be the result of free cations, Fe^{++} and Ca^{++}, reacting with sulphur.

Ibarra *et al* (1989) investigated the pyrolysis of weathered sub-bituminous coals to compare their thermal decomposition to raw un-weathered coal samples. Iron sulphate formed by the oxidation of pyrite was observed to decompose above 500°C and yield complex sulphides that accumulated in the chars. These sulphides were unaccounted for using chemical analysis, thereby interfering with the calculation of organic sulphur (calculated by difference that is, total sulphur minus inorganic sulphur). Significant weathering of coals, leading to an increase in the sulphate concentration also seriously affects their physio-chemical properties including their plastic stage during thermo-chemical treatment (Ibarra *et al.*, 1989).

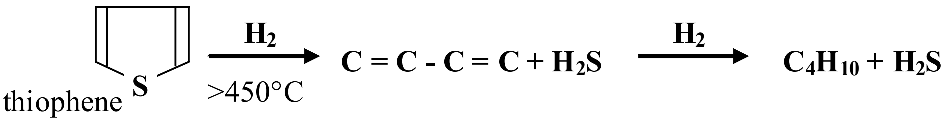
Organic sulphur

The term "organic" characterises that sulphur which is chemically bonded to the coal carbon matrix. Aliphatic thiols, disulphides and sulphides are organic compounds present in coal that tend to decompose easily to H_2S. These are believed to be the predominant organic sulphur compounds in South Australian lignite (Telfer, 1999). *Aromatic* thiols, disulphides and sulphides are much more stable than the former, as the type of substituent stabilises the carbon-sulphur bonding (Calkins, 1987). Thiophenic compounds are the most stable form of organic sulphur and it is unlikely that these exist in appreciable concentrations in South Australian low-rank coals (Telfer, 1999), as aromatic sulphur content usually increases with increasing rank while aliphatic sulphur forms decrease (George *et al.*, 1991; Huffman *et al.*, 1991).

Thiols and disulphides, being the least stable sulphur species in coal, decompose and are reduced easily in the presence of hydrogen. While it has generally been held that thiols in the products of pyrolysis and gasification are secondary products from reactions of H_2S with unsaturated compounds in the gas phase (Attar, 1978), it has recently been suggested that ethyl and methyl thiol are primary products from pyrolysis at fast heating rates (Miura *et al.*, 2001). Thiols can easily be reduced to H_2S and hydrocarbons by hydrogen, and oxygen readily oxidises them to sulphoxides and sulphanes (Robinson, 1978).

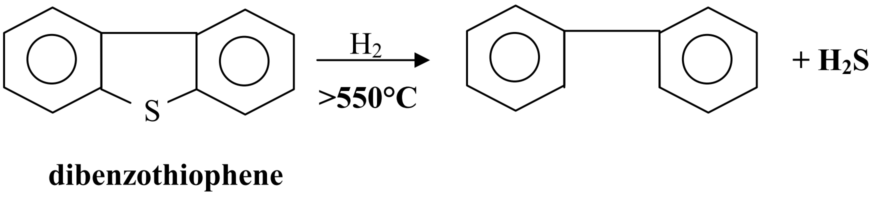
Aryl, cyclic and aliphatic sulphides are more stable organic sulphur compounds. Aryl sulphides are usually very stable due to the resonance of the aromatic ring adjacent the sulphur functional group.

Thiophenes are very stable organic sulphur species and do not readily decompose below 450°C. Alkyl thiophenes lose the alkyl group at temperatures over 500°C and the ring itself undergoes decomposition around 800°C (Attar, 1978). Hydrogenation of thiophene is described by equation 2.20 (Attar, 1978; Khan, 1989). Note that these are model compounds only and are designed to indicate the types of reactions that organically bound sulphur may undergo.



Eq 2-19

Hydrogenation reactions occur more rapidly as hydrogen is generated from the coal matrix during pyrolysis and gasification. Thiophene decomposition may also be catalysed by the presence of material such as alumina or aluminosilicates as is the case with dibenzothiophene in reaction 2.21. Thiophenes may also be formed by the reaction of sulphur or H_2S with organic molecules or by reaction of hydrocarbons such as ethylene with FeS_2.

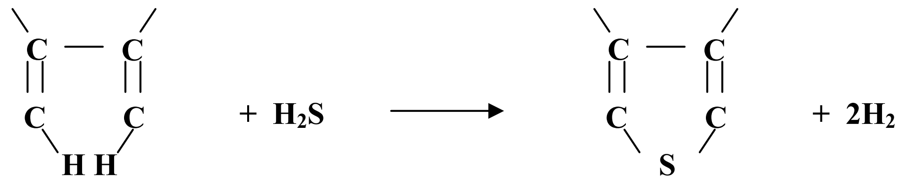


Eq 2-20

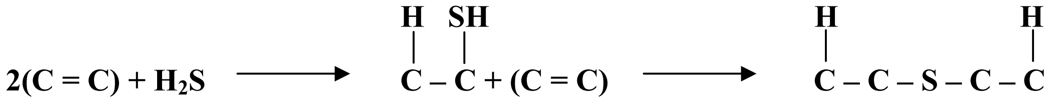
Sulphur fixation

Inter-conversions of various sulphur forms also play an important role in the release of sulphur during heat treatment. Sulphur fixation is the ability of the coal matrix to trap sulphur by forming strong organic bonds. This has been noted by a number of workers as an increase in the organic sulphur content of the coal at a particular stage in the treatment process (Attar, 1978; Cleye, 1984; Khan, 1989; Gryglewicz, 1992).

The decomposition of pyrite is affected by many factors, including the gas phase that is generated within the coal matrix as it decomposes. Cleye (1984) suggested that charge transfer, reaction and desorption at the surface of FeS, result in a number of compounds being formed. The decomposing coal matrix would also produce hydrogen leading to the formation of H_2S. As H_2S diffuses away from the FeS/coal interface through the pore structure, it reacts with active carbon sites that are being generated by the coincident devolatilisation of the coal matrix, forming organic sulphur. This process is described by equations Eq 2-22 and Eq 2-22.



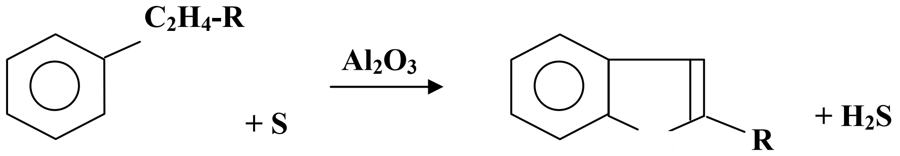
Eq 2-21



$$2(C = C) + H_2S \longrightarrow \overset{H}{C} - \overset{SH}{C} + (C = C) \longrightarrow \overset{H}{C} - C - S - C - \overset{H}{C}$$

Eq 2-22

Thiophenic structures may also be formed by the reaction of organic molecules with pyrite (Attar, 1978). Alumina, silica and other mineral matter may catalyse these reactions as indicated by the following reaction (where R is hydrocarbon):



Eq 2-23

Several researchers have observed that the increase in organic sulphur content of coal with heat treatment corresponds to a decrease in the sulphate content of the coal (Medvedev and Petropolskaya, 1966; Ibarra *et al* 1994; Telfer 1999).

The transformation of sulphate and pyrite to organic sulphur is more favourable than the formation of sulphide during pyrolysis (Kucukbayrak and Kadioglu, 1988). This is due to the stability of sulphide sulphur, which decomposes only at temperatures outside the normal operating range of combustors and gasifiers, as opposed to thiophenic structures, which decompose around 800°C.

Once thiophenic structures are formed during heat treatment it is very difficult to decompose or hydrogenate them (Attar, 1978). This is primarily because the sulphur group often takes part in the resonance of the hetero-ring it is a part of and thus stabilises the carbon-sulphur bonds. This is strengthened even further with aromaticity in the groups that are adjacent the sulphur atom.

2.3.3 Gas phase sulphur chemistry

The reactions of gaseous sulphur species that are released during pyrolysis and gasification also play an important role in determining the product gas concentrations in a fluidised-bed gasifier, and an understanding of these competing phenomena in the gas phase is essential.

Hydrogen sulphide, H_2S, is the most abundant form of gaseous phase sulphur detected during pyrolysis and gasification. The three main gas phase species that are formed other than H_2S are COS, CS_2 and SO_2, either as primary products or the result of secondary reactions of H_2S with mineral mater, the organic matrix or other gas phase species. This section details the gas phase reactions that determine the product composition during the thermo-chemical treatment of coal.

Carbonyl sulphide

Carbonyl sulphide, COS, has been detected by a number of researchers in a variety of pyrolysis and gasification studies (Khan, 1989; Furimsky *et al.*, 1991; Ibarra *et al.*, 1994a; Garcia-Labiano *et al.*, 1995; Garcia-Labiano *et al.*, 1996). Furimsky *et al.* (1991), however, found that COS was only observed during gasification experiments in CO_2 and not during pyrolysis or steam gasification. Attar (1978) suggested that the reaction of pyrite with carbon monoxide was a possible avenue for COS formation.

Ibarra *et al* (1994) suggested that the decomposition of organic matter was also a contributing factor in the formation of COS. During fixed bed pyrolysis studies, two temperature regions of COS formation were identified, the first due to pyrite decomposition. Using a low pyrite coal, the second peak was attributed to decomposing organic matter and its subsequent reaction with sulphur.

Furimsky *et al.* (1991) believed that COS formation did not occur during pyrolysis but only during gasification, implying that COS was formed from secondary reactions in the gas phase between H_2S and CO_2. These experiments were carried out in a fixed bed reactor at 1200K, in which COS was detected after five minutes, at which time pyrolysis was complete. Experimenting with mixtures of 1% vol H_2S in 50% vol CO, and 1% vol H_2S in 50% vol CO_2, Furimsky *et al.* (1991) observed that part of the COS formed in the latter decomposed to CO and elemental sulphur. This implied that while reaction with CO_2 was possible, reaction with CO was the most likely mechanism for stable COS formation:

$$H_2S + CO \Leftrightarrow COS + H_2 \qquad \text{Eq 2-24}$$

Work done by Garcia-Labiano *et al* (1996) on the devolatilisation of large coal particles suggested that COS *is* formed during pyrolysis, particularly of low-rank coals, from the decomposition of highly reactive organic coal matter containing relatively abundant oxygen groups. Ma *et al.* (1989) anticipated that with increasing temperature, the COS concentration would increase due to enhanced organic sulphur decomposition and an increased rate of the secondary reaction with CO_2:

$$H_2S + CO_2 \Leftrightarrow COS + H_2O \qquad \text{Eq 2-25}$$

Robinson (1978) proposed that COS may also be formed via the reaction of CO with free sulphur according to the following reaction:

$$CO + \frac{1}{n}S_n \rightarrow COS \qquad \text{Eq 2-26}$$

Carbon disulphide

Garcia-Labiano *et al.* (1995) observed that the yield of carbon disulphide, CS_2, increased during coal heat treatment with decreasing coal rank. Their experiments were carried out with four coals in a wire-mesh reactor, including two low rank coals, at heating rates comparable to those found in fluidised-beds. CS_2 was believed to be a primary product given that the small particle size and high sweep gas velocity are assumed to limit secondary reactions in such reactors.

Robinson (1978) proposed that CS_2 may also be formed by the reaction of CO with sulphur according to the following reaction:

$$CO + \frac{2}{n}S_n \rightarrow CS_2 \qquad \text{Eq 2-27}$$

CS_2 may be formed from gas-solid reactions involving pyrite and methane or carbon dioxide at temperatures around 800°C, however, for low-rank coals containing relatively little pyrite, this pathway would not contribute significantly.

Khan (1989) concluded that CS_2 formation was the result of secondary reactions involving H_2S, COS and CO_2 as follows:

$$2H_2S + CO_2 \rightarrow CS_2 + 2H_2O \qquad \text{Eq 2-28}$$

$$H_2S + COS \rightarrow CS_2 + H_2O \qquad \text{Eq 2-29}$$

$$2COS \rightarrow CS_2 + CO_2 \qquad \text{Eq 2-30}$$

Calkins (1987) noted a strong relationship between CS_2 and operating temperature during flash pyrolysis of coal in a fluidised-bed reactor. As the temperature increased above 750°C, CS_2 concentration continued to increase up to 1000°C.

Sulphur oxides

According to Furimsky (1991), the most obvious source of SO_2 during gasification or pyrolysis is sulphates, given that SO_x from any other source would require an oxidising agent. However, SO_2 has been detected during pyrolysis and gasification of low sulphate coals (Furimsky *et al.*, 1991; Ibarra *et al.*, 1994a; Miura *et al.*, 2001). According to Furimsky (1991), oxidation of coal prior to utilisation may impact on the SO_2 evolution, by promoting reactions between iron sulphide, from pyrite decomposition, and metal oxides. For example, FeS may be oxidised to FeO via reaction with calcium oxide. FeO would then decompose to iron and react with steam or CO_2 to form ferrous oxide (Fe_3O_4), which would then oxidise H_2S to elemental sulphur and sulphur dioxide.

According to Calkins (1987), SO_2 may be formed from the pyrolysis of organic sulphones in the coal as well as the oxidation of sulphides by chemisorbed oxygen in the organic matrix of the coal. The direct decomposition of $Fe_2(SO_4)_3$ may also lead to the formation of SO_3 in the gas phase, which can in turn decompose to SO_2.

Miura *et al.* (2001) observed the formation of SO_2 during pyrolysis and found that SO_2 formation was affected by the heating rate. During flash pyrolysis, no SO_2 was observed, however, during temperature-programmed pyrolysis at $20Kmin^{-1}$, SO_2 was observed to form below 400°C. It was concluded that the oxidation of thiols may have contributed to SO_2 formation at lower heating rates, however, given the amount of SO_2 formed, it was believed that part of the pyrite in the coal was oxidised to form SO_2 by H_2O and CO_2 that was produced at the low temperatures of the slow pyrolysis experiments.

The formation of gases other than H_2S during heat treatment can provide information about coal structure and the nature of the sulphur bonding in coal. While work has been done to elucidate the major gas phase reactions of the sulphur containing products of pyrolysis and gasification for simple systems, research is required into the factors affecting the sulphur in the product gas for larger scale fluidised-beds.

2.3.4 Factors affecting sulphur redistribution

Understanding what factors impact the form of sulphur in the gas phase is vitally important in the design of effective desulphurisation strategies. Attar (1979) pointed out that the redistribution of sulphur in the products of gasification is dependent on two factors: the initial coal conditions and experimental operating parameters.

Coal properties

A number of coal properties affect sulphur redistribution during pyrolysis and gasification. These include the volatile matter content and ash composition along with sulphur content and form. Mineral matter content and form also has an effect on sulphur evolution.

Coal rank

As coal rank increases, the relative complexity of the organic sulphur compounds present in the coal structure increases. Cernic-Simic (1962) examined the effect of coal rank on sulphur retention during coal carbonisation and concluded that the lower the coal rank:

- the greater proportion of organic sulphur released during carbonisation, depending on the composition and thermal stability of the sulphur group.
- the greater the effect of volatiles evolution on removing organic sulphur, that is, high volatiles flow rate from the coal particles means less opportunity for sulphur fixation.
- the higher the mineral matter content, typically, therefore there is more opportunity for sulphur to be fixed as metal sulphides that are retained in the ash during heat treatment.

Cernic-Simic (1962) also examined the effect of adding pyrite to the coal and then carbonising it at 900°C. While the pyrite retained in the char increased for increasing rank, organic sulphur retention decreased with increasing rank. This was due to the higher rank coals containing chemically stable and non-reactive carbon structures, not readily allowing fixation of the liberated sulphur. Low rank coals, having higher reactivity, reacted rapidly with the H_2S of pyrite decomposition to form highly complex carbon-sulphur bonds not easily reduced at 900°C. Other researchers have observed this phenomenon (Attar, 1978; Gryglewicz and Jasienko, 1988; Ibarra *et al.*, 1994b; Garcia-Labiano *et al.*, 1995).

Gryglewicz and Jasienko (1988) demonstrated that the thiophenic sulphur content in coals of varying rank, as determined by their volatile matter content, increased in complexity with increasing rank. For low heating rates, as in the work of Garcia-Labiano *et al.* (1995) for higher heating rates, it was found that as the rank of coal increased, the yield (to the gas phase) of sulphur during pyrolysis decreased. Garcia-Labiano *et al.* (1995) also observed that the yield of CS_2 during pyrolysis decreased with increasing coal rank, as the high reactivity of low-rank coals allowed for more rapid reaction of the carbon structure with the H_2S evolved. The COS evolved during pyrolysis was also found to be greater for low-rank coals than for coals of higher rank.

Sulphur form distribution

Correlating the distribution of initial sulphur forms and their corresponding pyrolysis products is difficult due to large variations in calculating sulphur mass balances during coal conversion processes (Khan 1989). H_2S absorbs onto metal surfaces, plastic tubing and other active sites found in quartz vessels, for example, leading to inaccuracies in gas and tar phase sulphur measurements.

Fixed bed studies by Kahn (1989) employing 100g of coal at a heating rate of 12.5 $Kmin^{-1}$ with final temperatures of 500°C, observed that the organic sulphur played a strong role in determining the amount of sulphur in the tar and gas products. The tar sulphur was primarily determined by the decomposition of thiophenes in the coal, implying that coals of higher rank, with a higher proportion of thiophenic structures, would lead to greater tar formation. It was believed that pyrite played an important role in the amount of sulphur remaining in the char. Kahn (1989) developed correlations between the sulphur product distribution and the total sulphur content and forms, however, these related only to the experimental conditions of low temperature and heating rate. Other workers have noted the effects of the different sulphur forms in coal during thermal treatment, however, no definitive relationships exist between the sulphur forms in coal and the sulphur forms in the product gas of conversion processes due to many complicated factors. These factors are discussed in the following sections.

Morphological behaviour

The amount of H_2S and other volatile sulphur compounds released during pyrolysis and gasification also depends on morphological changes, or the swelling, that the coal undergoes (Patrick, 1993; Garcia-Labiano *et al.*, 1995; Mondragon *et al.*, 1999). Coals vary greatly in their swelling propensity and in the porosity of the chars and cokes they produce when pyrolysed, with lignite and sub-bituminous coals showing low swelling, producing chars that possess more open pore structures and higher surface areas. The closed porosity of many higher ranking coals may trap gases during pyrolysis and play an important role in the overall H_2S release, particularly as this physical trapping often enhances chemical trapping in the organic matrix or via mineral matter (Mondragon *et al.*, 1999). No account of the swelling propensity has been made in the previous studies of H_2S evolution from the pyrolysis of coals over a range of rank.

The morphological changes that coal undergoes during pyrolysis are known to affect the gasification rate of the chars that are formed (Sharma *et al.*, 2002). These changes are brought about by the change in carbon structure that occurs as a result of thermal annealing at high temperatures and the catalytic effect of mineral matter. They lead to an increase in the ordering of the carbon layers within the matrix. This is why the heating rate is such a crucial factor in the release of volatile sulphur compounds from coal during pyrolysis and the reattachment and subsequent fixation of H_2S in the char.

Sulphur interactions with inorganic matter

The interactions between the sulphur species and the inorganic matter in coal are an important issue in fluidised-bed processes where alkali mineral matter formed of calcium and sodium prevents the evolution of sulphur in the gas phase. A large portion of the inorganic matter in low-rank coal is organically bound alkalines, freely dispersed in the organic coal matrix. Potassium, sodium, calcium, magnesium, aluminium and iron have been found attached as cations to carboxylic acid and phenolic functional groups. In low rank coals, silica and alumina generally constitute up to 60% of the ash where quartz (SiO_2) and kaolinite ($Al_4SiO_{10}(OH)_8$) are the most common forms.

Sodium may exist in the inherent water in coal, either as chlorides and/or sulphates. In Lochiel coal, NaCl has been found to crystallise as sub-micrometer particles and disperse itself evenly within the coal matrix. Sodium may also be found in clay minerals such as sodium aluminosilicates, which, during oxidation on exposure to the atmosphere, transform to release sodium that may then appear as an organically bound inorganic constituent in the coal.

Understanding the role that inorganic matter plays in fluidised-bed gasification is essential to developing stable operating guidelines. Sulphur is closely connected to the problem of ash agglomeration and defluidisation in that sulphur is found in many of the low melting point eutectics that are an issue with low rank coal utilisation.

Chen *et al.* (1999) examined the effects of mineral matter on the product yield and sulphur distribution in hydropyrolysis and pyrolysis of Chinese lignite using a fixed bed reactor. Demineralised samples were heated at $10Kmin^{-1}$ under 3Mpa to final temperatures between 450°C and 650°C. The demineralised samples, and samples with pyrite removed, were examined for conversion, tar yields and sulphur distribution over a range of temperatures and pressures. It was concluded from their study that basic alkaline-earth minerals can trap the released sulphur and increase the sulphur content in char, however, clays and other mineral matter may also catalyze the decomposition of sulphur containing compounds in tar. Mineral matter was also found to reduce the amount of COS and CH_3SH released in pyrolysis and hydropyrolysis, implying that pyrite may not be the only source of COS. Mineral matter plays a role, then, in catalysing the decomposition of organic sulphur groups during pyrolysis, as evidenced by the diminishing CH_3SH evolution with removal of mineral matter and pyrite.

Telfer (1999) conducted TPP experiments comparing raw and acid-washed Bowmans and Lochiel coal, observing that the acid-washed samples did not show the characteristic zone of increasing organic sulphur over 500°C. This indicated that the pyrite and sulphate forms were responsible for the reincorporation of organic sulphur.

Telfer (1999) also examined the effects of different inorganic species and different modes of inorganic attachment by pyrolysing water-washed and acid-washed samples of Bowmans and Lochiel coal that were ion-exchanged with $CaSO_4$, FeS_2 and Na_2SO_4. A summary of the effect of ion-exchanging on sulphur retention in the char after heat treatment to 900°C is given in **Table 2-3**, showing that acid washing resulted in the lowest sulphur retention – only one third of the original sulphur in the coal was retained at 900°C after TPP. Acid washing removed all sulphate and pyrite along with acid-soluble minerals and organically-bound inorganics, with the only minerals retained typically quartz and clay. Water washing, meanwhile, removed the water-soluble inorganics and this included most of the sulphates (98%).

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)

Treatment	Exchanged	Sulphur Retained wt % Total Sulphur
Raw	-	0.46
Acid Washed	-	0.33
Acid Washed	20% $CaSO_4$	0.49
Water Washed	-	0.40
Water Washed	20% FeS_2	0.46
Water Washed	20% Na_2SO_4	0.50
Water Washed	20% $CaSO_4$	0.53

Karaca (2003) investigated the effect of acid washing coal on the transformations of sulphur species during pyrolysis in inert and reducing atmospheres. After treating Turkish lignite with either HCl or HCl and HF, samples were heated to 600°C in a fixed bed reactor and the sulphur species in the char were monitored as a function of holding time and temperature. As a result of HCl treatment, $CaCO_3$, $FeCO_3$, $MgCO_3$ and chlorite minerals were removed from the coal, leading to a decrease in pyrolytic conversion. This treatment, however, enhanced the removal of pyrite but decreased the removal of organic sulphur implying that inorganic species catalyse organic coal decomposition. The combined HCl/HF treatment improved the organic sulphur and pyrite removal during pyrolysis, possibly due to the removal of clay minerals from the coal structure, which were not removed by treatment with HCl alone.

Weathering & coal oxidation

The exposure of raw coal to ambient air results in the oxidation of pyrite to iron sulphide has been observed by a number of workers. However, few investigations have examined the effect of weathering and oxidation on the sulphur transformations during thermo-chemical treatment.

Block *et al.* (1975) found that oxidation of coal samples - 300°C in air for 10 min prior to desulphurisation - had a remarkable effect on enhancing the sulphur removal in a variety of gas atmospheres. For example, oxidation pre-treatment followed by hydrogen treatment at 900°C in a horizontal tube furnace removed as much sulphur in 4 minutes as was removed in 60 min without the pre-treatment.

Ibarra *et al.* (1989) investigated the influence of weathering on the sulphur removal from Spanish low-rank coals by pyrolysis. Utilising chemical and X-ray analysis techniques, it was observed that iron sulphate, formed by the oxidation of pyrite, decomposed above 500°C to yield complex sulphides that accumulated in the chars. An important conclusion from this study related to sulphur determination: the sulphides that were formed, because of their lack of reactivity towards the acid, could not be determined completely by chemical analysis, meaning that the organic sulphur, when calculated by the wet-chemical difference method, was overestimated. Despite using relatively low heating rates for these experiments (7°C.min^{-1}) and operating to 600°C, no re-incorporation of organic sulphur was noted.

Alvarez *et al.* (1995) studied the effect of coal oxidation on char gasification reactivity using bituminous coals. Chars were prepared with forced air circulation at temperatures between 150-270°C. It was observed that char reactivity increased with the degree of coal oxidation. This was attributed to the modification of the porous char structure, along with the development of greater surface accessibility and more active sites. The active sites density increase was related to the increase in oxygen heteroatom density as a consequence of coal oxidation. This observation implies that oxidised coal samples of high sulphur content may show greater loss of organic sulphur compounds due to a more highly developed pore structure, and greater production of COS during pyrolysis and gasification. This would result in the organic matrix reacting more readily during gasification.

Mondragon *et al.* (2002) also conducted experiments to examine the effect of coal oxidation on the reaction of oxidised coal with elemental sulphur. Coal samples were oxidised at 30, 50, 80 and 150°C and then reacted with elemental sulphur in a temperature-programmed pyrolysis reactor. The H_2S evolved from the reaction was monitored by absorption into NaOH. The amount of H_2S produced was highly sensitive to the oxidation temperature, with the samples oxidised at 30°C losing 50-75% of their reactive hydrogen, limiting H_2S formation. Given that this is approximately the temperature at which lignite is stored, oxidation of the coal prior to utilisation may impact on the sulphur evolution characteristics of the coal during fluidised-bed gasification.

Operating conditions

In addition to being strongly related to the initial condition of the coal, sulphur transformations are highly dependent on the experimental conditions under which they are examined.

Heating rate

A number of researchers have examined the effect of heating rate on the evolution of sulphur products during pyrolysis and hydropyrolysis (Cai *et al.* 1993; Sugawara *et al.* 1994a; Miura *et al*. (2001), presented results for heating rates between 1 and 6000 Ks^{-1}.

Cai *et al.* (1993) investigated the nitrogen and sulphur partitioning between product phases for Illinois No. 6 and Tilmanstone (UK) coals as a function of heating rate and pressure in a wire-mesh reactor. These coals were chosen because they had similar organic sulphur contents at 56 wt % and 51 wt % of the total sulphur respectively. However, the two coals showed very different volatile sulphur yield profile, despite having similar total and organic sulphur content – the Illinois #6 coal releasing 60-70% of the original coal suphur to the gas phase, and around 20% to tar, while Tilmanstone pyrolysis resulted in 35-45% of the original coal sulphur evolving in the gas phase and around 10% as tar.

This was attributed to Illinois No. 6 coal having a lower proportion of thiophenic structures than Tilmanstone coal, structures which were more easily volatilised below 950°C. Tar yields, however, were not as sensitive to heating rate as the volatile yields, but the fact that Illinois No. 6 coal showed a greater proportion of sulphur in the tar than Tilmanstone was again indicative of the more complex nature of sulphur compounds in Tilmanstone coal.

Hydropyrolysis studies in a drop tube furnace by Sugawara *et al*. (1989) found that higher heating rates encouraged rapid release of volatiles from the coal, limiting diffusion of hydrogen into the structure to facilitate sulphur removal. This had the effect, however, of preventing pyrite reduction.

Sugawara *et al*. (1994a) pyrolysed a bituminous coal in a Thermo-Gravimetric Analyser (TGA) at heating rates of 20 and 100 $Kmin^{-1}$ with terminal temperature in the range 573-1173K. It was found that while the organic sulphur retained in the char decreased at higher heating rate, it passed through a minimum at 773K before increasing to the residual char level. During rapid pyrolysis in a free fall pyrolyser at 6000 Ks^{-1}, with terminal temperature 1233K, this behaviour was not noted and organic sulphur content decreased as temperature increased.

Miura *et al*. (2001) examined the gaseous products of slow and flash pyrolysis in order to ascertain the heating rate effect on the product distribution. Ten bituminous coals were pyrolysed in a TGA with mass spectrometer (TGA-MS), and a Curie-point pyrolyser. At low heating rate (20 $Kmin^{-1}$), H_2S, COS and SO_2 were observed. At higher heating rate (3000 Ks^{-1}), the total sulphur released was equal to or greater than that at the lower heating rate, however, SO_2 was not observed in the gas products. Methyl and ethyl mercaptan were detected in significant amounts. It was stated that this reflected the primary product distribution for pyrolysis at high heating rates. In a gasifier, however, or at the slow heating rates of the TGA, H_2O and CO_2 would facilitate the decomposition or reaction of methyl and ethyl mercaptan to H_2S or SO_2. The SO_2 formed under slow heating rate conditions was found to exceed the thiol sulphur component, meaning that SO_2 originated from sources additional to thiols. Miura *et al*. (2001) believed that part of the pyrite was oxidised by H_2O and CO_2 to form SO_2 at low temperatures under the conditions of slow pyrolysis.

In order to clarify these results, Miura *et al*. (2001) used a modified controlled-atmosphere-programmed-temperature-oxidation (CAPTO) method to monitor the sulphur form distribution in the char. This method is a modified version of that developed by LaCount *et al*. (1993). Pyrite and three forms of organic sulphur were determined and a relationship between the decomposition behaviour of each form and the formation of sulphur containing gases developed.

Particle size

Heat and mass transfer rates impact on the sulphur evolution from coal during coal thermo-chemical treatment (Garcia-Labiano *et al.*, 1996). For a particle of size 0.5mm or less, it has been found that thermal decomposition is generally controlled by chemical kinetics (Devanathan and Saxena, 1986; Sugawara *et al.*, 1990), however, for particles of the size 30mm or greater, mass diffusion and intra-particle heat transfer effects dominate.

Garcia-Labiano *et al*. (1996) used a non-isothermal wire mesh pyrolysis technique to study the sulphur products of lignite pyrolysis for large particles - sized 353, 894 and 1788 μm – showing that the time required to achieve the same degree of sulphur removal increased with particle size.

Operating pressure

The effect of operating pressure on the sulphur transformations during pyrolysis has been examined in hydrogen atmospheres by Sugawara *et al.* (1989). With increasing hydrogen pressure, the decomposition of pyrite and complex organic sulphur, referred to as refractory organic sulphur, was found to increase. The reduction of iron sulphide, FeS, to iron, was also observed at higher H_2 pressures and back reactions of H_2S and the organic coal matrix were suppressed because the partial pressure of H_2 lead to an increase in secondary gas phase reactions with increasing intra-particle residence time.

The investigation of Cai *et al.* (1993) found that for Illinois No. 6 coal, the total sulphur yield remained constant (65-70%) with increasing pressure, whereas the distribution of sulphur between the tar and gas phase changed markedly, with the proportion of sulphur in the tar dropping significantly with increasing pressure. The high rank Tilmanstone coal showed an increase in the total sulphur yield with pressure and a corresponding decrease in tar sulphur yield.

A recent study by Xu and Kumagai (2003), utilising a continuous free fall pyrolyser, indicated similar results. However, in their study the reduction of inorganic sulphur species was affected only by the temperature and not by H_2 partial pressure. No sulphur compounds other than H_2S were detected, this being attributed to the high-pressure environment leading to high gas residence times, thereby increasing secondary reactions of primary sulphur products.

Gasifying agent

The gas atmosphere surrounding the coal particle plays an important role in the transformations of sulphur compounds during gasification. Much of the earlier literature on the effect of various gas atmospheres on desulphurization was concerned with upgrading the coal for use in combustion furnaces (Snow, 1932; Sinha and Walker, 1972; Block *et al.*, 1975).

Snow (1932) found that at 1000°C, carbon monoxide, nitrogen, carbon dioxide, methane and ethane removed 50-60% of coal sulphur; hydrogen removed 87%; ammonia 82% and water gas 76%. At 800°C, steam removed 84% while water gas with hydrogen chloride removed 72.5%. These experiments were carried out in a fixed bed apparatus consisting of a fused silica reaction tube in which a 15 gram sample was placed and heated in the gas stream. Cernic-Simic (1962), experimenting with coals of different rank in a horizontal tube furnace, found that steam at 600°C achieved greater desulphurisation than hydrogen at 900°C. Sinha and Walker (1972) found the sulphur reducing capacity of gases in the range 400-600°C to be: air> steam-CO>CO>N_2.

Lolja (1995) found that steam had a negligible desulphurisation effect on coal below 600°C. Tsai (1986) believed that steam reduced the oxidation of the organic matrix of coal and increased the oxidation of pyrite, finding that an optimum steam-to-air ratio existed at which coal desulphurisation was maximised and oxidation considerably reduced. For fluidised-bed experiments carried out up to 375°C, a steam-to-air mass ratio of between 4 and 5 g_{steam}/g_{air} (85-90% vol steam) achieved optimum desulphurisation.

Fixed-bed gasification studies by Furimsky *et al.* (1991) using sub-bituminous and bituminous coals examined the evolution of H_2S, COS and SO_2 under three atmospheres: pure N_2, N_2 and steam, and pure CO_2. Most of the H_2S and SO_2 evolved during the pyrolysis stage and continued to evolve at much lower concentrations in steam and CO_2 gasification. COS, however, was only detected in low concentrations and only during gasification in CO_2. Low concentrations of H_2S were detected during gasification in pure CO_2, and COS formation was attributed to the gas phase reaction between H_2S and CO (reaction 5.1). Sulphur removal from coal during heat treatment was found to increase in the order of inert, reducing and oxidising atmospheres.

Karaca (2003) investigated the removal of sulphur from Turkish lignite in a fixed-bed in nitrogen and carbon dioxide atmospheres at atmospheric pressure. It was found that pyrolysis in carbon dioxide had a greater effect on the organic sulphur removal at higher temperatures. Experiments were carried out for six different holding times, eight different temperatures and a range of gas flows. A 15g sample of coal was preheated to remove the volatile sulphur compounds and then inserted into a furnace in which the gas was set to a specific flow rate. The flow rate of nitrogen had little effect on the organic sulphur removal at 350°C, while pyrite removal increased with increasing flow. The opposite behaviour was observed for 700°C where organic sulphur removal was affected by the nitrogen flow. Increasing the CO_2 flow rate at 350°C enhanced organic sulphur removal, while pyrite removal was unaffected. At 700°C, the increasing flow rate of CO_2 had little effect on the organic sulphur and pyrite removal. This work suggested that it was also the residence time of reactive gas species in the reactor, hence in contact with the coal particles, that affected the desulphurisation characteristics of coal at various temperatures and that chemical reaction kinetics were the rate controlling steps at higher temperatures.

2.4 Analytical and experimental methods

Adequate knowledge of the total sulphur and the distribution of its forms in coal is essential because all sulphur, regardless of its form, has the potential to contribute to SO_x emissions during coal utilisation.

How experimental conditions affect the degree of sulphur evolution during pyrolysis and gasification has been discussed previously, with the heating rate, particle size, operating pressure and atmosphere as key parameters. These factors must be considered in order to design experimental systems that allows for accurate and effective analysis of the sulphur redistribution during pyrolysis and gasification.

This section outlines the methods of determination for the total sulphur and sulphur forms, presenting the advantages and disadvantages of each. Its aim is to demonstrate the necessity of having accurate coal analysis when investigating the behaviour of coal sulphur during thermo-chemical treatment. It also describes the various experimental studies, categorised by reactor type, that have been conducted in order to examine sulphur transformations, with specific reference will be made here to the experimental conditions under which the transformations were examined and how they were monitored.

2.4.1 Feedstock and product analysis

While wet chemical and electron microscopy techniques have been shown to estimate the total sulphur and forms with an acceptable degree of accuracy, determination of the forms of organic sulphur is much more difficult. Electron microscopy techniques do not allow for the identification of specific organic sulphur forms in coal. This creates large uncertainties in attempting to characterise the transformations of sulphur from (and between) their various forms during heat treatment by examining the solid phase alone. Attar and Hendrickson (1982) have suggested this as a possible reason for the limited understanding in the literature of the transformations of sulphur during coal utilisation

Indirect techniques to determine the form of organic sulphur species in coal consist of analysing the release of sulphur, or the sulphur remaining in the coal, during thermo-chemical treatment under specific conditions. The sulphur functional groups present are inferred, then, from the temperature zone in which gas phase sulphur is released.

The wet chemical method for determining the total sulphur and forms has two major disadvantages. The first of these is the inability to determine the organic sulphur directly. The determination by difference suffers from the accumulated errors from pyrite, sulphide and sulphate sulphur determination. When comparing the wet chemical methods to electron microscopy methods such as EPM and SEM-EDX there is good agreement for low pyrite coals, however for coals of higher pyrite content, organic sulphur content is largely overestimated by classical methods, due to inaccurate measurements of pyrite, occurring due to insufficient HNO_3 leaching of the coal sample.

While EPM, SEM-EDX and TEM allow for direct and non-destructive determination of organic sulphur content in coal, the need to average the organic sulphur content over a large number of measurements is a disadvantage. Due to the direct nature of these measurements, electron microscopy techniques are often considered more accurate, however, this accuracy is only evaluated when compared to the standard wet chemical procedures.

Destructive and non-destructive organic sulphur analysis techniques require deconvolution procedures in interpreting the data. This means that the results are very sensitive to the type of model employed. Also of vital importance is the interpretation of the chemical or X-ray analyses with respect to 'model' sulphur compounds. A report by Davidson (1994) asked whether the structures of non-thiophenic models were representative and whether the behaviour of thiophenic and non-thiophenic compounds was representative of the coal sulphur behaviour. Improving the deconvolution procedures and grasping the uncertainties in assigning 'model' sulphur compounds to those sulphur forms in coal requires greater investigation in order to answer these questions.

Flash pyrolysis experiments were performed by Calkins (1987) in order to provide insight into the organic sulphur structures in coal. A temperature programmed pyrolyser (TPP) connected to a GC/MS (Gas chromatography/mass spectrometer) allowed the quantification of volatile sulphur species from a range of coals. Solutions of 16 model sulphur compounds were prepared in benzene, at concentrations similar to those of organic sulphur in high sulphur coals, and these solutions were pyrolysed under the same conditions as the coals so that the organic sulphur forms in the coal could be related to the model compounds. In addition to H_2S, COS, CS_2, CH_3SH and SO_2, many compounds such as thiophenes, benzothiophene and methylthiophene were observed to be released, in specific temperature ranges. It was expected that heavier weight heterocyclic sulphur compounds would form, but this was not observed, owing mainly to the trapping of heavier compounds in tar traps. Removal of mineral matter by solvent extraction greatly lowered the amount of SO_2, CS_2 and COS detected. The results of this work, showing decomposition temperatures for various sulphur forms, are shown in **Table 2.4.**

Table 2-4 Decomposition ranges for organic sulphur groups in coal.

Technique	**Flash Pyrolysis**	**TP Reduction**	**TP Oxidation**
Researcher	**Calkins (1987)**	**Mitchell et al. (1994)**	**La Count et al. (1987)**
Atmosphere	**Nitrogen**	**Hydrogen**	**Oxygen**
Aliphatic, aryl thiols	775-800°C	200-320°C	-
Aliphatic sulphides	775-800°C	200-320°C	300°C
Cyclic sulphides	-	-	-
Aromatic sulphides	-	-	420-430°C
Aryl sulphides	850-900°C	320°C	-
Thiophenes	>900°C	400,470°C	420-430°C

Temperature Programmed Reduction (TPR) combines slow heat treatment with a reducing agent. This reducing agent can be liquid or gaseous, with the former referred to as solvent TPR. Work with solvent TPR (Attar, 1979) has proven difficult in the determination of thiophenic sulphur groups due primarily to the low boiling point solvents used. Solvent TPR experiments reported by Attar (1979) showed improvement over normal heat treatment TPR since distinction could be made between simple and complex thiophenic structures.

Mitchell *et al.* (1994) conducted high pressure TPR in a hydrogen atmosphere at 15MPa. Using high pressures enabled the determination of non-thiophenic and thiophenic forms of sulphur and estimated the type of ring structure of the thiophenes because of the temperature peak at which it was reduced. The high-pressure environment, however, could not prevent back reactions completely. These results are also shown in **Table 2.4**. Difficulties arising in TPR include not being able to quantify the sulphur forms that are soluble in tar due to condensation in reactors that are not well swept, that is, with too high gas residence time (Lafferty *et al.*, 1993).

LaCount *et al.* (1987) suggested that the organic sulphur in coal does not respond as well to reductive techniques as to oxidative techniques. Their work monitored the SO_2 evolution profiles from samples of coal heated at a constant heating rate in the presence of 10% v/v oxygen in argon. These results were then compared with TPO profiles of model sulphur compounds in order to ascertain the organic sulphur source responsible for the evolution of SO_2 at a particular temperature. This method was termed the CAPTO (Controlled-atmosphere programmed-temperature oxidation) method, and was used, when analysing the profiles of CO_2, CO, O_2, and H_2O effluent, to provide insights into the structural characteristics of the organic matrix. Other than the effect of pyrite, mass transfer caused broadening of the observed SO_2 evolution peaks while the low exit gas flow caused broader peaks to appear sharper. The results of this study are also shown in **Table 2.4**.

2.4.2 Determining experimental conditions

To study pyrolysis and gasification, a variety of reactors have been employed, depending on the research aim. Since most experiments are designed to determine kinetic rates and reaction mechanisms, it is important to consider the accuracy with which the pyrolysis time, temperature and primary product distribution can be determined in each experimental system (Solomon *et al.*, 1992).

Fixed Beds

The TGA or Thermo-Gravimetric Analyser, using a microbalance to measure coal sample weight variation with time, is one of the most common types of fixed-bed apparatus. The heating rate is set and an atmosphere selected under which the weight loss and products are to be examined. Another more commonly used fixed-bed apparatus is the Horizontal Tube Furnace (HTF), which consists of an externally pre-heated ceramic tube in which a sample of coal is placed for a given time.

A number of studies have been conducted to examine the redistribution of sulphur during pyrolysis and gasification in fixed-beds. This work has focused on characterising the sulphur functionalities by examining the formation of the gaseous and tar sulphur evolved (LaCount *et al.*, 1987; Sugawara *et al.*, 1988; Khan, 1989; Furimsky *et al.*, 1991; LaCount *et al.*, 1993) and the functional groups present in coal-char after heat treatment (Cernic-Simic, 1962; LaCount *et al.*, 1987; Gryglewicz and Jasienko, 1988; Sugawara *et al.*, 1988; Khan, 1989; Gryglewicz and Jasienko, 1992; Gryglewicz *et al.*, 1994; Ibarra *et al.*, 1994; Gryglewicz, 1995; Yperman *et al.*, 1995; Gryglewicz, 1996; Gryglewicz *et al.*, 1996; Gryglewicz and Rutkowski, 2001). However, no fundamental kinetic data has been obtained for these studies.

Sugawara *et al.* (1988) pyrolysed three kinds of non-caking steam coals under hydrogen in fixed-beds, believing hydrogen availability to be the determining factor in sulphur evolution (as H_2S). These experiments were carried out at either atmospheric pressure or 30 kg.cm^{-2} (2942kPa). The reactors, consisting of a 36mm i.d. stainless steel tube for pressurised experiments, and a 21 mm i.d. fused-silica tube for atmospheric pressure treatment, were packed with particles of diameter 0.35-0.5mm. The reactor was then heated to either 500°C or 900°C, at a rate of 10°Cmin^{-1} for the pressurised treatment, or 40°Cmin^{-1} for the atmospheric treatment. A cold trap captured tar and H_2S was absorbed in a 0.05M zinc amine complex solution. The sequential changes in char yield and sulphur form distribution were monitored over the course of the experiments in order to examine the desulphurisation effect of reaction temperature and the how this influenced the product distribution. A coal desulphurisation scheme was proposed that could kinetically explain the complex behaviour of organic and inorganic sulphur forms.

Sugawara *et al.* (1989) conducted similar experiments with a terminal temperature of only 500°C in order to simulate the changes in sulphur forms using the reaction scheme proposed in the earlier paper (Sugawara *et al.*, 1988). Using the kinetic parameters for desulphurisation derived from the work of Yergey *et al*. (1974), the changes in sulphur forms during hydropyrolysis were successfully simulated for eight non-caking steam coals. Increasing the hydrogen pressure increased the reduction of pyrite and the decomposition rate of organic sulphur, while suppressing the capture of hydrogen sulphide. It was noted that the extent of volatile organic sulphur release increased linearly with an increase in the internal surface area during heat up.

Sugawara *et al.* (1994b) also conducted TGA studies at atmospheric pressure in nitrogen for two coals. Approximately 200mg of sample was loaded on SiO_2-Al_2O_3 wool in a perforated basket and heated to final temperatures up to 900°C. The heating rates were either 20Kmin^{-1} or 100Kmin^{-1} with a constant nitrogen flow of 120cm^3 NTP/min. As with earlier work (Sugawara *et al.*, 1988; Sugawara *et al.*, 1989), the sequential changes in sulphur form distribution were monitored analytically and successfully simulated using the parameters of Yergey *et al*. (1974).

Bassilakis *et al.* (1993) studied the sulphur evolution from Argonne premium coals using TG-FTIR where temperature programmed pyrolysis products were combusted and the SO_2 evolution monitored. A 20mg sample of coal was loaded into a platinum sample pan and heated to 150°C at 30°Cmin^{-1} in helium for four minutes to drive off the moisture. The sample was then heated at 30°Cmin^{-1} to a final temperature of 900°C and held for 3 minutes. After cooling to 250°C over about 20 minutes, the sample was finally heated to 900°C with 20cm^{3}min^{-1} O_2 in order to burn out the remaining char. To study the sulphur species evolution, oxygen (10cm^3.min^{-1}) and heat (900°C) were added to the volatile stream in order to convert tar and H_2S to SO_2. Each SO_2 peak, along with the COS detected in the evolution profile, was modelled using the FG-DVC (Functional Group – Depolymerisation, Vaporisation, and Cross-linking) model in order to derive the evolution kinetics, using a distributed activation energy approach.

Kelemen *et al.* (1993) also examined the evolution of H_2S from the pyrolysis of Argonne premium coals released from Temperature Programmed Decomposition (TPD) studies. The TPD apparatus consisted of an Ultra High Vacuum (UHV) reaction vessel in which a 0.5 to 5mg sample was placed. A chromel-alumel thermocouple at the centre of the sample bed monitored temperature and the top of the vessel was packed with quartz wool. Using a method of heating rate variation, data from experiments using at least five different heating rates could be used to determine the activation energy and pre-exponential factors for particular gas phase species, in this case H_2S, CH_4 and light hydrocarbons. A Distributed Activation Energy Model (DAEM) was developed to describe the evolution of gaseous pyrolysis products as a function of time or temperature relying on the derived kinetic data from the TPD experiments. Typical activation energies ranged from 44.7kcal.mol^{-1} to 53.2kcal.mol^{-1}.

Miura *et al.* (2001) conducted fixed bed experiments using a TG-MS and Curie-point pyrolyser, estimating the changes in sulphur distributions using a modified Controlled Atmospheric Programmed-Temperature Oxidation (CAPTO) method. Six Japanese coals, three Argonne premium coals, and one Chinese coal, each in 3mg samples less than 74μm, were pyrolysed in a TGA from room temperature to 900°C at 20Kmin^{-1}. The formation rates of H_2S, COS, CS_2, SO_2, CH_3SH, C_2H_5SH were measured continuously using a mass spectrometer. For the Curie-point experiments, 2mg of coal particles wrapped in ferromagnetic foil were placed in a 4mm i.d. quartz reactor and heated at a rate of 3000Ks^{-1} to final temperatures up to 920°C. Tar was completely trapped by quartz wool placed just after the foil and gas products sampled by a gas-chromatograph with flame photometric detector (FPD). The yields of char and tar were measured by the weight change in the reactor and quartz wool respectively. Employing a modified Distributed Activation Energy Model (DAEM) to analyse the pyrolysis reactions of coal, the distribution of activation energy was between 150-300kJmol^{-1} for aliphatic sulphur forms and between 150-400kJmol^{-1} for aromatic forms. Whereas LaCount *et al.* (1987) deconvoluted the CAPTO SO_2 profiles into three peaks, assigned to non-thiophenic, pyretic and thiophenic sulphur, Miura *et al.* (2001) assigned four deconvoluted peaks at 320, 400, 450 and 500°C representing aliphatic, aromatic, inorganic and thiophenic sulphur respectively. Organic sulphur groups showed this distribution of activation energies whereas the inorganic sulphur forms such as pyrite showed sharp decompositions.

The primary advantage of many fixed bed experiments is that the coal particle temperature can be accurately determined at low heating rates, and residence times can be precisely known. Experiments in a TGA are also relatively easy to perform, providing reliable kinetic data for weight loss or individual species at low heating rates. The major disadvantage of using low heating rate kinetics is that they are applicable only at low heating rate and extrapolating them to higher heating rate is not recommended (Solomon *et al.*, 1992).

Entrained Flow Reactors

The most widely used version of the entrained flow reactor is the drop tube furnace, or free-fall pyrolyser (Solomon *et al.*, 1992) in which coal particles entrained in a carrier gas are injected along the axis of a hot furnace tube into a flowing preheated gas stream. The advantage of using the drop tube furnace in these types of studies is that they can be designed for the complete collection and separation of char, tar and gas products and can be used at high temperature for very high heating rates. Residence times can be well known and controlled and particle velocities accurately calculated.

A series of papers has been published following the sulphur transformations that take place during pyrolysis and hydropyrolysis in a free-fall pyrolyser (Sugawara *et al.*, 1991; Sugawara *et al.*, 1994a; Sugawara *et al.*, 1994b; Sugawara *et al.*, 1997; Sugawara *et al.*, 2003). These papers follow the redistribution of sulphur in coal among the solid, gas and tar phase under a variety of conditions including variations in heating rate, pyrolysis temperature, gas atmosphere (H_2, N_2 and H_2S) and coal pre-treatment.

Sugawara *et al.* (1991) studied the behaviour of seven bituminous and sub-bituminous coals in a drop tube furnace at atmospheric pressure for temperatures up to 1233K. The reactor consisted of a 36mm i.d. fused silica tube surrounded by an electric furnace composed of five heating sections. Adjusting the number of coils of heater wire and altering the position of the heating section in the furnace changed the temperature profile of the reactor. Coal particles were added from a hopper situated above the reactor at a feed rate of 0.2gmin^{-1} and encountered hydrogen gas flowing upwards at $2\ \text{L-NTP.min}^{-1}$. Changing the number of heating sections controlled the residence time of particles in the heating zone. In order to calculate the particle residence time and particle temperature, momentum and energy balances were solved, assuming an average particle heat capacity and average coal emissivity. A cold trap captured the tar formed and hydrogen sulphide was analysed by an ion electrode method. Sulphur species in the various phases were determined as in previous work (Sugawara *et al.*, 1988; Sugawara *et al.*, 1989). The release rate of volatile organic sulphur to tar and gas was found to increase with increasing release rate of volatile matter and with increasing surface area.

Sugawara *et al.* (1994a) also studied the effect of coal density on the behaviour of sulphur forms in a drop tube furnace. A non-caking bituminous coal was separated into three groups by flotation in aqueous zinc chloride and then rapidly pyrolysed up to 1253K in nitrogen carrier gas. The lowest density fraction of coal showed the highest rate of release of volatiles and the greatest desulphurisation, while the highest density fraction evolved no gas phase sulphur products but only sulphur in the tar phase.

More recently, Sugawara *et al.* (2003) examined the effect of hydrogen sulphide on the organic sulphur behaviour during rapid hydropyrolysis. Using the experimental set up described above, hydrogen sulphide was introduced into the hydrogen carrier gas at a concentration of 0.288 vol %. Although the volatile matter content of the coal samples rapidly decreased, the organic sulphur content of the char increased by almost 100% in one case.

Xu and Kumagai (2003) conducted a more recent study utilising a free-fall pyrolyser. At temperatures between 650°C and 850°C with hydrogen pressures up to 5Mpa, the yields of gas, tar and char sulphur were determined for three bituminous coals. The coals were first ground to 75-90μm and fed at a rate of 0.15gmin^{-1} from the top of the reactor with a constant hydrogen gas flow *downwards*. This apparatus differs from that developed and described by Sugawara *et al.* (1990) in that the gas and tar phase were extracted from the bottom of the reactor, not the top (Xu and Kumagai, 2002). Part of the gas product bypassed the tar traps and was analysed either online using a GC with a flame photometric detector (FPD) or removed to a gas-bag for analysis with detector tubes. The tar traps were washed with tetrahydrofuran, followed by filtration with a 0.45μm Teflon membrane to remove any char particles. The tar was obtained by evaporating the solvent, followed by treatment in a vacuum. However, this method may have removed low-molecular weight sulphur compounds from the residue. A global reaction model was assumed and Arrhenius pre-exponential factors, activation energy and reaction orders were calculated for 3 different bituminous coals. The activation energies for total and organic sulphur removal were between 17-26kJmol^{-1} and 13-55kJmol^{-1} respectively, values the authors considered very low, suggesting that the transformation and removal of sulphur from the coal may have been controlled by the diffusion and/or thermodynamic equilibrium during hydropyrolysis under the high-pressure conditions used.

One disadvantage of the drop tube furnace is that volatile products remain hot during the experiment and undergo secondary reactions. This explains why, in the studies mentioned, no gas phase products other than H_2S were detected. The main disadvantage of the drop tube furnace is that the coal particle temperature histories are difficult to determine. They are usually calculated from heat transfer/fluid mechanics models where details of coal and carrier gas mixing with the entrained gas are not well understood. These factors are vitally important in predicting particle temperatures. Work has been done to validate these calculations by attempting to measure the actual particle temperature, however, complete temperature histories of the particle were not validated due to experimental limitations (Solomon *et al.*, 1992).

Wire Mesh Reactors

Wire mesh experiments involve the pyrolysis or gasification of a small amount of coal (~10mg) in an electrically heated wire grid. The heating rate and holding time can be controlled well and the temperature history of the coal can be approximated as equal to a thermocouple bead placed on the mesh or in its folds. Wire mesh experiments allow heating rates from 0.5 to 10^3 Ks^{-1} and the collection of both tars and gases facilitate good material balance closure.

Cai *et al.* (1993) examined the distribution of nitrogen and sulphur among the phases of wire mesh pyrolysis, for two bituminous coals, as a function of heating rate and pressure. Coals of size 106-150μm were prepared and dried overnight at 105°C in nitrogen, after which they were stored under nitrogen. A total of 5-10mg of coal was spread as a 15mm diameter circle at the centre of a 30mm diameter section of stainless steel wire mesh. The wire mesh was folded to give a single layer above and below the coal sample and placed in a pressurised vessel. Two thermocouples, one at the centre and the other 1mm from the edge of the sample, were used to record and control temperature. The sweep gas was directed perpendicular to the wire mesh then through a column cooled by liquid nitrogen for tar collection. Tar and char yields were determined by the weight difference of the tar trap and sample holder before and after each experiment. The helium sweep gas was $0.3ms^{-1}$ for pressures up to 2.0MPa and $0.1ms^{-1}$ for pressures above 2.0MPa. The heating rate for atmospheric pressure tests was varied between 5 and 5000 Ks^{-1} up to final temperature of 950°C with a 5 sec holding time, whereas for pressurised tests, the heating rate was 1000Ks^{-1} with final temperature of 700°C and 10 second hold. Pressure was varied between 0.1 and 7.0MPa.

The tar yields of nitrogen and sulphur were found to increase with increasing heating rates and decrease with increasing pressure. Despite the coals having similar organic sulphur content, the proportion of sulphur in the volatiles differed significantly, demonstrating that the nature of organic sulphur bonding in the original coal structure played a crucial role in determining the volatile release.

Garcia-Labiano *et al.* (1995) also examined the distribution of sulphur among the phases of wire mesh pyrolysis, using two lignites, a bituminous coal and an anthracite. In an argon atmosphere (1dm^{3}min^{-1} flow rate), 10mg of coal was heated at 1100 Ks^{-1} to final temperatures between 700°C and 1200°C and held for 0.5s. The coal particles, of size 75-100μm, were loaded onto the stainless steel grid and held in place by brass electrodes. No tar was collected and all gas channelled to a gas syringe connected to the reactor. This syringe expanded as the products formed in order to prevent an increase in pressure in the system. The product gases were then analysed by GC using FPD. In order to estimate the proportion of tar released, fixed-bed experiments in a horizontal tube furnace were used to estimate the tar yield, calculated by the difference between the char and volatile products. Despite this being undertaken at a heating rate of 5 Ks^{-1}, qualitative conclusions were made regarding the behaviour at higher heating rates.

H_2S, COS, CS_2 and thiophenes were observed for the pyrolysis of each coal, and it was found that the lower the rank, the greater the concentration of COS, CS_2 and thiophenes. In order to derive kinetic data from these experiments, a single reaction model for sulphur evolution in the gas phase was used, and Arrhenius pre-exponential and activation energies obtained. Kinetic parameters were also derived for each specific sulphur compound evolved in the gas phase, however, this was only possible for one of the lignites as the yields of COS, CS_2 and thiophenes were too low for other coals to allow meaningful analysis.

Garcia-Labiano *et al.* (1996) also conducted wire mesh pyrolysis experiments using larger coal particles, the results of which have been outlined in this review (Section 2.3.4). These experiments were carried out using the same procedure as described above, with particles of size 353, 894 and 1788 μm. Using a global reaction model with energy balance for spherical particles, the temperature response of the coal and the sulphur yield during pyrolysis was successfully predicted Further details of the modelling aspect of this study are found in section 2.5.3.

The advantages of these types of experiments are that the pyrolysis times can be precisely controlled, good material balances can be obtained, and secondary reactions are nearly eliminated with a sweep gas and good coal loading technique. The main disadvantage, however, is that coal particle temperatures are not well known during heat-up and cannot be easily measured. A number of factors influencing the temperature recorded by the thermocouple bring into doubt the validity of the assumption that the coal temperature follows that of the wire-mesh. Solomon *et al.* (1992) provides a detailed list of these factors.

Fluidised Beds

Fluidised-bed systems are not usually designed for obtaining data on the primary kinetic mechanisms or rates of pyrolysis and gasification (Solomon *et al.*, 1992). Due to the use of larger particles (>1mm) and heating rates that are not easily calculated or measured, the results of these studies need to be interpreted in terms of coupled reaction and transport models (Agarwal *et al.*, 1984b). The main disadvantages of fluidised-bed systems include: the difficulty of obtaining mass balance closure; variable volatile residence times; secondary reactions of primary pyrolysis products and; unknown particle residence times due to particle elutriation. Fluidised-bed systems have been most useful, however, in determining volatile yields and evolution rates (Solomon *et al.*, 1992).

A number of experimental studies have been carried out to examine coal devolatilisation in fluidised-bed systems (Morris and Keairns, 1979; Jung and Stanmore, 1980; Agarwal *et al.*, 1984a; Stubington and Sumaryono, 1984; Calkins, 1987; Peeler and Poynton, 1992; Czaplicki and Smolka, 1998; Telfer, 1999), however, only a few of these studies have examined the distribution of sulphur in the various products (Calkins, 1987; Czaplicki and Smolka, 1998; Telfer, 1999).

Calkins (1987) conducted flash pyrolysis experiments in a fluidised-bed pyrolyser in order to examine the sulphur containing components in coals of various ranks. Coal particles, fluidised in nitrogen in a coal feeder at room temperature, were entrained and carried into a fluidised-bed of sand held at pyrolysis temperature. The coal pyrolysed in the reactor and the volatiles passed through cellulose thimbles to remove the tar before being sent to a GC for analysis via FPD. These experiments were designed to examine the yield of H_2S, COS and CS_2 with respect to pyrolysis temperature.

Czaplicki and Smolka (1998) used a pilot scale, continuous circulating fluidised-bed reactor to study the sulphur distribution in coal pyrolysis products for a non-coking and brown coal. Process variables were changed in order to examine what effects they would have on the sulphur content of the gas and char products. The process temperature was varied between 910-930°C, while the volumetric flow rate of air supplied to the reactor was set between 100 and 200 m^3hr^{-1}. The feed rate of coal was varied from 78 to 268 $kghr^{-1}$ without char recirculation. Steam was added at 2 % (on supplied coal) for certain experiments, as was dolomite (3%). It was found that the addition of steam enhanced the desulphurisation of the char while the addition of dolomite enhanced sulphur retention in the char. Increasing the coal to air ratio resulted in an increase in the sulphur retained in the char, particularly for tests completed with the addition of dolomite. This study resulted in the development of linear empirical correlations based on the coal-to-air feed ratio in order to predict the sulphur partitioning in the gas and char phase for standard conditions, with the addition of dolomite and the addition of steam. The correlations indicated that neither coal rank or the addition of dolomite or steam had a marked effect on the absolute value of the slope of the line relating the sulphur partitioning to the coal to air ratio.

A number of experimental studies have also been carried out in fluidised-beds under gasification conditions (Maa *et al,.* 1975; Kolodney *et al.*, 1976; Morris and Keairns, 1979; Ma *et al.*, 1989; Marinov *et al.*, 1992; Mason, 1992; Brooker and Oh, 1995; Sue-A-Quan *et al.*, 1995; Middleton *et al.*, 1997; Czaplicki and Smolka, 1998; Hoppesteyn *et al.*, 1998; Molina and Mondragon, 1998; Telfer, 1999; Fang *et al.*, 2001; Hanson *et al.*, 2002; Sciazko and Kubica, 2002; Ocampo *et al.*, 2003) however, as with the devolatilisation studies, little work has been done to examine the fate of sulphur under these conditions and few papers look at sulphur transformations in detail (Maa *et al.*, 1975; Ma *et al.*, 1989; Middleton *et al.*, 1997; Czaplicki and Smolka, 1998). Of these studies, only Ma *et al.* (1989) attempted to model the sulphur evolution in the gas phase.

Maa *et al.* (1975) examined the sulphur transformations of Western Kentucky coals using a quartz fluidised-bed reactor in atmospheres of nitrogen, hydrogen and hydrogen/hydrogen sulphide mixtures. A 22mm i.d. quartz reactor was connected to a sampling syringe that collected the gaseous products for analysis with a GC. 10g of oven dried (105°C for 2 hours) Kentucky No. 9 coal was added to the reactor and heated up in nitrogen to the reaction temperature where it was maintained for 1 hour. Pure hydrogen or hydrogen/hydrogen sulphide mixtures were then added to replace the nitrogen flow. Once a constant hydrogen sulphide concentration was achieved, the bed was quenched with dry nitrogen and discharged for analysis of sulphur forms. The procedure was repeated for different H_2S:H_2 ratios in order to obtain an inhibition isotherm, that is, the point at which the hydrogen sulphide concentration is sufficient to reverse the reaction between ferrous sulphide and hydrogen and thus inhibit desulphurisation. Maa *et al.* (1975) also examined the relationship between the various sulphur forms in coal and treatment temperature, along with additional H_2S concentration, in order to identify the optimum conditions to achieve maximum desulphurisation. It was concluded that maximum desulphurisation could be achieved in hydrogen at around 870°C. The formation of metal sulphide accounted for about half of the sulphur remaining in the char after heat treatment.

Ma *et al.* (1989) examined the H_2S evolution from the fluidised-bed gasification of sub-bituminous coal, lignite and a bituminous coal char. The gasifier consisted of a 15cm i.d. stainless steel pipe encased in a 61 cm i.d. carbon steel pipe. This design enabled the vessel to be pressurised up to 765kPa. The height of the reactor was roughly 4m, with a typical bed height of 1m. Coal was fed at the freeboard and char removed by a nitrogen purged screw conveyor. Downstream from the cyclone, tars and solids were trapped in a steel wool filter while condensable and water-soluble species were removed in a cold water quench. Gas was then either depressurised and vented or drawn into stainless steel glass bombs for analysis with GC. Typical coal feed size was 0.2-0.6mm and the operating variables such as steam to carbon ratio and percentage carbon conversion were varied. The concentration of H_2S and COS were measured and a model constructed to predict these and other product gas concentrations, using the kinetic parameters of Yergey *et al.* (1974).

Middleton *et al.* (1997) conducted pyrolysis and partial gasification studies in a fluidised-bed reactor of 70mm i.d. and 1m height with heating capabilities up to 1200°C. Coal was injected into the freeboard and the tars present in the product gas condensed in a water-cooled condenser or, if in droplet form, in an electrostatically charged polymer filter. Tars were then recovered by dissolution in solvent and subsequent evaporation. Prior to coal injection, a 200mm bed of 250-355μm sand was fluidised in a pre-heated flow of nitrogen to the desired temperature. The coal was first dried in air at 200°C for 1 hour in order to reduce the plastic properties and avoid agglomeration. The product char was then calculated from the ash yields of coal and char and the volatiles yield obtained by difference. This allowed the water generated during pyrolysis to be neglected. The partial gasification experiments were carried out using oxygen-nitrogen mixtures as the fluidising medium. All the coals studied showed a consistent pattern with respect to sulphur release. Expressed as a ratio of sulphur gasified to coal gasified, the pyrolysis behaviour showed enrichment of sulphur in the coal while the partial gasification conditions resulted in an equal gasification conversion of sulphur and carbon.

2.5 Previous work on SA lignite

2.5.1 Behaviour of sulphur

Telfer (1999) conducted a number of experiments using Bowmans and Lochiel coal in order to examine the behaviour of the sulphur groups present during devolatilisation. This section presents the major findings of her work and highlights areas that require further investigation.

Temperature Programmed Pyrolysis (TPP)

TPP experiments were aimed at elucidating the effect of the distribution and nature of the sulphur forms in coal on the subsequent transformations and evolution of sulphur during pyrolysis (Telfer, 1999). They were carried out in a standard muffle furnace where pulverised coal samples of approximately 3 grams each were heated at a constant rate of 17 Kmin^{-1}. When the desired temperature was reached, they were removed, quenched with dry ice and stored for analysis. Standard methods were used to calculate the inorganic and total sulphur values and the organic sulphur was estimated by difference. The results of these experiments were presented as the decomposition of the sulphur forms in coal as a percentage of the total initial sulphur, versus the pyrolysis temperature. These were referred to as TPP profiles.

Lochiel versus Bowmans Lignite

The results of Bowmans and Lochiel TPP experiments are shown in **Figure 2-2**. The profiles show similar distribution of sulphur forms in both. However, the rate of decomposition of organic sulphur in the temperature range 300-500°C is clearly greater for Lochiel coal, implying that Lochiel had a greater proportion of aliphatic sulphides and disulphides than Bowmans (Telfer, 1999). Note also that the reincorporation of sulphur into the organic coal matrix was not as pronounced for Lochiel as for Bowmans lignite, distinguishable between 600 and 900°C.

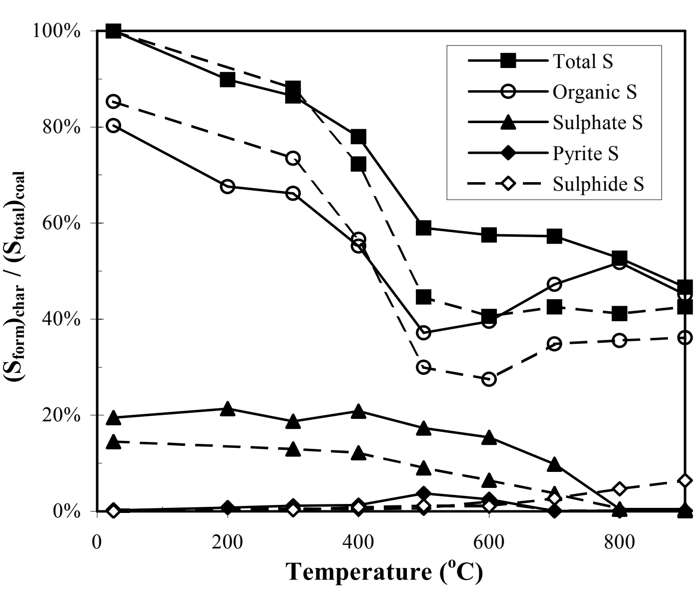


Figure 2-2 Retention of various sulphur forms in the char during TPP of raw Bowmans (————) and raw Lochiel (---------) coals (Telfer, 1999).

The decrease in sulphate concentration occurred sooner for Lochiel coal, indicating that the sulphate compounds are more volatile. It is possible that the release of these more volatile components prevented solid-state transformations to organic sulphur, this being why Lochiel did not show an increase in organic sulphur after 500°C. The pyrite concentration for Lochiel coal peaked at 600°C (the data point is indistinguishable from that of sulphide) as opposed to 500°C for Bowmans, possibly indicating a delayed solid-state sulphate transformation (Telfer 1999).

Sulphide sulphur increased in Lochiel coal from 500°C but not for Bowmans coal in which the sulphide content (FeS, CaS) remained negligible throughout the experiment. As previously discussed (Section 2.3.4), atmospheric oxidation of the coal prior to utilisation may have lead to the formation of complex sulphides not determinable by standard methods. These sulphides may have been the result of decomposing organic sulphur compounds in this region (Telfer, 1999). Telfer (1999) suggested that this indicated a greater proportion of less complex organic sulphur in Lochiel lignite, allowing for the formation and subsequent decomposition of more complex sulphur compounds, that facilitate reactions of local organically bound inorganic matter with the organic sulphur, forming sulphides.

Effect of Inorganic Sulphur Forms

Telfer (1999) also investigated the effect of water-washing followed by the addition of 20% of the original total sulphur content as inorganic sulphur compounds: Na_2SO_4, $CaSO_4$ and FeS_2. The decomposition of added Na_2SO_4 led to an increase in organic sulphur at higher temperatures, but did not lead to a significant pyrite increase, as occurred with raw Bowmans. Sulphides were not observed to form. In the case of added $CaSO_4$, a different decomposition profile was shown whereby sulphur preferentially transformed to sulphide after 700°C, showing a significant increase in char organic sulphur content. Added pyrite, FeS_2, showed decomposition to FeS, as expected, with only a small amount of organic sulphur reincorporation beyond 500°C.

Acid-washing was also undertaken followed by the addition of both 20% and 50% of the original total sulphur content as $CaSO_4$, indicating that the greater added sulphate sulphur suppressed the decomposition of organic sulphur when compared to the raw coal TPP.

These results indicated that the retention of sulphur during pyrolysis was primarily due to the water-soluble sulphate compounds present in the raw coal. The removal of these water-soluble sulphates, therefore, is anticipated to significantly enhance the removal of sulphur from Bowmans and Lochiel coal during heat treatment.

Effect of Inorganic Constituents

TPP experiments were also conducted on water-washed, acid-washed and acid-washed calcium and sodium ion-exchanged Bowmans coal samples in order to understand their effect on sulphur transformations. These results are shown in **Figure 2-3**. Water-washed, acid-washed calcium-exchanged and acid-washed sodium-exchanged samples all began to retain sulphur between 500 and 600°C, whereas the acid washed samples did not.

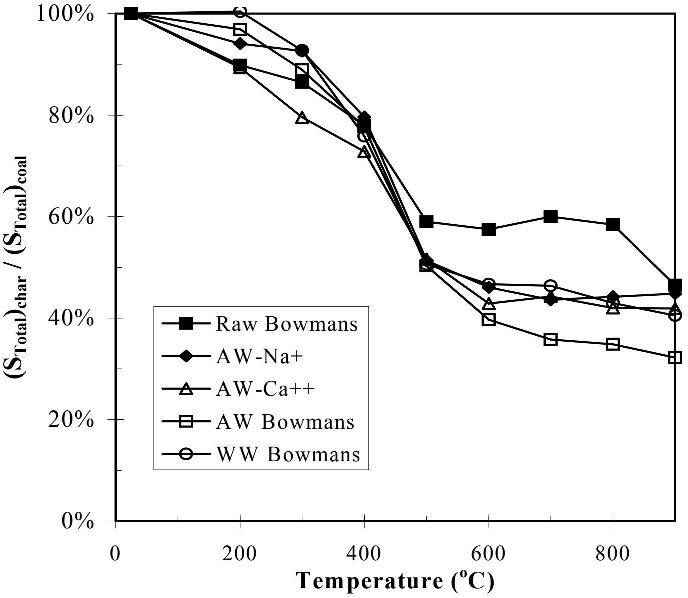


Figure 2-3 Comparison of the retention of total sulphur in the char during TPP of Bowmans coal after various treatments (Telfer, 1999).

Between 200 and 400°C, the sodium had a retaining effect on the total sulphur while calcium appeared to have enhanced the decomposition. This decomposition was not enhanced when coal samples were doped with calcium carbonate to the same calcium concentration as the ion-exchanged coal, implying that the organic bonding of calcium was important in determining the sulphur behaviour. Extensive SEM investigations revealed that sodium and sulphur formed constituents not easily removable by acid-washing, implying that this is why the sodium doped coal samples showed little retention of sodium sulphide in the chars after heat treatment.

Conclusions of TPP Experiments

Telfer's (1999) study enabled a number of conclusions to be made about Bowmans and Lochiel lignite and their behaviour after various pre-treatments. Three main conclusions are listed below:

- Sulphide formation was significant in Lochiel lignite at temperatures over 700°C whereas sulphide formation was negligible for Bowmans, possibly due to the formation of sulphides not determinable using chemical methods. These sulphides may be acid-insoluble compounds resulting from reactions with organically bound sodium.

- The presence of water-soluble and acid-soluble inorganics encouraged retention of sulphur in the char during TPP, however, it was the presence of water-soluble sulphates that enhanced the retention of sulphur in the char post-pyrolysis. Removal of these sulphates would improve the removal of sulphur during heat-treatment.

- Organically bound sodium was reactive towards silica during pyrolysis (more so than calcium) and formed a large portion of water-soluble silicates in the char, on which a coating containing high concentrations of sulphur was found. This may be the start of ash coating that is responsible for agglomeration during fluidised-bed processes.

Fixed-bed Pyrolysis Experiments in HTF

Telfer (1999) conducted fixed-bed pyrolysis experiments using a Horizontal Tube Furnace, pyrolysing pulverised raw Bowmans and Lochiel lignite at 700°C and 900°C in order to examine the effect of heating rate on the sulphur transformations. The results of these experiments confirmed the results of the TPP experiments in terms of the organic sulphur forms found in the raw lignite and the transformations that took place. **Figure 2-4** shows a comparison between the sulphur forms remaining in the char during 5 minutes of fixed-bed pyrolysis at 700°C and 900°C for both Bowmans and Lochiel lignite. The heating rates were predicted using the heat transfer model developed by Heidenreich (1999) and the particle temperature prediction is shown on the secondary y-axis. The peak heating rates were 5.69 and 7.88 Ks^{-1} within the first 30 seconds of pyrolysis for 700°C and 900°C, respectively.

The total sulphur decrease in the early stages of pyrolysis was due to rapid decomposition of organic sulphur and to a lesser extent, the decomposition of sulphates. The rapid decomposition of sulphates also inhibited the solid-state sulphate transformations to organic sulphur, evident when examining the difference in behaviour between 700 and 900°C. The following conclusions were made from these experiments:

- The decomposition of all sulphur forms was directly related to heating rate, with sulphate sulphur showing an increase in its ability to decompose when introduced to an inert atmosphere at 900°C as opposed to 700°C.

- Slower volatiles release favoured the solid-state sulphate transformation to organic sulphur, and this was greatest for Bowmans coal. Even at higher heating rate, solid-state transformations occurred once the bulk volatiles release is finished, at around 500°C.

- The formation of sulphide sulphur was negligible for Bowmans coal at high heating rates, but significant for Lochiel coal. This sulphide formation was likely the result of interactions of inorganic alkali metals with sulphur in the char, as opposed to sulphate decomposition.

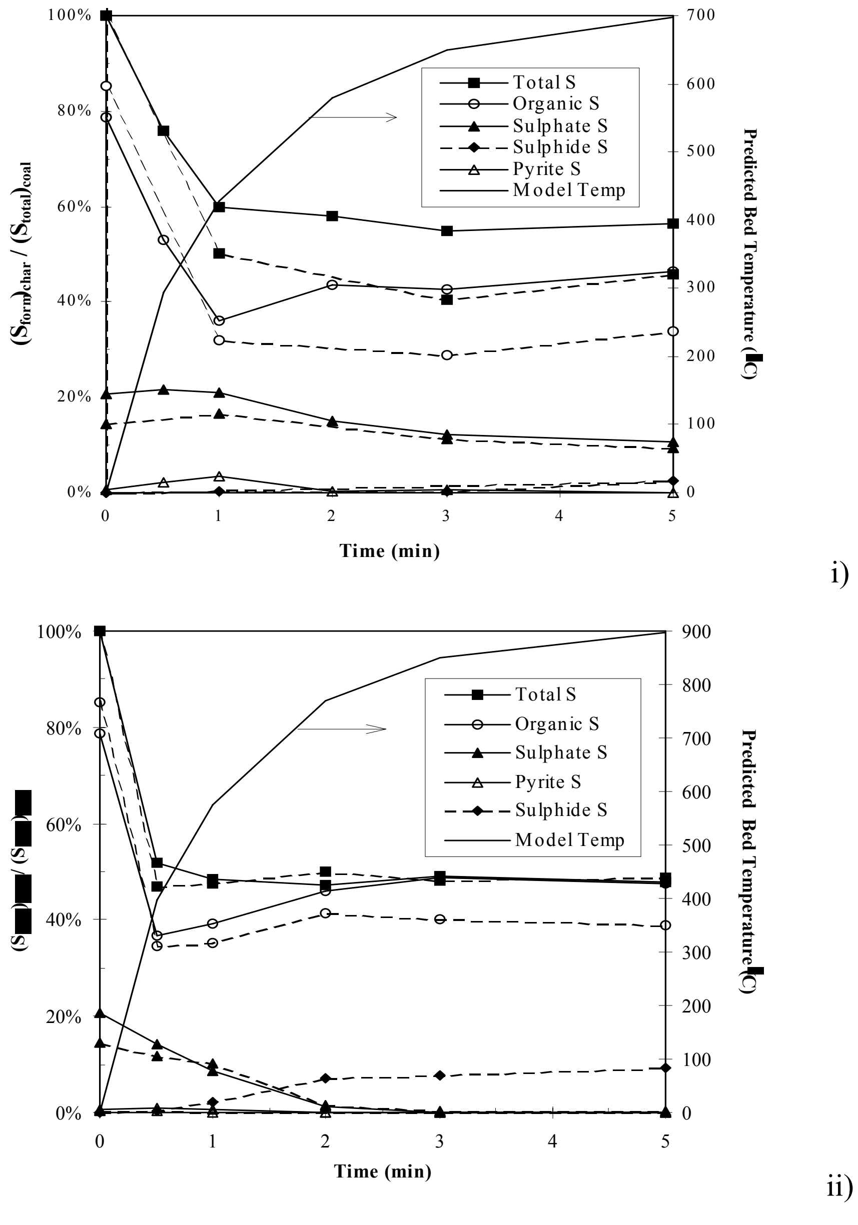


Figure 2-4 Comparison of the sulphur forms remaining in the char during 5 minutes of fixed-bed pyrolysis at 700°C (i) and 900 °C (ii) for Bowmans (——) and Lochiel (-----) lignite (Telfer, 1999).

Bulk Fluidised-bed Pyrolysis

Raw lignite pellets were pyrolysed by Telfer (1999) in a 102mm fluidised-bed reactor at constant temperature in order to examine the role of particle size on sulphur evolution. **Figure 2-5** shows the results of one such experiment for Lochiel and Bowmans coal. The average heating rates calculated by the heat transfer model (Heidenreich, 1999) were 25, 20 and 13 Ks^{-1} for 6,8 and 10mm particles respectively.

The organic sulphur concentration in the fluidised-bed particles reached a minimum before the end of devolatilisation, when comparing the mass loss data to the sulphur species data, suggesting that most of the labile organic sulphur species were decomposed and transported away from the coal matrix. This suggested that the evolution of organic sulphur was dominated by the higher heat transfer rates of the fluidised-bed as opposed to the mass transfer limitations of the larger particles. Telfer's (1999) observation was unexpected since it was considered likely that the fixed-bed experiments, in which decomposition occured under kinetic control, would evolve more sulphur. The larger fluidised-bed particles, on the other hand, were expected to restrict volatiles evolution due to a possible pressure build up in the pores. Further investigation into the effect of pelletising did not indicate that this phenomenon occurred.

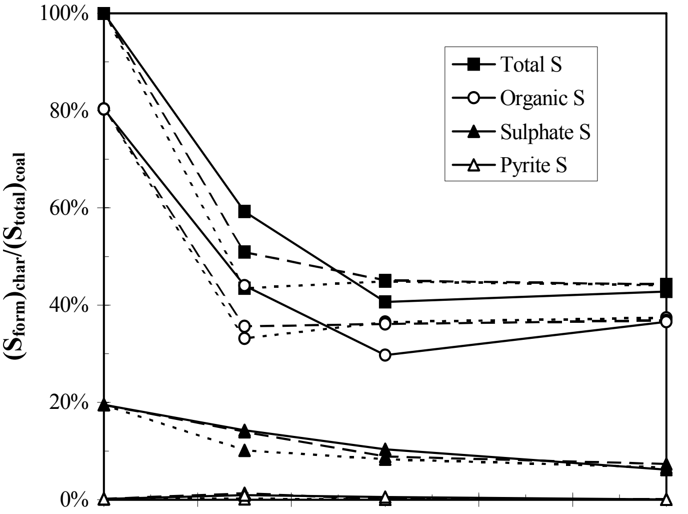


Figure 2-5 Retention of various sulphur forms during two minutes of fluidised-bed pyrolysis at 800°C. Comparison between 6 mm (--------), 8 mm (-----) and 10 mm (———) pellets of Bowmans coal (Telfer, 1999).

An important result from these experiments is that sulphate decomposition was not enhanced by the increased heating rate of the fluidised-bed experiments. In fact, at final temperature of 800°C, almost half of the original sulphate remained. The larger particles appeared to have inhibited sulphate decomposition and the very small differences between the decomposition of the 6-10mm particles support the notion that sulphate transformations were not only affected by heat transfer but mass transfer effects as well.

Single Particle Fluidised-bed Pyrolysis

Telfer (1999) also conducted fluidised-bed pyrolysis experiments in a 20mm reactor using cylindrical coal pellets of 2mm diameter, and 4mm length. The purpose of these experiments was to investigate the intra-particle transformations of sulphur during thermal decomposition. A cylindrical pellet was chosen so that a suitable cross-section of sulphur concentration could be examined. The heat transfer model predicted that sulphur would most likely evolve from the edge of the particle due to the temperature gradient across the cross section, the result of which would be a sulphur concentration lowest at the particle edge.

However, X-ray maps of the cross-sectional sulphur concentration indicate the opposite. High concentrations of sulphur were distributed towards the edge of the particle and the central sulphur concentrations were low, as shown in **Figure 2-6**. The diagram represents three identical X-ray maps of sulphur in the particle before (a) and after (b) pyrolysis featured as dark green areas on the maps. The minimum sulphur concentration detection limit was gradually increased from 1.50 wt% (i) to 4.0wt% (ii) and 5.0 wt% (iii) for the same particle. Pockets of high concentration existed at the particle edge (b, ii) and b, iii). Telfer (1999) explained this phenomenon as a function of back reactions of H_2S with active carbon sites causing reattachment and subsequent reincorporation of the sulphur into the organic coal matrix as the sulphur diffused outwards from the centre of the particle, in support of the earlier work of Zielke *et al.* (1954) who observed similar phenomena for hydro-pyrolysis of coal briquettes of 11mm diameter

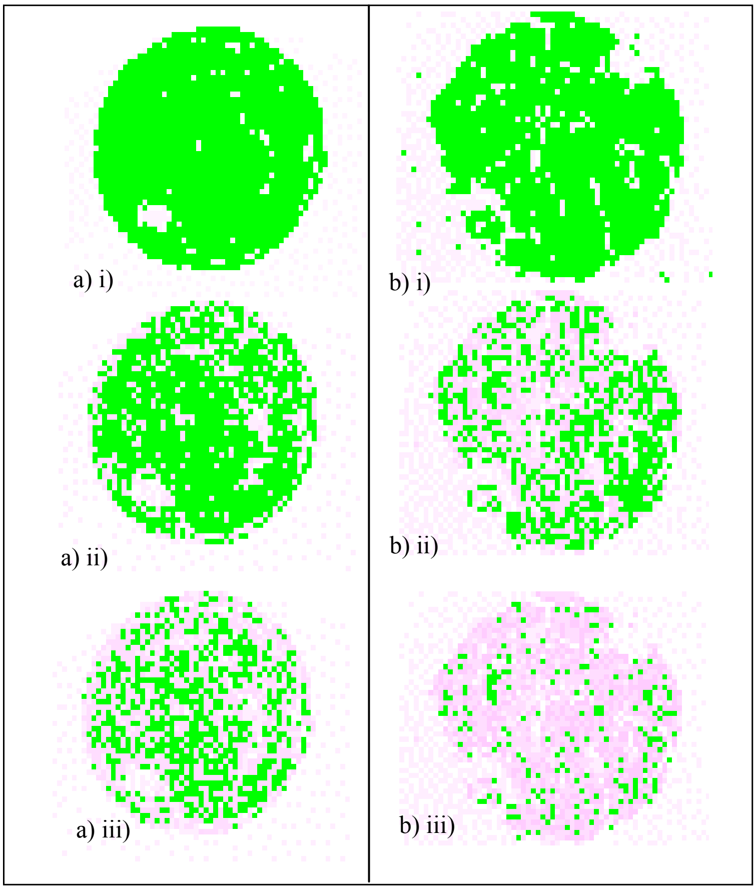


Figure 2-6 Comparisons of the distribution of sulphur in (a) unpyrolysed and (b) pyrolysed raw Bowmans coal for concentrations ranges (i) 1.50 - 33.41 wt%, (ii) 4.0 - 33.41 wt% and (iii) 5.0 - 33.41 wt% (Telfer, 1999) Sulphur appears as dark green in these images.

Conclusions from Telfer's Work

Telfer's (1999) study enabled a number of conclusions to be made about Bowmans and Lochiel lignite and the behaviour of the sulphur forms during pyrolysis in a number of environments. These are summarised as follows:

- Organic sulphur content increased in Bowmans and Lochiel char between 500°C and 800°C, due to the formation of aromatic sulphides, and simple thiophenic sulphur forms from the solid-state decomposition of water-soluble sulphates present in the raw coal.

- Solid-state decomposition of water-soluble sulphates was enhanced by higher heating rates, however, was also strongly affected by mass transfer limitations imposed by the larger particles employed in fluidised-beds.

- The presence of water-soluble and acid-soluble inorganics encouraged retention of sulphur in the char during TPP, with organically bound sodium showing the least propensity for sulphur retention.

- Organic sulphur decomposition in Bowmans and Lochiel coal was proportional to heating rate, showing little relation to the mass transfer limitations imposed by the larger particles of fluidised-beds.

- Larger particles associated with fluidised-beds showed high sulphur concentrations close to the particle surface, with lower sulphur concentration at the particle centre, indicating that the trapping of H_2S as it diffused through the tortuous coal pore structure played a role in its retention.

Recommendations from Telfer's Work

Telfer (1999) suggested that future work regarding SA low-rank coals should involve research into the bonding nature and structure of the organic sulphur functionalities present. More detailed knowledge regarding the exact nature of the inorganic sulphur compounds retained in the char was suggested as an important step in identifying the mechanisms of sulphur retention and ash deposition during FBG.

Telfer (1999) also recommended the extension of study into smaller particle sizes, of the range 1 to 4 mm, and run-of-mine particles where mass diffusion and heat transfer effects are more representative of the actual coal particles to be used in FBG processes.

The most important aspect, according to Telfer (1999), in the development of a suitable model for the sulphur emissions during fluidised-bed gasification, is the extension of investigations into gasification environments to examine the effect of the gasifying agent on sulphur transformations. It was stated that this work needs to be coupled with accurate analysis of the gas phase products, with the intention of deriving the organic or inorganic sulphur forms in the raw coal from which they originate. This work would aid in the development of a suitable reaction scheme for gasification conditions, which coupled to a heat and mass transfer model for a fluidised-bed, would lead to predictions of sulphur concentration in the product gas.

2.5.2 Ash agglomeration and deposition in fluidised-bed gasification

Mitigating the problems of ash agglomeration and deposition associated with high sulphur coals is a major challenge in fluidised-bed gasification. Particularly with low rank coals, the presence of sodium and chlorine in the ash enhance their agglomeration propensity and therefore increase the probability of more rapid defluidisation and shutdown. This section presents the role that sulphur plays in these problems.

Mechanism

During combustion and gasification processes, inorganic constituents are exposed to the surrounding gas environment due to receding carbon surfaces on the coal particle. The interaction of these constituents on the surface of the char allows the formation of low melting point eutectics – compound mixtures that melt at temperatures much lower than the individual melting point of each component. Song and Kim (1993) found that much lower melting points could be obtained for alkali salts and their mixtures when measured in a steam atmosphere as opposed to an inert atmosphere. Therefore, during the steam gasification of low-rank coals, it is expected that the propensity for low-melting point eutectic formation will be enhanced.

Agglomeration within a fluidised-bed occurs as a result of particles adhering to each other under specific conditions. (Yerushalmi *et al.*, 1975) suggested the following steps for agglomeration in a fluidised-bed:

- Small molten beads occur on the surface of the char particles.

- Beads grow by further char gasification or by capturing molten ash from other particles during collisions.
- Beads separate from char during growth due to the existence of high interfacial tension between the molten phase and the char.
- Remaining sticky at the gasifier temperature, beads continue to grow either by coalescence with other agglomerates or with other beads.

The Role of Sulphur and Inorganics

The role that sulphur compounds play in this mechanism is uncertain during gasification, however, several literature studies have investigated its effects (Kolodney *et al.*, 1976; Marinov *et al.*, 1992; Mason, 1992; Brooker and Oh, 1995). Transformations and interactions of inorganic constituents are not as well understood under gasification conditions as under combustion conditions. Fixed-bed gasification studies using the high sulphur South Australian Lochiel coal found that both organically bound sodium and sodium found as NaCl react with silica and kaolin to form sodium silicates and aluminosilicates respectively (Kosminski, 2001). He observed that sodium silicates in gasified chars appeared fused while the sodium aluminosilicates appeared sintered but not fused, and therefore unlikely to create agglomerates as in combustion systems.

Kolodney *et al.* (1976) investigated the behaviour of mineral matter in the Ignifluid Process. While the Ignifluid process consists of a fluidised-bed, it is supported on a travelling grate and operates at temperatures between 1200°C and 1400°C. At these temperatures, evidence of the fusion of iron sulphides was found, their product being a pyrrhotite-pyrite fusion ($Fe_{(1-x)}S$-FeS_2).

Marinov *et al.* (1992) studied the agglomeration of ash during fluidised-bed gasification of a high sulphur Bulgarian lignite, identifying two kinds of ash agglomeration centres: melting and sintering. The first was believed responsible for the ash agglomeration in their study, given that it coincided with the melting temperature of the FeS-FeO eutectic at around 930°C.

Mason (1992) studied the contribution of sulphur to agglomeration during fluidised-bed gasification in the U-GAS® gasifier. The behaviour of iron-sulphur species, derived from pyrite, was the focus of this study. It was observed that pyrite, FeS_2, decomposed to FeS, oxidised to FeO, and then reacted with silica material in the coal to produce low melting point silicate mixtures. This contributed to ash agglomeration in the oxygen rich regions of the gasifier, regions where the local temperature was high. More recent work observed that FeS oxidation to FeO resulted in an iron eutectic compound, FeS-FeO, that had a melting point less that 900°C. Given that the typical operating temperature of a lignite fluidised-bed gasifier is around 900°C, high sulphur content will most likely contribute significantly to agglomeration in oxygen rich zones.

Brooker and Oh (1995) analysed the ash generated during coal gasification using a high calcium coal, suggesting that iron sulphide was the dominant sulphide species in the system. A high iron Pittsburgh No. 8 coal also showed the formation of iron sulphide crystals on the outer surface of ash particles. The mode of formation of these sulphides was believed to be one or more of the following mechanisms:

- During gasification, some pyrite may have been converted to both FeS droplets with small amounts of FeO and Fe within them along with fumes. The oxy-sulphide droplets then migrated to the outer surface of the siliceous ash and those particles with sufficient iron sulphide became sticky enough to deposit in the gasifier.
- After particles left the gasifier, ash particles began cooling to a temperature at which the gas temperature may have exceeded the solidification point of FeS but was still at the softening point of the ash. Additional fume particles then collected on the ash and FeS formed on the outside of the particles due to the combination of H_2S with iron in the siliceous glass.
- FeS fume particles may have collected on the cooler surfaces of the gasifier, forming a fouling layer on which ash particles that had the thickest FeS layer adhered. Once this occurred, the glass, which was low melting, sintered and

devitrified, forming anorthite ($CaAl_2Si_2O_8$) and an iron-magnesium alumina silicate.

- During sintering, the oxy-sulphide particles on the outside of the siliceous particles migrated to pores in the deposit. Above 1000°C, the iron sulphide already deposited re-crystallised and combined with the FeS generated from H_2S reacting with iron from the silicates, forming large crystals of FeS.

Recent studies by McCullough (2007), utilising Lochiel coal in a spouted fluidised-bed gasifier with air and steam as the gasifying medium, found that sulphur was observed primarily as sulphates deposited at the inlet to the spouted bed, where the atmosphere was oxygen rich. These sulphates were sodium, calcium and magnesium, similar in appearance to the coatings found on sand particles observed in the fluidised-bed combustion work of Manzoori (1990). It was observed that at higher operating temperatures, sodium sulphate was preferentially formed at the inlet to the spouted bed.

Conclusions

Sulphur has been found to play an important role in ash agglomeration and deposition in fluidised-bed gasifiers. This work suggests that the formation of an FeS-FeO eutectic is responsible for these phenomenon when pyrite concentration in the coal is high (Kolodney *et al.*, 1976; Marinov *et al.*, 1992; Mason, 1992; Brooker and Oh, 1995). Agglomeration has been observed due to sulphur in the low pyrite South Australian coal, although this coal contains high quantities of organic sulphur and sulphates. Sulphur containing deposits were only observed to form in oxygen rich zones during gasification, however, with sodium sulphate preferentially formed at higher temperatures (McCullough, 2007). Understanding the fate of sulphur in the ash during fluidised-bed gasification processes will assist in the development of suitable in-bed strategies for sulphur capture and removal.

2.5.3 Kinetic modelling of sulphur and gasification

Mathematical modelling is a cost effective method of predicting process performance. Several mathematical models of fluidised-bed coal gasifiers exist in the literature, however, there is a lack of relevant chemical kinetic data for gasification reactions of Australian high-moisture low-rank coals that is suitable for use within the gasification kinetic sub-models (Briedis and Ashman, 2003). This section outlines the literature studies concerned with the development of a suitable kinetic sub-model for sulphur transformations.

CRC Gasifier Model

The Centre has previously developed a mathematical model of a bubbling fluidised-bed gasifier (Yan *et al.*, 1999). This model is based on the two-phase theory of fluidisation and incorporates empirical relationships describing heterogeneous and homogeneous reactions in the emulsion and bubble phases. The model simplifies sulphur chemistry to three reactions. These reactions are as follows:

$$Coal - S + H_2 \rightarrow H_2S \qquad \text{Eq 2-31}$$

$$FeS_2 + H_2 \rightarrow FeS + H_2S \qquad \text{Eq 2-32}$$

$$H_2S + CO_2 \rightarrow H_2O + COS \qquad \text{Eq 2-33}$$

The most serious limitation of the model in terms of the treatment of sulphur, however, is the assumption that all coal-sulphur is instantaneously converted to H_2S during devolatilisation after Eq 2-32. While a useful approximation for relatively low sulphur coals (<0.5 wt% d.b.), more detailed predictions of the sulphur redistribution among the various phases and an understanding of gas-phase sulphur partitioning are required for coals with higher sulphur content. In addition, the kinetic expressions related to the decomposition of pyrite (Eq 2-33) and the gas phase reaction between H_2S and CO_2 (Eq 2-34) are not included.

As demonstrated in this review, the sulphur reaction chemistry is much more complex. Given the substantial fraction of fuel-sulphur released during the pyrolysis stage of coal conversion processes, the development of a suitable model for gasification should begin with a suitable model for the devolatilisation behaviour of coal sulphur. At this stage, however, it is difficult to construct a fundamental model of sulphur transformations in coal gasification due firstly to incomplete knowledge of the transforming reactions, and secondly to limited availability of kinetic data for those reactions that are known (Garcia-Labiano *et al.*, 1996).

Modelling Sulphur Species Transformations

Yergey *et al.* (1974) conducted experiments utilising finely ground bituminous coal in a hydrogen or helium atmosphere. Ten bituminous coals were individually loaded into a 0.5cm quartz reaction tube and inserted into a furnace at room temperature. The temperature inside the furnace was increased linearly at heating rates between 1°Cmin^{-1} and 100°Cmin^{-1}. It was found that the temperature of the tube was unaffected by gas flow rates under 400 scc.min^{-1}, and gas residence times were calculated at approximately 7.5 x 10^{-2} sec. H_2S evolution curves were obtained using a mass spectrometer, giving intensity versus temperature and regions of high H_2S evolution were assigned to the reaction of a particular sulphur functional group with hydrogen. The reaction orders, activation energies and pre-exponential factors were determined for each of these reactions. The back reaction, whereby H_2S adsorbs to an active carbon site, was also assigned a reaction order, activation energy and pre-exponential factor from these observations.

The sulphur functional groups present in the coal were of pyrite and organic origin. Using pure pyrite, two distinct peaks were observed, one relating to the reduction of pyrite to FeS and the other, the decomposition of FeS to iron. At low temperature, for all coals used, a peak appeared at 685°C, which was attributed to organic sulphur decomposition. Not knowing the exact functional group, this was termed Organic I sulphur. Closer inspection of the peak revealed that its shape varied for each of the ten coals used and that it was actually a superposition of at least two desulphurisation processes producing H_2S. The other peak was then termed Organic II sulphur. Common to all coals was a peak at high temperature, which was designated Organic III sulphur, referring to the highly stable thiophenic structures present in coals, in concentrations dependent on their rank.

Kinetic parameters for the hydrodesulphurisation of each of these groups were determined, including the back-reaction of H_2S with the coal matrix. These are shown in **Table 2-5**.

Table 2-5 Kinetic parameters for hydrodesulphurisation reactions (Yergey *et al.* 1974)

Reaction	Reaction Order	$E_{apparent}$	$k_{o\ apparent}$	E kcal/mol	k_o
Org I + Org II + H_2 > H_2S	1	22.0	2×10^6	22.0	2×10^6
Pyrite + H_2 > H_2S	0.5	42.1	1.3×10^{11}	42.1	1.3×10^{11}
Sulphide + H_2 > H_2S	1	25.1	1.8×10^5	43.1	9.7×10^8
Org III + H_2 > H_2S	2	38.1	2.5×10^7	56.1	1.3×10^{11}
Fe + H_2S > FeS + H_2	1	-	-	18.0	6.5×10^4
C + H_2S > $H_2S_{adsorbed}$	1	-	-	38.0	4.7×10^{13}

Sugawara *et al* (1994b) developed a kinetic model of sulphur transformations incorporating the sulphur evolution parameters proposed by Yergey *et al.* (1974). This consisted of a set of competing reactions between release and uptake of H_2S to predict the changes of sulphur forms in coal with temperature, and is depicted graphically in **Figure 2-7**. Experiments were conducted in a TGA for slow heating rates ($20Kmin^{-1}$ and $100Kmin^{-1}$) and a free fall pyrolyser for rapid heating ($6000Ks^{-1}$), using particle sizes between 0.35 and 0.5mm. Frequency factors for desulphurisation and devolatilisation, along with activation energy for volatiles release were varied to simulate the experimental results at the lower heating rates. Small particle sizes were chosen to minimise the effects of internal mass and heat transfer.

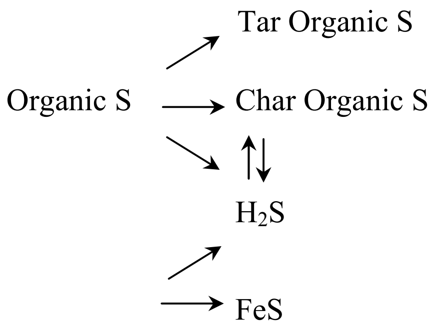


Figure 2-7 Coal desulphurisation scheme incorporating the H_2S uptake reaction (Sugawara *et al.*, 1994b)

These simulations clarified the proposed mechanism and confirmed the validity of the reaction orders and activation energies calculated by Yergey *et al.* (1974). At a heating rate of 6000Ks^{-1}, the residence time of volatiles in the coal particle was so short that negligible uptake of H_2S was observed, suggesting that to extend this method to fluidised-bed systems would require the incorporation of a mass and heat transfer model. Given that Telfer's (1999) work clearly suggests sulphates transformations play an important role in the heat treatment of Bowmans and Lochiel coal, this scheme would not be suitable in predicting their pyrolysis behaviour.

Garcia-Labiano *et al* (1995) employed a single reaction model to describe the sulphur release from rapid coal pyrolysis. A wire mesh reactor was used to simulate heating rates similar to those in fluidised-beds and to minimise secondary reactions. The rate of production of sulphur species, representing the summation of all possible sulphur evolution pathways, was determined by the following equation:

$$\frac{dV_s}{dt} = k\ (V_s^* - V_s) \qquad \text{Eq 2-34}$$

Where V_s^* is the maximum concentration of sulphur precursor in the coal and V_s is the concentration of that precursor at a given time, *t*. The rate constant, *k*, is expressed in the usual manner:

$$k = Ae^{-(E/RT)} \qquad \text{Eq 2-35}$$

The pre-exponential factors, A, and the activation energy, E, were determined for the four coals investigated. High-pressure hydropyrolysis studies by (Xu and Kumagai, 2003) also used this approach. More recent studies by Garcia-Labiano *et al.* (1996) used the kinetic data obtained to accurately predict sulphur product yield during the devolatilisation of larger particles (0.35-2.0mm), where internal heat and mass transfer rates are important factors. Kinetic data were also obtained for the gas-phase sulphur product distribution among COS, CS_2 and thiophenes between 800-1000°C. While accurately depicting the experimental sulphur yield, this method necessitates the use of separate sulphur release/capture kinetics to accurately describe the sulphur species temperature history.

Heat and Mass Transfer Treatment in Devolatilisation Modelling

For larger coal particles, the devolatilisation mechanism changes with the introduction of primary product reactions as they are transported out of the particle. The reactions that can occur during this stage are enhanced by the temperature gradient that exists within the particle. As the volatiles are formed at the particle centre and migrate out, they encounter higher temperatures and undergo secondary reactions.

The unsteady-state heat conduction equation in spherical co-ordinates has been used to predict the temperature response of coal particles during devolatilisation where α represents the coal thermal diffusivity and r, the particle radius (Agarwal *et al.*, 1984a; Garcia-Labiano *et al.*, 1996):

$$\frac{\delta T}{\delta t} = \frac{\alpha}{r^2}\frac{\delta}{\delta r}\left(r^2\frac{\delta T}{\delta r}\right) \qquad \text{Eq 2-36}$$

When modelling the heat transfer in solids, however, the thermophysical properties of specific heat and thermal conductivity play a major role in controlling the accumulation and transfer of heat through the solid (Heidenreich, 1999). With respect to the coal thermal diffusivity, this is related to the coal properties by the following relationship:

$$\alpha = \frac{k_c}{\rho_c C_{p,c}} \qquad \text{Eq 2-37}$$

Where k_c, ρ_c and $C_{p,c}$ represent the coal thermal conductivity, density and specific heat capacity respectively. Therefore, assuming constant thermal diffusivity, α, is inherently dependent on constant thermophysical properties and density. The thermophysical properties of coal reported in the literature for a variety of coals, however, vary significantly. The model of Heidenreich (1999) used suitable literature correlations to predict these properties.

Gasifier Modelling

No large-scale gasification studies have attempted to model the gasification of sulphur except that of Ma *et al.* (1989). The rates of evolution of H_2S were measured for the steam/oxygen gasification of lignite, along with sub bituminous coal and bituminous coal char, and a model formulated to correlate the results. The model assumed instantaneous devolatilisation and partial combustion of the coal followed by rate limited gasification of the char in a single well-mixed stage.

Organic I and II sulphur, as described by Yergey *et al.* (1974), were assumed to be released to the gas phase by hydrogenation during pyrolysis. Pyrite was partially reduced during pyrolysis but this was dependent on the peak temperature and the residence time of coal particles in the freeboard. The pyrite remaining after devolatilisation was reduced to FeS in the gasification stage. FeS, along with Organic III sulphur, was then reduced at a rate described by the kinetics of Yergey *et al.* (1974).

The H_2S-COS shift reaction,

$$COS + H_2O \Leftrightarrow H_2S + CO_2 \qquad \text{Eq 2-38}$$

was assumed to attain equilibrium instantaneously in the gas phase, with the equilibrium constant a function of temperature

$$\ln(K) = A + \frac{B}{T} \qquad \text{Eq 2-39}$$

A and B were determined for temperatures above and below 900°C.

The model successfully simulated the experimental results for sulphur evolution with most predictions deviating by no more than 20% from the measured values. For comparison, the model was evaluated by assuming that sulphur conversion was equal to carbon conversion. The results indicated that the mean deviation of the measured H_2S evolution rates from predictions based on the equal conversion assumption were less reliable than those based on the evolution kinetics of Yergey *et al.* (1974), again reinforcing the validity of the calculated kinetic parameters.

Conclusions

The development of a model to predict the sulphur transformations occurring in fluidised-bed gasification has received little attention in the literature. While models exist to predict the pyrolysis behaviour of coals, few studies have predicted the release of sulphur during pyrolysis. Assuming instantaneous devolatilisation during gasification may be useful as a first approximation, however, suitable correlations regarding the devolatilisation yield of Bowmans and Lochiel coal in a fluidised-bed have not been developed for sulphur functional groups. In order to incorporate a sulphur transformation mechanism and validate the devolatilisation model of Heidenreich (1999) for fluidised-bed pyrolysis, and Yan and Heidenreich (1999) for fluidised-bed gasification, considerable experimental data are required relating to the sulphur yield during pyrolysis and the rate of sulphur gasification in steam and air.

2.6 Literature evaluation

Perhaps make this section a summary of dot points highlighting the gaps in the literature and how this thesis aims to address those gaps. Sulphur is found in coal in both organic and inorganic forms, and while the behaviour of the inorganic sulphur forms is well understood, the reactions of the organic portion of coal sulphur are poorly known. Inter-conversion between inorganic and organic sulphur forms, and the reaction of sulphur in the gas phase with the coal matrix to reform complex sulphur species, are phenomena observed by a number of workers which affect the sulphur remaining in char after pyrolysis.

Pyrolysis is the first step of coal conversion processes, including gasification. During pyrolysis, sulphur evolves as H_2S, COS, SO_2 and a host of other more complex compounds that may undergo secondary cracking to these more simple species. The reactions of coal sulphur have been thoroughly reviewed by a number of researchers and there exists wide agreement in the literature regarding the most important transformations that occur.

Organic sulphur in coal decomposes over a wide temperature range, with simple, less complex compounds devolatilising at temperatures as low as 200°C. Pyrite and sulphates begin decomposing around 400-500°C while more complex organic compounds are sensitive to temperatures over 700°C. Metal sulphides are the most stable species formed during thermal treatment, forming complexes that are not easily removable from coal even at temperatures over 1000°C. The sulphur species evolved as these compounds decompose may re-incorporate into the organic coal matrix to form more complex species, or react with metal ions in the char to form sulphides. The competing and opposing reactions, as well as these interconversions, are affected by a number of factors.

The two main factors that affect sulphur transformations relate to the initial condition of the coal and the process parameters under which they are examined. Coal characteristics including rank, volatile matter content, total sulphur content and form, along with inorganic matter content and form, impact on the coal sulphur behaviour remarkably. Experimental operating conditions such as temperature, pressure and gas atmosphere also affect the degree of sulphur evolution during pyrolysis and gasification. Particle heating rate is a major influence on how sulphur is released. Higher heating rates lead to an increase in the volatile sulphur yield, decreasing the back reaction of evolved sulphur with the organic coal matrix and inorganic matter. Coupled with this is the effect of particle size, with larger particles evolving less sulphur. Recent work at the Cooperative Research Centre for Clean Power from Lignite has identified that this is primarily due to mass transfer effects and not the slower thermal response of the larger particle. Operating pressure is also important in the release of coal sulphur, particularly in the formation of volatile sulphur products, although no large-scale fluidised-bed studies on its effects have been undertaken. Crucial to the study of sulphur gasification rate is the impact of gas atmosphere on the extent of sulphur evolution. Literature studies reveal that sulphur removal from coal is enhanced in the order of inert, reducing and oxidising atmospheres. No large-scale studies have been undertaken to examine the effect of gas atmosphere on sulphur transformations during fluidised-bed gasification. Crucial to any experimental study, though, is effective monitoring and analysis of the sulphur transformations.

A great deal of literature exists regarding sulphur species analysis. Difficulties arise in completely accounting for pyrite and sulphates using standard methods and it has been found that oxidation of coal prior to utilisation, particularly in storage, leads to the formation of complex sulphides during thermochemical treatment that are not determinable using standard procedures. The organic portion of coal sulphur, which is classically determined by the difference between the total sulphur in a coal sample and the inorganic forms, is dramatically affected by these difficulties. As such, organic sulphur determination has recently been the focus of wide literature study centred on both direct and indirect methods of determination. While these methods have enabled the determination of total organic sulphur, including the classification of organic sulphur forms, their accuracy is still evaluated in comparison with standard methods.

Further development of these analytical techniques is required in order to aid the development of suitable gasification studies to examine sulphur redistribution.

A number of experimental studies have been carried out to examine devolatilisation and gasification in a variety of reactor configurations, however, few of these studies have examined the distribution of sulphur in the various products and while several researchers have obtained kinetic data on the primary sulphur forming mechanisms, larger scale fluidised-bed systems have not been used for obtaining these on the primary mechanisms or rates of pyrolysis and gasification - volatile sulphur yields and sulphur evolution rates during gasification have been evaluated for only one study involving a pressurised fluidised-bed. There is a significant lack of data in the literature describing the volatiles yield and sulphur gasification rate from larger rigs, information that is essential in developing strategies to mitigate the adverse effects of utilising high sulphur coals. These effects include the release of sulphur species to the gas phase and the formation of low-melting point compounds involving sulphur in the ash phase.

Several studies in the literature suggest that the formation of an FeS-FeO eutectic is responsible for these phenomenon utilising coals of high pyrite concentration. Agglomeration has been observed, however, due to sulphur in low pyrite Lochiel coal, with the formation of sulphur containing agglomerates observed in the oxygen rich zones of a spouted-bed gasifier. Sodium sulphate was preferentially formed at higher operating temperatures. What impact the addition of bed material for in-situ desulphurisation has on this phenomenon has not been investigated.

Previous pyrolysis studies at the Centre have enabled a number of conclusions to be made about the behaviour of the sulphur forms in Bowmans and Lochiel lignite, having a number of implications for fluidised-bed gasification. This provided a detailed quantitative and qualitative understanding of the behaviour of the coal sulphur under a variety of pyrolysis conditions and evaluated the effects of heating rate, particle size and intra-particle diffusion effects. Given the complex nature of the fluidised-bed gasifier system, decoupling and modelling the transformations that take place will prove challenging. What is the gap?

The development of a model to predict the sulphur transformations occurring in fluidised-bed gasification has received little attention in the literature, due firstly to incomplete knowledge of the transforming reactions that take place, and secondly to the limited availability of kinetic data for the reactions that are known. While models exist to predict the pyrolysis behaviour of coals, only one literature study exists in which the sulphur transformations occurring during gasification were modelled. While the assumption of instantaneous devolatilisation employed in this study may be useful as a first approximation, suitable correlations regarding the devolatilisation yield of sulphur and the gasification rate are required for a more accurate treatment of gasification behaviour.

3 EXPERIMENTAL WORK

3.1 Introduction and Objectives

This chapter presents a description of the experimental equipment, techniques and materials used in the present study.

The experimental programme for this work is designed to achieve a better understanding of the behaviour of sulphur during the pyrolysis and gasification of low-rank coals, with objectives to determine:

- the extent of volatilisation of sulphur from coal during pyrolysis and gasification, particularly with respect to carbon evolution.
- the influence of the sulphur distribution (organic-inorganic) on the transformations of sulphur and its re-distribution during pyrolysis and gasification.
- the influence of mineral matter and particle size on the transformations of sulphur during pyrolysis and gasification.
- the rate of conversion of sulphur (and carbon) during gasification with steam and obtain a relation of the conversion and reaction time for sulphur (and carbon) gasification under various conditions.

Two different experimental systems were used in this programme, the first consisting of a horizontal tube furnace for fixed bed operation and the second a 50mm atmospheric pressure fluidised bed apparatus. Both allowed either pyrolysis or gasification experiments to be undertaken.

All gas phase analysis work was completed on-site, while solid phase analyses were performed by third party commercial entities, and this is noted where appropriate.

3.2 Coal Preparation

In the 1980's, considerable work was done in finding viable coal deposits in South Australia's mid north region by the then Electricity Trust of South Australia (ETSA). This work included core sampling to delineate the resources and a trial open cut pit at Lochiel.

Large quantities of Lochiel and Bowmans coals are stored in woven polypropylene bulker bags with polyethylene lining. It is from these bulk storage bags that as mined coal samples are obtained and transferred to sealed bins in discreet quantities prior to the drying step.

Dry coal is prepared by laying a sufficient quantity of as-mined coal on drying trays in 10 mm thick layers and allowing the samples to sit until equilibrium with the laboratory atmosphere is achieved. The coal is placed in a dry part of the lab away from direct sunlight and draughts, and stirred periodically in accordance with Australian Standard method AS 1038.1–1992, Section 2. Dried samples are typically obtained after two to three days drying time. Equilibrium moisture content, at typically between 10-15% weight basis, is indicated within two to three days by cracking of the coal layers.

Air-dried samples of these coals are sieved to size fraction 1.0-1.7mm in order to obtain a size typical of fluidised-bed applications. Post drying and sizing, the coal is stored in 2L, air-tight plastic containers until utilisation.

In order to prepare coal that is free of mineral matter (except silica), prolonged leaching with ambient temperature acid is undertaken - in this study for the Lochiel coal only. This acid-washing is carried out by mixing 80g of as received coal, sieved to exclude less than 1mm particle size, with 400mL of 0.5M hydrochloric acid (HCL) solution in an 800mL Erlenmeyer flask. The mixture is stirred continuously using a magnetic stirrer and left for two to three days before being washed and filtered with demineralised water until chlorine is not detected in the solute by silver nitrate solution. The water is then decanted and the acid-washed coal recovered by filtration under vacuum using filter paper. The acid-washed coal is then air-dried according to the previously described procedure and sieved once more to obtain a 1-1.7mm and less than 500micron particle size fraction. Post drying and sizing, the coal is stored in 2L, air-tight plastic containers until utilisation.

3.3 Analytical Methods for Coal and Char

3.3.1 Wet Chemical Methods

Several standard techniques and confidential methods are employed for characterising the feed coal for experiments. Moisture and ash yield are determined according to HRL method 1.6, an in-house confidential method used by HRL Pty Ltd. Fixed carbon and volatile matter are determined according to Australian Standard method AS 2434.2. Sulphur and chlorine content are carried out according to AS 2434.6 and AS 1038.8, respectively. A confidential HRL method was used to determine the coal mineral content. Analysis of the AW-LL sample, air-dried, is shown in **Table 3-1**.

3.3.2 X-Ray Diffraction (XRD) Analysis of Chars

X-Ray Diffraction (XRD) analysis provides mineralogical information, giving the crystalline structures existing in the ash. Analysis is carried out by the CSIRO Division of Land and Water. Samples for analysis are oven dried to 60°C then ground with mortar and pestle before being lightly pressed into aluminium sample holders. The XRD patterns are recorded with a Philips PW1800 microprocessor-controlled diffractometer using Co Kα radiation, variable divergence slit, and graphite monochromator. The diffraction patterns are recorded in steps of 0.05° 2θ with a 3.0 second counting time per step, and logged to data files for analysis with CSIRO technicians interpreting the patterns.

Table 3-1 Analysis of Lochiel (LL) and Bowmans (BW) coal

Component	Description	Lochiel	Bowmans	Acid-washed Lochiel
Moisture (% as received)	Moisture	13.76	17.48	10.33
Proximate analysis (% dry basis)	Volatile matter	46.61	48.1	50.38
	Ash Yield	14	13.8	4.42
	Fixed Carbon	39.39	38.1	45.2
Ultimate analysis (% dry basis)	Carbon	58.6	55.7	63.4
	Hydrogen	4	3.4	4.3
	Nitrogen	0.46	0.43	0.48
	Sulphur	2.96	5.07	2.7
	Chlorine	0.42	1.48	0.1
Sulphur form (%db)	Sulphate	0.51	1.25	0.06
	Pyrite	0.032	0.014	0.012
	Inorganic S	0.54	1.26	0.07
	Organic S	2.42	3.83	2.63
Elemental ash analysis (%db)	Si	1.62	0.56	1.31
	Al	0.55	0.46	0.27
	Fe	0.43	0.87	0.19
	Ti	0.068	0.005	0.14
	K	0.031	0.025	0.006
	Mg	0.77	0.96	0.05
	Na	0.8	1.82	0.02
	Ca	1.29	0.46	0.13

3.4 Experimental Equipment

3.4.1 Fixed bed apparatus

It was decided to use a simple reaction system to pyrolyse and gasify the coal in the first instance, and move to the more complex fluidised-bed gasification environment to validate and build on that first stage. A simple reaction system was chose in the form of a horizontal tube furnace, as it has the advantage over a fluidised bed of being able to:

- minimise secondary reactions of volatiles with other volatile species and/or char
- prevent the loss of catalyst/product with fines carry over
- more accurately predict residence times and calculate mass balances

The HTF used in this study was a Carbolite Model CFM 14/2 furnace, controlled by Eurotherm 91e temperature controller/programmer. A 25mm internal diameter by 500mm length non-porous “Pythagoras” type ceramic tube, housed inside the refractory lined furnace, is heated by four Kanthal silicon carbide heating elements capable of delivering a maximum of 2.25kW. The HTF can be heated to 1400°C for a range of heating rates 5-50°Cmin^{-1}. An 80mm hot zone is maintained along the centre of the ceramic tube at uniform temperature, within which the coal samples are placed, secured either within a 10mm ID quartz tube (for pyrolysis experiments) or 10mm ID stainless steel tube (206L, for gasification experiments).

Gas supply

Gases are supplied to the reactor (argon and nitrogen) from G size ultra-high purity gas bottles, through 1/8th inch copper tubing, while 1/8th inch Teflon tubing directs the flow of products from the reactor to the sampling system. The flows of argon and nitrogen are regulated by Brooks 5850S mass flow controllers (MFCs), and a stainless steal chamber inserted in series after a moisture trap, to ensure a consistent and constant flow of reactants and carrier gas to the vessel

Steam System

In order to generate a steady and consistent flow of steam to the reaction vessel for steam gasification experiments, a peristaltic pump, the Masterflex C/L Pump System, is connected to a 1/16th inch stainless steel line feeding water to the hot zone of the reactor via connection to a Swagelock Cajon fitting. The steam generator consists of a 10mm 206L stainless steel line with two 30mm internal diameter stainless steel pressurised sample bulbs welded in series to ensure sufficient homogenisation of the water feed (pumped at 180RPM). Using 0.0099 inch i.d. Tygon tubing gives a demineralised water flow rate of 0.1mL/min to be accurately fed to the steam generator. This system is shown schematically in Figure 3-2.

3.4.2 Fixed-bed methodology

The experimental system for the Temperature Programmed Pyrolysis (TPP) and Fast Pyrolysis experiments is depicted in Figure 3-1.

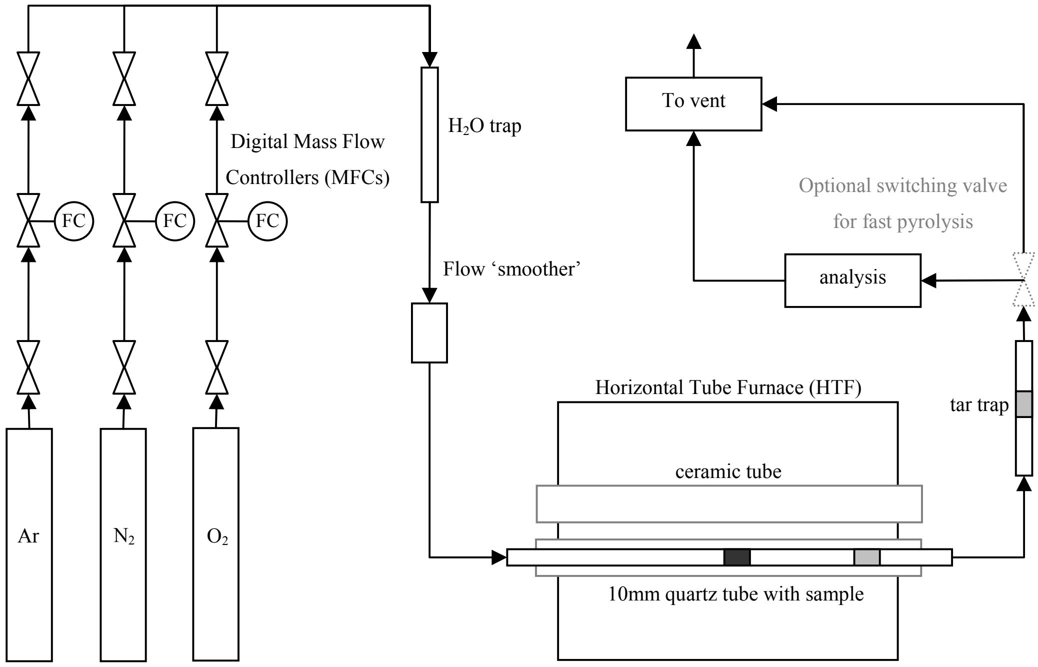


Figure 3-1 Schematic diagram of the Horizontal Tube Furnace (HTF), configured for Temperature Programmed Pyrolysis (TPP).

Temperature Programmed Pyrolysis

For the TPP work, the 500mg sample of coal, packed between quartz wool in the quartz tube, is inserted into the reaction zone of the HTF and heated to 50°C. At this point, gases are analysed for O_2 to ensure that the reaction vessel is inert. After this check, the vessel temperature is set to 1200°C and the gases analysed continuously while the temperature-programmed stage of pyrolysis took place at 15Kmin^{-1} heating rate. At 1200°C, after a 5 minute holding time, the coal sample is withdrawn to cool, still under inert conditions, then weighed and stored in 5mL glass vessels with hard plastic screw-top sealers to prevent contamination.

Fast Pyrolysis

For the fast pyrolysis work, a 50mg coal sample is prepared as above, however, the sample is not inserted into the hot zone of the HTF until the furnace is brought to reaction temperature (700°C to 1000°C) and the vessel intertised. After confirming that no oxygen is present, the coal sample is plunged into the hot zone and pyrolysed for 5 minutes before being withdrawn and allowed to cool, still under inert conditions. When analysing via Mass Spectrometry, continuous profiles are obtained under a 95% He/5% Ar mix. In order to determine the yield of compounds from pyrolysis, all gaseous products are collected in Teflon bags and analysed using the micro GC immediately after the experiment is completed.

Steam Gasification

The experimental system for the steam gasification experiments is depicted in Figure 3-2.

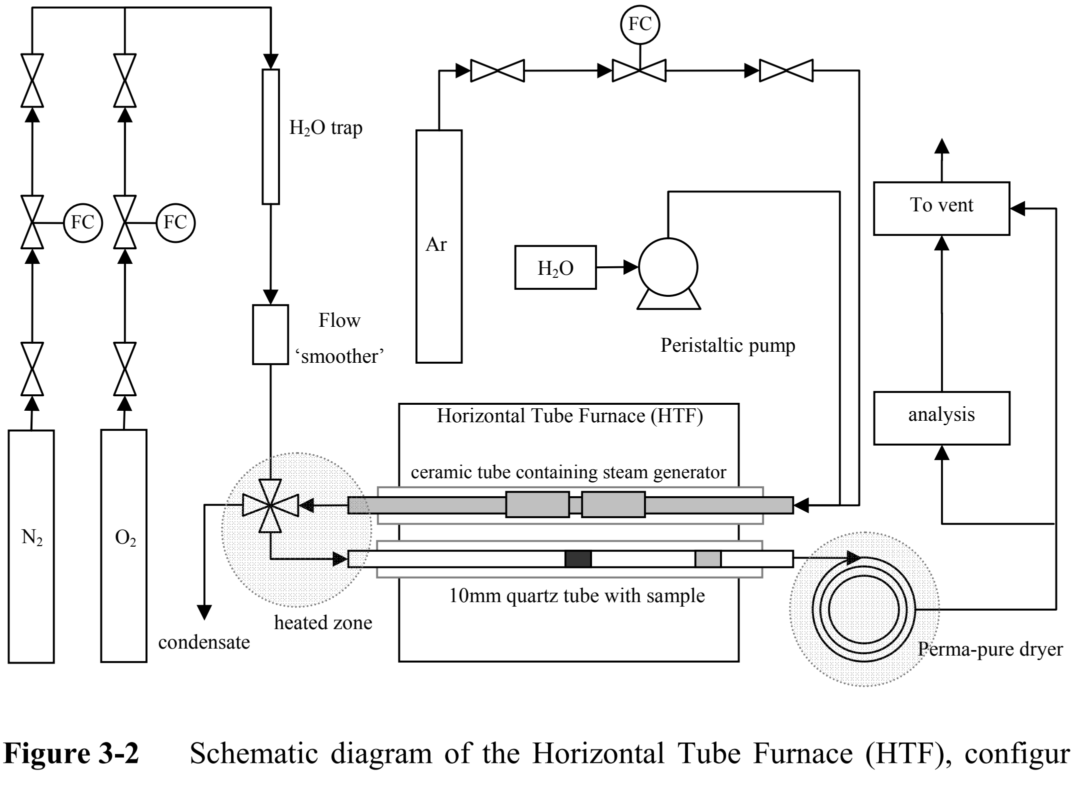


Figure 3-2 Schematic diagram of the Horizontal Tube Furnace (HTF), configured for gasification in steam.

Char Preparation

In order to make char suitable for conducting steam-gasification experiments in the HTF, a 2 gram sample of air-dried Bowmans, Lochiel and acid-washed Lochiel coals is loaded in a 10mm quartz tube as above, however, as during the fast pyrolysis experiments, it is not inserted into the hot zone of the HTF until the furnace is brought to the char making temperature of 800°C. Upon confirming that the atmosphere in the tube is inert (N_2 at 400mL/min) the sample is plunged into the reactor for 5 minutes of pyrolysis. After 5 minutes the sample is removed and cooled, still under inert conditions, and the char recovered for further experimentation.

Steam production

To confirm an accurate steam flow rate, prior to each experiment, a measuring cylinder is filled with deionised water from the feed tank and the feed tubes are placed into the vessel. The volume of water pumped out of the measuring cylinder over 10 minutes is measured, and a mass flow rate of water calculated for a given pump setting. The process was repeated until the pump setting acquired gives an accurate and repeatable flow rate of 0.1mL/min.

A switching valve positioned outside the HTF, and heated by a 400W magnetic stirrer/plate heater to external metal temperature of 200°C, ensures that the steam does not condense at any point prior to its introduction to the reaction tube.

A sample of char (500mg) is packed in quartz wool and positioned within a 10mm ID 206L stainless steel tube. The tube is then placed in a horizontal tube furnace (HTF) at ambient temperature and connected to both the steam generator and gas-dryer in order to conduct steam gasification experiments. It is inertised using 100% Ar and heated to reaction temperature (800°C) while a mixture of 25% vol steam in N_2 (N_2 400mLmin^{-1}) is prepared in the steam generator. Using the switching valve, the mixture is swapped with Argon at the commencement of an experiment and the product gases dried and analysed via micro-GC and MS.

Gas Conditioning

The product gases, leaving the reaction vessel, pass through a quartz wool plug to ensure that no particulate matter is passed through to the gas drying unit. This section of the system is electrically heated using a silicone rubber cable heater, with metal temperature maintained at 200°C, to ensure that no condensation of water occurs before entry into the drying unit.

A Perma Pure drier, MD-110-96-S-4, is used to ensure that a dry gas sample was delivered to the micro-GC and that no moisture condensed during the drying process. This drier consists of a single Nafion tube (0.086" i.d. by 96" length) in a stainless steel casing. These dryers were specifically developed by DuPont to transfer moisture from one gas stream to a counter-flowing purge gas stream (N_2 at 500mLmin^{-1}) without condensation. Water molecules permeate through the Nafion tube wall, evaporating into the purge gas stream. The water concentration differential between the two gas streams drives the permeation, rapidly drying the air or gas, but without species such as H_2S dissolving (since no condensation occurs). A schematic diagram of the Perma Pure drier is shown in Figure 3-3 .

For this work, the drier is heated using a silicone rubber cable heater from Helios, such that the purge gas outlet stream from the drier was held between 90-100°C. Temperature was controlled manually via a Helios HC1 Simmerstat Controller. From the Permapure drier, product gases are sampled periodically via the micro-GC system.

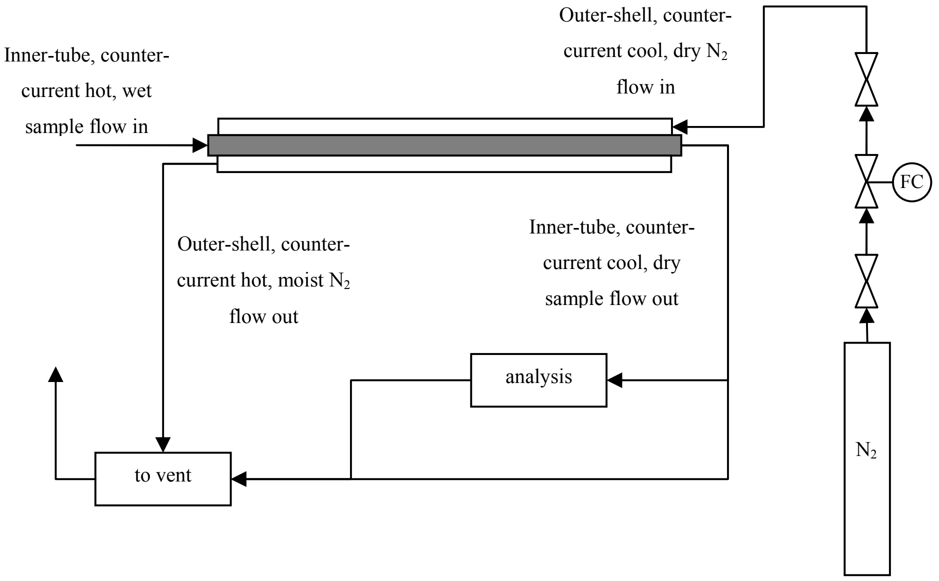


Figure 3-3 Schematic diagram of the Perma Pure dryer gas conditioning system for steam gasification.

3.4.3 Fluidised-Bed

Reaction Vessel and coal feeding

The 50mm atmospheric-pressure fluidised-bed gasifier consists of a 253MA stainless steel 50mm i.d. reaction zone expanding to a 200mm i.d. freeboard. Below the reaction zone suspends a 50mm i.d. plenum chamber that is mated via a 200mm flange in which is set an 80mm stainless steel sintered disc that acts as a distributor. A Leister Air Tool (5.0-6.7kW type) conducts preheated air or nitrogen (23LPM) to the plenum chamber, the flows of which are controlled using Alicat Scientific mass flow controllers (MC-100SLPM-D). Steam is generated in the plenum chamber fed demineralised water via a Masterflex C/L Pump System with 1mm i.d. silicon microbore tubing at $5.6 mL.min^{-1}$. The flows of air, nitrogen and oxygen (for burnout) are regulated by Brooks 5850S mass flow controllers (MFCs).

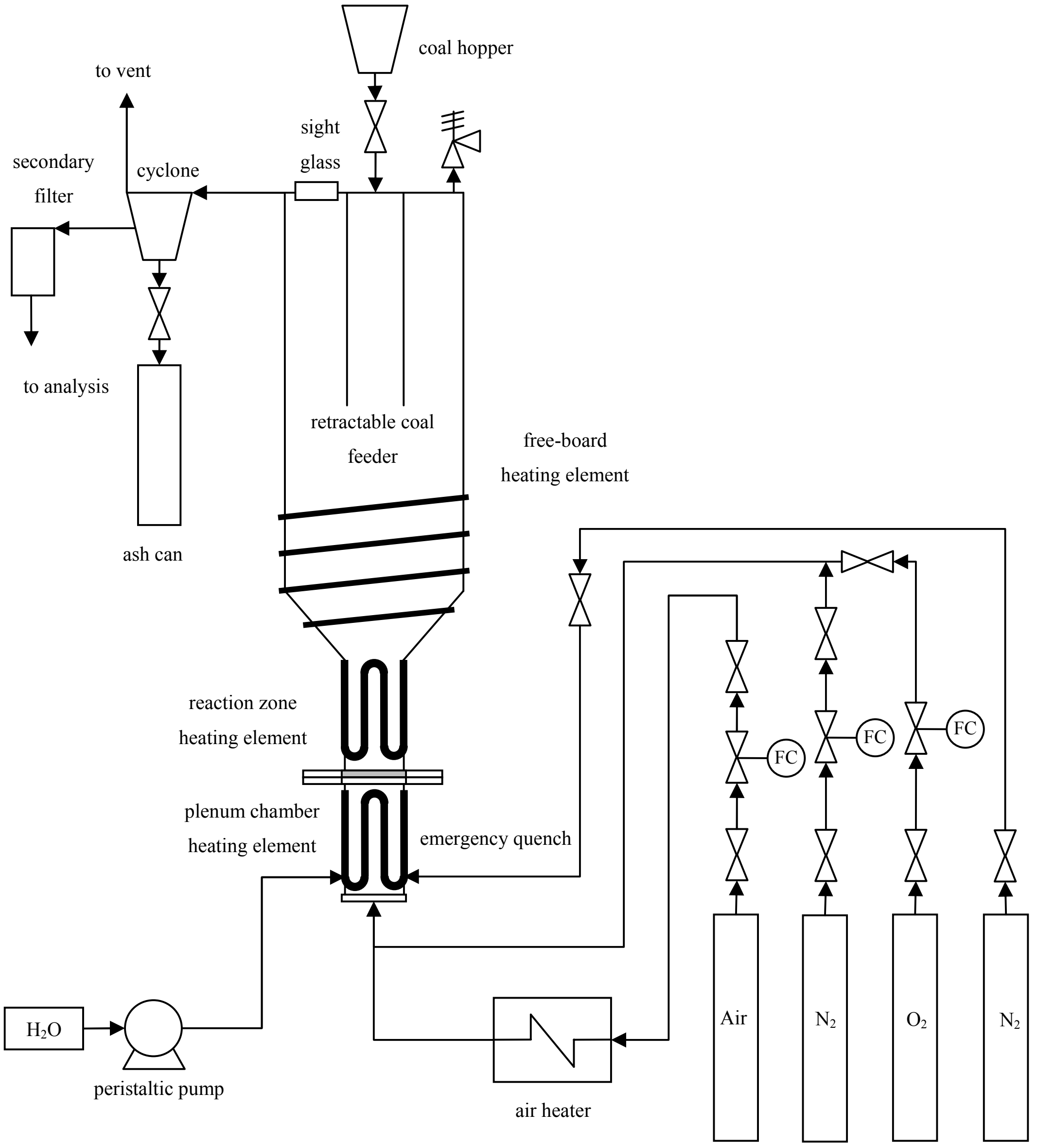


Figure 3-4 Schematic diagram of the 50mm atmospheric-pressure fluidised-bed gasifier system.

Heating Elements

The vessel heating is achieved by using 3 electrical heating elements. The plenum chamber is heated using an 800W Incoloy 8.0mm diameter tubular heater from Helios. This is controlled by a Shimaden SR73 Controller in conjunction with a Shimaden PAC-15P thyristor. The reaction zone uses a 1200W heater of the same type, controlled via a Yokagawa UT320 controller in conjunction with a Shimaden PAC-15-C thyristor. The reaction zone, however, uses a 3kW cable heater, 4.8mm diameter, controlled by a Shimaden SR73 Controller in conjunction with a Shimaden PAC-15P thyristor.

Thermocouples are located at three points in the reaction zone, one point in the freeboard and one point in the plenum chamber. All thermocouples reach the centre of the reaction vessel. A thermocouple is also used to monitor the metal temperature of the reaction zone heating element. The location of these thermocouples is shown in **Figure 3-5**.

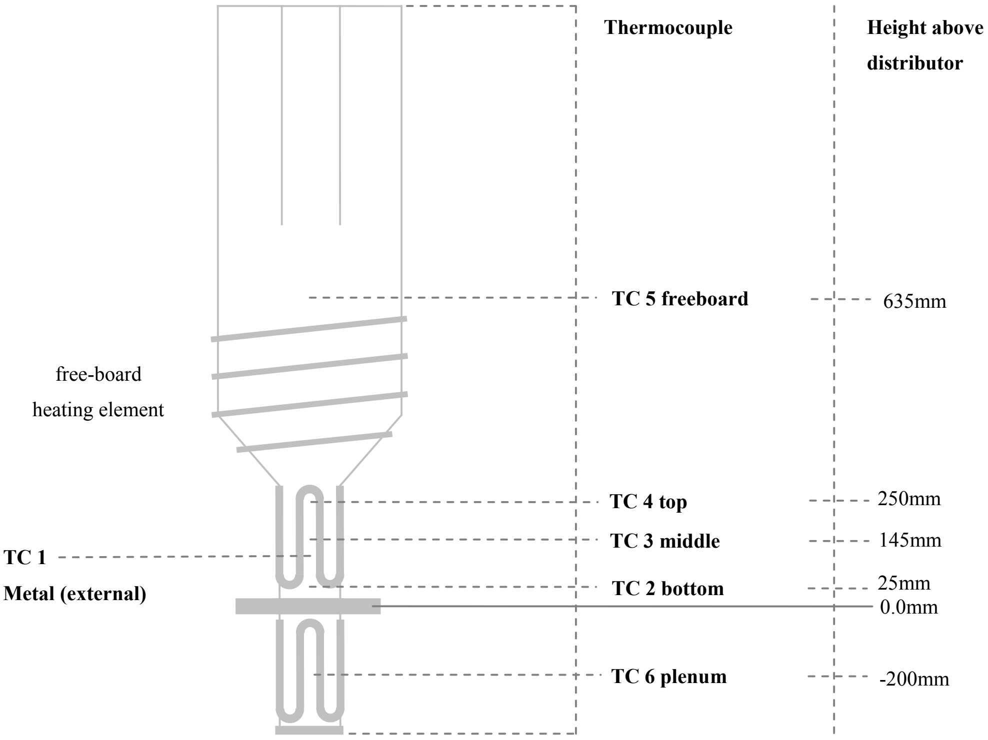


Figure 3-5 Schematic diagram of the reaction vessel, showing location of thermocouples.

Steam System

Demineralised water is introduced at a rate of 5.65 ml/min through a 1/8” stainless steel tube into the plenum chamber by a Masterflex C/L Pump System. The plenum chamber, held at 900°C, immediately vaporises the demineralised water and mixes it with the nitrogen flow to create a 25% v/v steam gasification mixture. This gasification mixture is then fed via the sintered stainless steel distributor plate into the reaction zone.

Gas Conditioning

Product gases exit the gasifier at the top of the freeboard and fines are removed from the stream via a cyclone. Just above the cyclone, a custom made heated particulate filter was installed to prevent particles >10 micron from entering the sample line. The filter was heated to 150°C using a silicone rubber cable heater controlled by a Helios HC1 Simmerstat Controller. The gas sample (approximately 2.5 LPM) is drawn through the filter assembly and heated sample line (400W coiled element) to an ADC (Analytical Development Company Limited) WA-584 analysis system. The ADC unit consists of heated particulate filter (10 micron) and Perma Pure drier (PD series). The PD series drier consists of a bundle of Nafion tubes and is designed to handle the higher flow rate of this system.

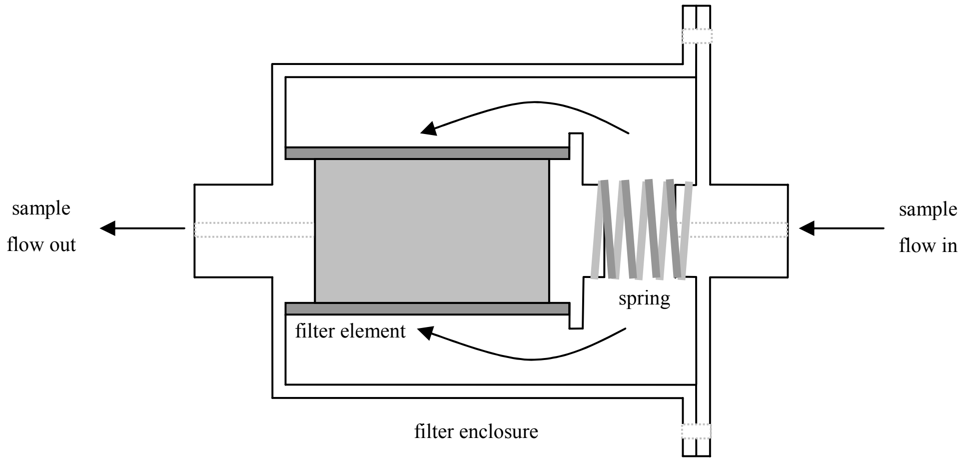


Figure 3-6 Schematic diagram of the gas conditioning and sampling system

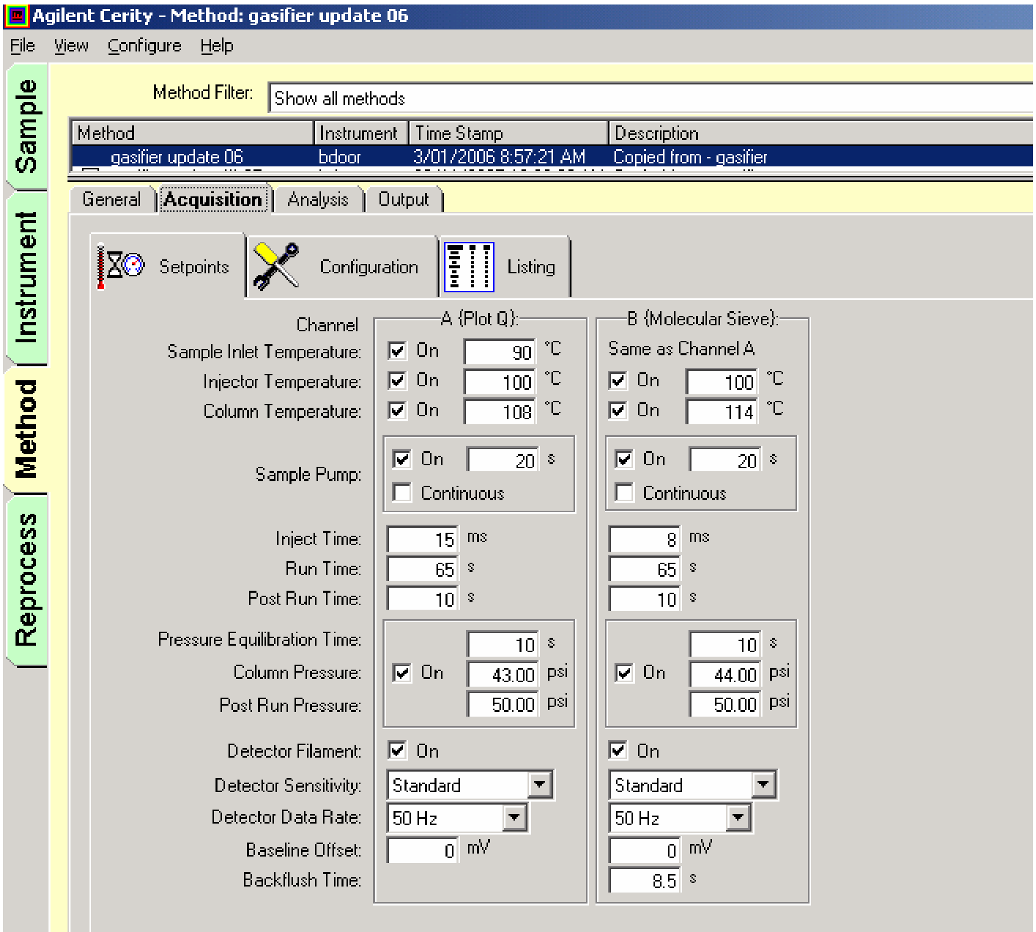
Coal addition

Once the vessel is heated to temperature, it is inertised using a flow of nitrogen. This is determined by analysing the gases for oxygen concentration. At this point, depending on the pyrolysis mode desired, steam can be introduced into the plenum chamber to generate a 25% vol flow of H_2O in N_2. At the desired time, the retractable coal feeder is lowered into the vessel and 300g of air-dried coal is dropped into the reaction vessel. The temperatures stabilise in the reaction zone after approximately 10 minutes.

3.4.4 Gas analysis

The micro GC consists of two independent ‘channels’, that is, individual capillary tubes (PoraPLOT Q on channel A and Molecular Sieve 5A with PoraPLOT U pre-column on channel B) designed to achieve an optimum separation of a given set of gas components. Each of these columns has a different carrier gas: for the PLOT Q, UHP Helium and for the Mol. Sieve 5A with PLOT U pre-column, UHP Argon. Carrier gases are in constant supply to the columns, their inlet pressure set to 80PSI (+/-2PSI).

Coupled with the use of small-scale thermal conductivity detectors (TCDs), elution time of gas species is much more rapid than conventional GC. Channel A is primarily used to identify air, methane, carbon dioxide, C2 and C3 hydrocarbons along with sulphur species, whereas channel B detects hydrogen, oxygen, nitrogen and carbon dioxide. The temperatures and pressures of the channels are optimised such that, in automation mode, the micro GC can take one sample every 1.6 minutes, determining all species of interest up to C3. The instrument method settings are shown in Figure 3-7 and the column specifications in Figure 3-8.

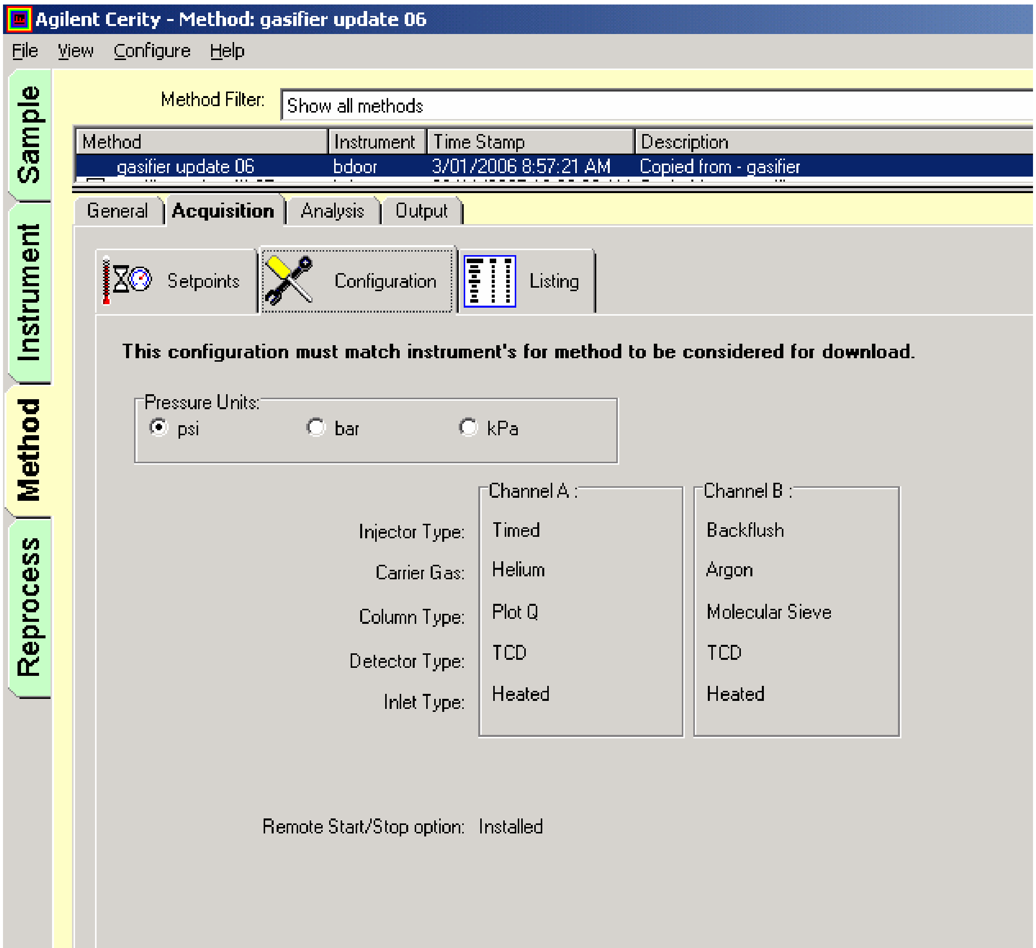


Method Filter: Show all methods

Method	Instrument	Time Stamp	Description
gasifier update 06	bdoor	3/01/2006 8:57:21 AM	Copied from - gasifier

Channel	A (Plot Q)	B (Molecular Sieve)
Sample Inlet Temperature:	☑ On 90 °C	Same as Channel A
Injector Temperature:	☑ On 100 °C	☑ On 100 °C
Column Temperature:	☑ On 108 °C	☑ On 114 °C
Sample Pump:	☑ On 20 s ☐ Continuous	☑ On 20 s ☐ Continuous
Inject Time:	15 ms	8 ms
Run Time:	65 s	65 s
Post Run Time:	10 s	10 s
Pressure Equilibration Time:	10 s	10 s
Column Pressure:	☑ On 43.00 psi	☑ On 44.00 psi
Post Run Pressure:	50.00 psi	50.00 psi
Detector Filament:	☑ On	☑ On
Detector Sensitivity:	Standard	Standard
Detector Data Rate:	50 Hz	50 Hz
Baseline Offset:	0 mV	0 mV
Backflush Time:		8.5 s

Figure 3-7 Micro-GC instrument method settings panel



Method Filter: Show all methods

Method	Instrument	Time Stamp	Description
gasifier update 06	bdoor	3/01/2006 8:57:21 AM	Copied from - gasifier

This configuration must match instrument's for method to be considered for download.

Pressure Units: ● psi ○ bar ○ kPa

	Channel A :	Channel B :
Injector Type:	Timed	Backflush
Carrier Gas:	Helium	Argon
Column Type:	Plot Q	Molecular Sieve
Detector Type:	TCD	TCD
Inlet Type:	Heated	Heated

Remote Start/Stop option: Installed

Figure 3-8 Micro-GC instrument configuration panel

3.4.5 Calibration

In order to calibrate the micro-GC, a number of calibration gases are utilised, in either nitrogen or helium. Only the multilevel calibration for CO does not result in a linear calibration curve. The concentrations are chosen based on the predicted concentrations for the fluidised bed results and are therefore higher than the actual concentrations obtained for the fixed bed experiments. When obtaining results for the peak area at a given retention time, the micro-GC applies the response factor (concentration per unit area under the curve) to estimate the concentration of species. This calibration data is shown in **Table 3-2**, while sample chromatograms for calibration of hydrocarbons using a mixture of hydrocarbons in nitrogen are shown in **Figure 3-9**.

Table 3-2 Micro-GC calibration data

Species	channel	concentration (% v/v)	retention time (min)	response area	response factor (v/v% per unit area)
CH4	1	3.4	0.298	35210.23	9.66E-05
CO2	1	10.3	0.317	151938.19	6.78E-05
		23.9	0.317	348594.22	6.86E-05
C2H4	1	0.93	0.346	27078.36	3.43E-05
C2H6	1	1.14	0.367	18476.76	6.17E-05
H2	2	19.2	0.396	99764.99	1.92E-04
H2S	1	1	0.417	14176.145	7.05E-05
O2	2	21	0.462	12212.38	1.72E-03
COS	1	1.5	0.485	28079	5.34E-05
N2	2	41.68	0.528	20933.24	1.99E-03
		100	0.528	51229	1.95E-03
		89.7	0.528	46388	1.93E-03
		79	0.528	38839.8	2.03E-03
		85	0.528	43679.72	1.95E-03
C3H6	1	0.99	0.553	18973.17	5.22E-05
C3H8	1	0.99	0.581	20603.98	4.80E-05
SO2	1	0.0481	0.599	406.61	1.18E-04
CH4	2	3.4	0.644	6263.93	5.43E-04
CO	2	20.6	0.77	9831.16	2.10E-03
		10.3	0.77	4904	2.10E-03
CH3SH	1	0.0477	1.036	897.34	5.32E-05
C2H5SH	1	0.0469	2.617	871.53	5.38E-05
CS2	1	0.0494	2.653	968.36	5.10E-05

For sulphur species, individual calibration gases for H_2S, COS and SO_2 at 1%v/v, 1.5%v/v and 489ppm in nitrogen respectively are used. The micro GC is calibrated for methyl (CH_3SH) and ethyl mercaptan (C_2H_5SH), along with carbon disulphide (CS_2), using a combination mix of 477, 469 and 494ppm in nitrogen respectively. Calibration of the unit is undertaken on a weekly basis for all these species.

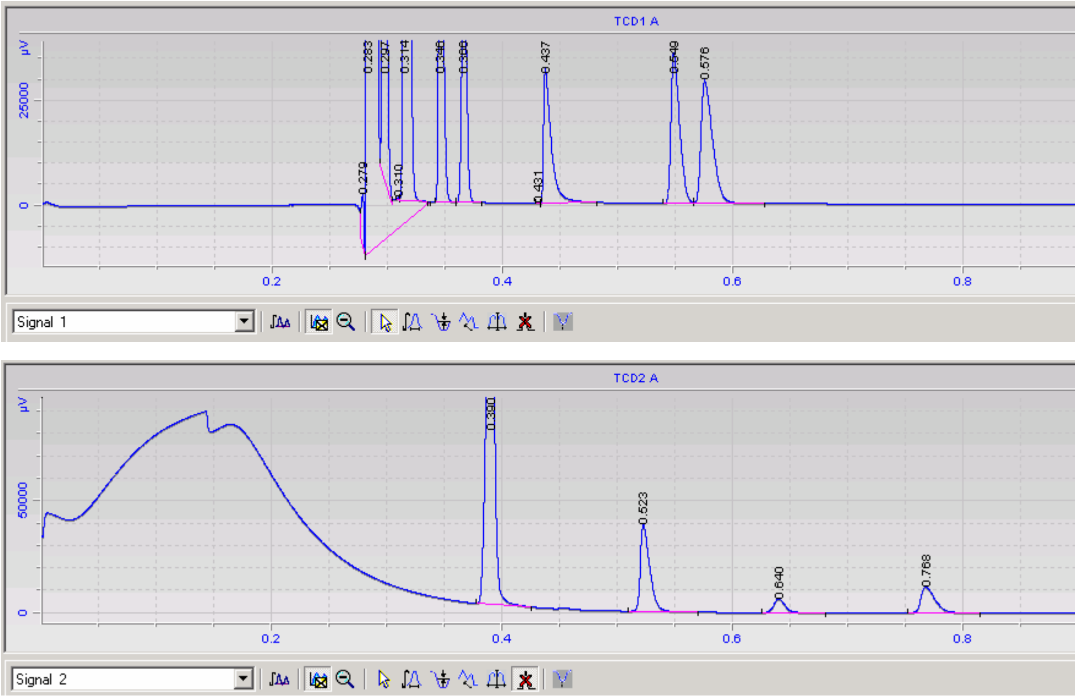


Figure 3-9 Chromatograms obtained for calibration data using hydrocarbon mix in nitrogen, for channel 1 (top) and channel 2 (bottom). Note the presence of nitrogen as the large peak at 0.282 minutes and the presence of moisture at 0.432 on channel 1.

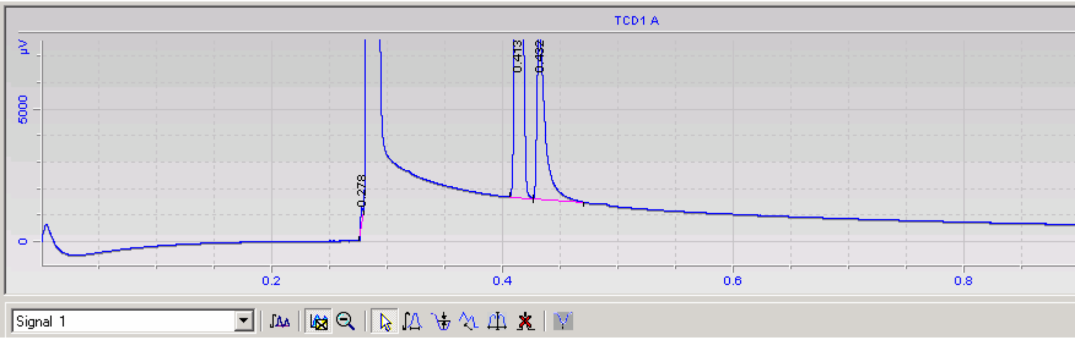


Figure 3-10 Chromatogram obtained for calibration of H_2S (1% v/v) in nitrogen. Note the presence of nitrogen as the large peak at 0.282 minutes and the presence of moisture at 0.432.

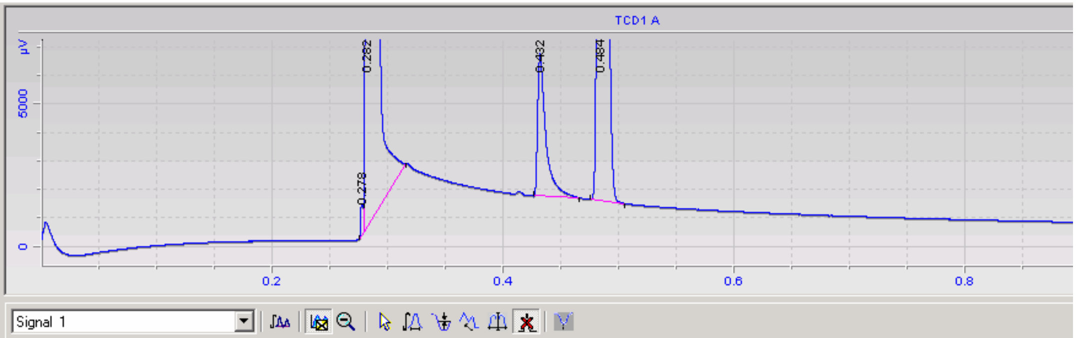


Figure 3-11 Chromatograms obtained for calibration of COS (1.5% v/v) in nitrogen. Note the presence of nitrogen as the large peak at 0.282 minutes, the presence of moisture at 0.432.

3.5 Mass balance calculation methodology

A normalised molar concentration (moles of species to moles of nitrogen) is obtained in order to calculate the instantaneous molar flow rate of species, based on the known flow rate of nitrogen to and from the reactor. It is assumed that nitrogen is not involved in any reaction mechanisms during either pyrolysis or gasification, and as such, the total flow rate of nitrogen out of the system is equal to the inflow.

Having obtained the instantaneous molar flow of species at a given time, this enables the calculation of the total molar flow of species over a given sampling period, the timing of which is precisely known, using the trapezoidal integration rule to calculate the area under the curve.

From this total molar flow rate of each gas species comes the total molar flow rate of carbon and sulphur, which are then compared to the initial carbon and sulphur content of the coal to obtain values of conversion of species to the gas phase.

A detailed Uncertainty Analysis section is included in Appendix A, outlining the uncertainties associated with this work.

4 TEMPERATURE PROGRAMMED PYROLYSIS

4.1 Introduction and Objectives

This chapter examines the transformations of sulphur during fixed-bed pyrolysis in nitrogen under both slow and fast heating rate, for both air-dried and acid-washed Lochiel and Bowmans coal. The need for data on the gas phase sulphur products of pyrolysis has been highlighted in the literature review. Temperature programmed pyrolysis, by employing a relatively low heating rate, reveals the onset decomposition temperatures for individual sulphur compounds, providing insight into the relative bond strength of individual species.

The body of literature reviewed for the analysis of sulphur forms in coal has focused on either Temperature Programmed Oxidation (TPO) or Temperature Programmed Reduction (TPR) as methods to disseminate the various sulphur structures. The premise behind this methodology is that since hydrogen is believed to facilitate the removal of sulphur as hydrogen sulphide, H_2S, and oxygen as sulphur dioxide, SO_2, then the total sulphur can more easily be evaluated using simple, cheap and robust methods of analysis. A significant resource also exists in the Temperature Programmed Pyrolysis (TPP) work of Telfer (1999), as to the characterisation of South Australian coals. As pointed out in the literature review, that work examined the solid phase transformations. This chapter aims to examine precisely what gas phase compounds are associated with the decomposition of specific coal-sulphur functional groups, utilising the same low-rank coals, and extending that work under slow heating rate pyrolysis conditions. The results in this TPP work are presented with respect to Lochiel coal's sensitivity toward coal pre-treatment and particle size, and results for Bowmans coal are included by way of comparison.

4.2 Concentration profiles

A 500mg sample of coal is packed in quartz wool and positioned within a 10mm internal diameter (ID) quartz tube. The tube is then placed in the horizontal tube furnace (HTF), at ambient temperature, and inertised using either ultra-high purity (UHP) nitrogen (99.999% N_2) when using Gas Chromatography for analysis, or a mixture of UHP helium and UHP argon (to achieve 5 % v/v Argon concentration) when analysing using Mass Spectrometry. Carrier gases are analysed for oxygen to ensure that the reaction vessel is completely inert, with flow regulated by Brooks 5850S mass flow controllers (MFCs) to give 150mL.min^{-1} overall volumetric gas flow rates. The vessel temperature is set to 1200°C and the gases analysed continuously while the temperature-programmed stage of pyrolysis takes place at 15Kmin^{-1} heating rate. At 1200°C, after a 5 minute holding time, the tube is withdrawn to allow the sample to cool, still under inert conditions, then the residue is weighed and stored in a 5mL glass vessel. Concentration profiles for sulphur species evolution during air-dried Lochiel coal TPP are shown in **Figure 4-1**.

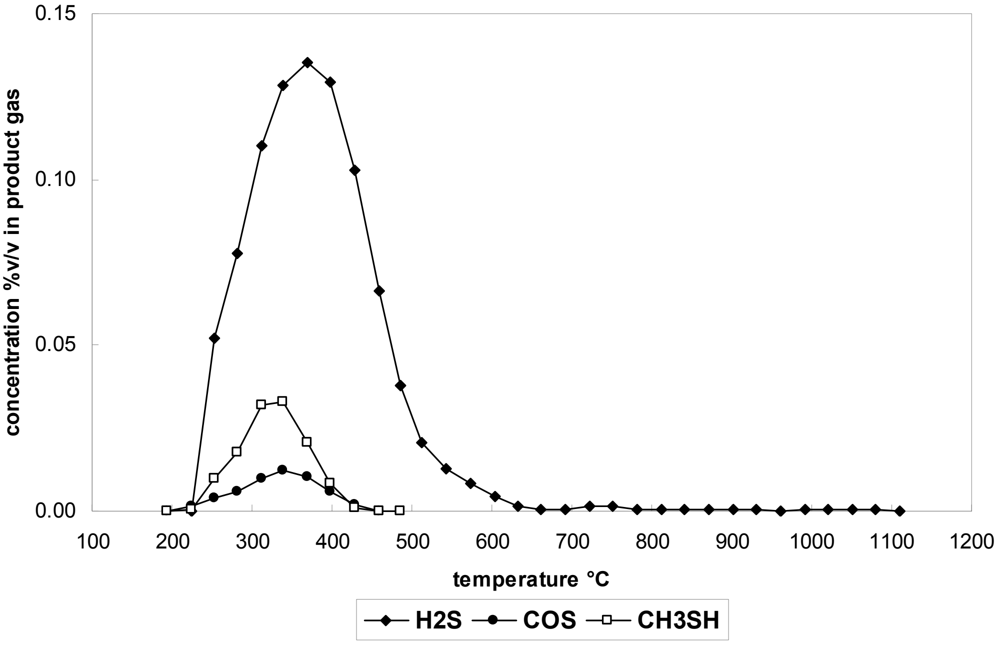


Figure 4-1 Sulphur species concentration in the product gas (%v/v) of air-dried Lochiel coal TPP at 15Kmin^{-1}

The concentration of H_2S increases from less than 0.05% at 250°C to a peak of 0.135% at 370°C, before diminishing to less than 10ppm by 660°C. This increases slightly to 13ppm by 750°C before again dropping to less than 10 pm levels until no further H_2S is detected at 1100°C.

COS is first detected at approximately 220°C at a concentration of 0.002%, increasing to 0.0120% by 340°C. The concentration then declines to zero by 460°C. For CH_3SH, first detection also corresponds to a temperature of 220°C (0.006%) with a peak concentration of 0.0330% at 340°C before declining to zero at 490°C.

To determine whether or not other sulphur compounds are evolving, the product gas is also analysed using mass spectrometry. Trace amounts of heavier sulphur compounds (such as sulphur dioxide (SO_2), ethyl mercaptan (C_2H_5SH) and carbon disulphide (CS_2)) are inferred by m/z readings at 64 (SO_2), 62 (C_2H_5SH) and 76 (CS_2), however, it is difficult to quantify these accurately due to the extensive ionisation and product mix associated with the devolatilisation process. Given that these species are not detected using micro-GC, the maximum concentration in the product gas is estimated to have been less than 1 ppm, based on the minimum detection limits for the micro-GC as specified in Chapter 3.

The implications of these concentration curves for sulphur are discussed below with reference to a calculated evolving rate, that is, the mole of sulphur species released per unit mole of sulphur in the original sample as a function of time. It should be noted, however, that re-absorption of the evolving sulphur gases can occur immediately after they are released, hence the TPP concentration and evolving rate profiles are only an indication of the type and nature of sulphur forms, since they may be a superposition of competing release-reattachment mechanisms.

4.3 Calculating evolving rate

Based on the precisely known flow rate of UHP nitrogen to the reactor (150mLmin^{-1}), the total volume of nitrogen is estimated between each sample period, and the normalised molar concentration (moles of species to moles of nitrogen) used to calculate the total mole of species released during each analysis period. This total mole of gas phase species is then converted to a total mole of sulphur and total mole of carbon and compared to the mole of sulphur and carbon in the initial coal, giving the conversion to the gas phase at any point in time. This is termed the evolving rate. **Figure 4-2** shows the evolving rate profile for sulphur species H_2S, COS and CH_3SH for air-dried Lochiel TPP detected using micro-GC, along with the cumulative sulphur conversion to the gas phase.

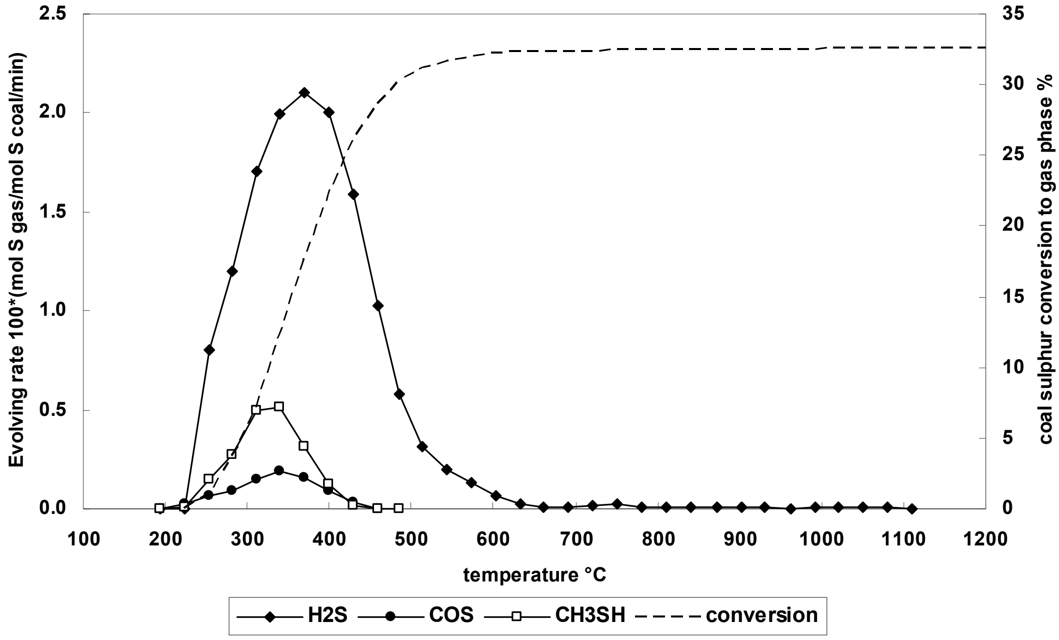


Figure 4-2 Sulphur gas phase evolving rate for individual sulphur species as a product of air-dried Lochiel TPP, along with cumulative coal sulphur conversion to the gas phase (secondary y-axis).

Each of the sulphur containing gases detected show a single peak evolving rate in the range 200-500°C, with the maxima for COS and CH_3SH occurring at approximately 330°C, at 0.2%min^{-1} and 0.5%min^{-1} respectively, while the maximum for H_2S occurs at approximately 370°C at 2% per minute. Only the H_2S profile shows a peak above 500°C, from 650-800°C, but this reaches a maximum evolving rate of <0.05%min^{-1}, making a contribution to overall sulphur conversion of less than 0.1%. Sulphur conversion to the gas phase is essentially complete at 500-600°C, as shown by the curve on the secondary y-axis, and while sulphur is detected as H_2S out to 1100°C, the maximum conversion of 32.6% at that temperature is only 0.4% higher than the conversion at 600°C, and the evolving rate negligible. This result compares well with Telfer's (1999) analysis of the char sulphur conversion for Lochiel coal which was observed to occur rapidly between 300-500°C and complete by 600°C. The total contribution to sulphur conversion to the gas phase from H_2S is 27% of the initial coal sulphur, while COS and CH_3SH contribute 1.6% and 3.7% respectively, bringing the total conversion to just over 31%.

In terms of the progenitor species for sulphur in the coal, thiols (R-SH) are believed to be the major source of H_2S at lower temperatures and the loss of organic sulphur by Lochiel coal in the region 200-300°C has been assigned to these species by various studies in the literature (Calkins, 1989; Attar, 1978; Telfer, 1999). While it has generally been held that mercaptans are the result of reactions of H_2S with unsaturated compounds in the gas phase (Attar, 1978), recent work by Miura *et al* (2001) suggests that mercaptans are primary products from pyrolysis, albeit not detected during slow heating rate experiments (20Kmin^{-1}) when they are believed to react with oxygen in CO_2 and H_2O to form SO_2.

Carbonyl sulphide, COS, is believed to result from the decomposition of highly reactive organic coal matter containing relatively abundant oxygen groups (Garcia-Labiano *et al.*, 1996), and also from pyrite (Attar, 1978; Ibarra *et al.*, 1994), however, since Lochiel coal contains negligible pyrite, the former source is believed to be most likely. It is also possible that COS is the result of secondary reactions of H_2S with either CO_2 or CO (Furimsky *et al.*, 1991; Ma *et al.*, 1989) although the reaction rate at temperatures less than 400°C is believed to be too slow to result in the formation of substantial quantities (Ma *et al.*, 1989).

In the range 400-600°C the signal for sulphur species drops significantly. In this temperature zone, Telfer (1999) noted a small increase in the organic sulphur content of the solid phase corresponding to the decomposition of sulphates, implying that sulphate did not release H_2S to the product gas but that it was retained as more complex organic sulphur compounds. That there is limited evolution after 600°C may be due to cross-linking and reattachment mechanisms such that the released sulphur does not easily escape from the char intra-particle surface and is retained in either the organic coal structure or as metal sulphides (Attar, 1978; Cleye, 1984; Kucukbayrak and Kadioglu, 1988; Khan, 1989; Gryglewicz, 1992). Between 650°C and 800°C, the small amount of sulphur detected as H_2S (corresponding to only 0.1% of conversion to gas phase) may correspond to the final decomposition of the sulphate sulphur, while the continued release up to 1100°C (albeit with almost negligible contribution to total conversion to gas phase) may be the result of the net decomposition of more complex sulphur compounds such as aryl, cyclic and aliphatic sulphides after re-reaction with the organic coal matrix or metals to form metal suphides (Attar, 1978).

No measurement is made of the sulphur contained in the tar, given the difficulty in collecting the entire mass of tar accurately. It is also not possible to determine via wet chemical methods the char sulphur content for Lochiel coal after TPP because of the sample sizes involved (recovered residues are consistently 0.2-0.22g from a sample size of 0.5g representing between 40-45 wt% char yield).

While wet chemical means are not suitable for analysis of this residue, XRD can be performed on the relatively small samples that are obtained. The results indicate that the dominant phase (>60 wt%) remaining in the char is cristobalite (SiO_2) with minor (<20 wt%) oldhamite (CaS), trace (<5 wt%) quartz (SiO_2) and possible gypsum ($CaSO_4$). That calcium plays a significant role in the fate of sulphur during pyrolysis of Lochiel coal has been observed previously by a number of workers, particularly for South Australian lignites (Telfer, 1999; Ross, 2000; Kosminski, 2001; McCullough, 2007). In order to elucidate the effect of mineral matter on the release and speciation of sulphur compounds, it is necessary to undertake experiments using acid-washed coal, where the discrete inclusions of mineral matter, along with organically bound inorganic species are removed.

4.4 Effect of acid-washing

4.4.1 Large particles (1-1.7mm)

The TPP profile for acid-washed Lochiel coal aids the interpretation of the air-dried profile since the inorganic compounds that are responsible for the formation of metal sulphides that remain bound in the coal particle are removed (Attar, 1978; Gryglewicz and Jasienko, 1992; Patrick, 1993; Telfer, 1999). As performed for the air-dried TPP results, concentration data is converted to evolving rate profiles to allow suitable comparison between samples with different sulphur content. The results of this work are presented in Figure 4-3, page 108.

There are subtle differences between the profiles for the air-dried and acid-washed Lochiel TPP experimental results. Examining first the profile for H_2S, the evolving rates for air-dried and acid-washed TPP reaches an equivalent peak of 2%min^{-1} at approximately 400°C, but in the 250-350°C region the evolving rate is greater for the acid-washed sample.

For H_2S there is a significant difference between the two profiles from 450-800°C, with the acid-washed sample showing a prominent secondary peak from 450-600°C, and a small tertiary peak from 600-800°C (at peak evolving rate of 0.2%min^{-1}). For the acid-washed sample, the evolution of sulphur in this temperature zone contributes 8% of the total sulphur conversion to the gas phase, while for the air-dried sample, the total conversion of sulphur to the gas phase of between 450-600°C is only 3.5%.

The tertiary peak for the acid washed sample represents approximately 2% of conversion, while, as mentioned previously, the conversion to the gas phase of the air-dried sample was almost negligible in this range at approximately 0.1%. The total conversion of the acid-washed sample due to H_2S represents a relative increase of over 30% compared with the air-dried sample, at 41% *cf* 32%.

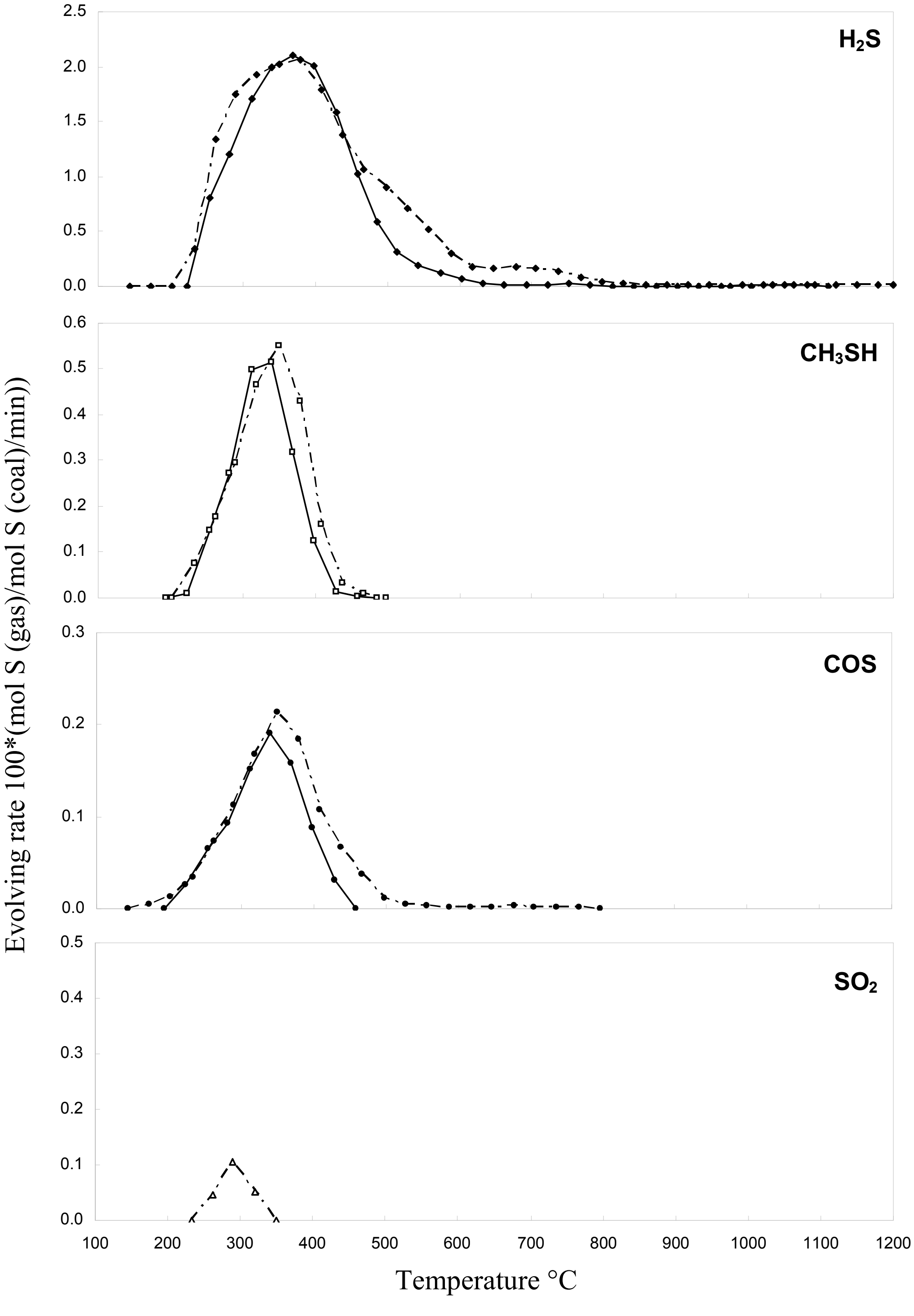


Figure 4-3 Evolving rate of sulphur species as a function of temperature for Lochiel (——) and acid washed Lochiel (– · –) coals.

The peak for methyl mercaptan (CH_3SH) evolving rate is translated slightly to a higher temperature region for the acid-washed sample, and reaches a slightly higher peak evolving rate of just over 0.5%min^{-1}. This represents an increase in conversion of sulphur to the gas phase of 0.6%, or 15% relative to the conversion for the air-dried sample.

The evolving rate for carbonyl sulphide (COS), however, shows prolonged evolution out to 800°C, after a pronounced primary peak between 200-500°C (although this occurs at an evolving rate of less than 0.01%min^{-1}). Like the methyl mercaptan peak, the carbonyl sulphide curve for the acid-washed sample reaches a maximum of 0.5%min^{-1} at approximately 350°C and maintains a higher evolving rate over the 350-500°C temperature range than the air-dried sample. Given the relative magnitude of the carbonyl sulphide to hydrogen sulphide evolving rate (H_2S is a an order of magnitude greater), between 350°C and 500°C, this increase only results in an additional 0.4% conversion of sulphur to the gas phase. Relative to the carbonyl sulphide conversion in the air-dried sample, however, this represents an increase of over 30%.

The most prominent feature of the acid-washed profile is the presence of sulphur dioxide (SO_2), which shows a simple single peak that reaches a maximum evolving rate of 0.1%min^{-1} at 300°C and accounts for approximately 0.4% of the total conversion. The narrow window of evolution, resulting in only three sample points from the micro-GC, means that there is uncertainty as to the shape of this curve, and accordingly, the calculated percentage conversion and peak evolving rate.

The increase in evolving rate for all the major gas phase species (H_2S, CH_3SH, COS and SO_2) resulting from acid-washing, increases the overall conversion to the gas phase, and demonstrates that the the evolution of sulphur under slow heating rate pyrolysis conditions is retarded by inorganic species present in untreated Lochiel coal.

Literature studies have demonstrated that by removing Alkali and Alkaline Earth Metal (AAEM) species from coal, the released sulphur has less chance to become 'fixed' as sulphidic or sulphatic structures (Cernic-Simic, 1962; Attar, 1978; Gryglewicz and Jasienko, 1988; Telfer, 1999). Telfer (1999) noted that sulphide sulphur concentration increased in Lochiel coal during TPP from 500°C onwards, and concluded that sulphides were most likely the result of less complex organic sulphur forms facilitating reactions with organically bound inorganics such as calcium. In addition, Telfer (1999) noted a pronounced increase in pyrite concentration (FeS_2) for TPP experiments in the 400-700°C region, believed to be an intermediate in the solid-state transformation of sulphate to organic sulphur. By removing the inorganics, these reactions are impeded and organic sulphur, which would ordinarily be retained for air-dried samples, is released. Telfer's solid phase experiments revealed an increase in conversion of between 15% and 20% for acid-washed samples undergoing TPP in the 800-900°C region when compared to air-dried samples of Lochiel and Bowmans.

In terms of the structures from which the detected species evolve for acid-washed coal, they are all likely to be organic in nature, since the treatment step removes close to 100% of the inorganic sulphur species (pyrite and sulphate, see Chapter 3). That sulphur dioxide is detected during TPP of the acid-washed coal and not the air-dried coal, however, is a point of interest since the literature suggests that SO_2 could be the result of the decomposition of sulphates (Ibarra *et al.*, 1994), the concentration of which wet chemical analysis indicates is negligible.

Oxidised sulphur groups are likely to come from organically bound species, for example sulphonic acids (RSO_2OH), sulphones (RSO_2R') and sulphoxides ($RSOR'$) (Attar, 1978; Calkins, 1987; Marinov *et al.*, 2005) where R is any hydrocarbon. It is possible that air-dried Lochiel contains these species. On decomposition during pyrolysis, however, they may be rapidly taken up by inorganic species found in the structure, species that are subsequently removed during acid-washing. Given that Lochiel coal, and low-rank coals in general, contain an abundance of oxygen functional groups, and that such groups are one of the primary reasons why the coals are so reactive during gasification processes (Takarada *et al.,* 1985), sulphur may indeed be bound in abundance to oxygen functional groups in these coals. Therefore the SO_2

during TPP may be an indication of their presence. This type of structural arrangement for organic sulphur groups in low-rank coals has been previously proposed by several researchers (Attar, 1978; Calkins, 1987; Miura *et al.*, 2001; Marinov *et al.*, 2005).

The literature also suggests that the progenitor species for SO and SO_2 may be the result of coal sulphur oxidation via exposure to the atmosphere (Ibarra et al, 1995). These studies, however, conclude that it is the oxidation of pyrite (FeS_2), to sulphate that is the source, not the oxidation of organic structures. Other investigators (Block *et al.*, 1975; Ibara *et al.*, 1989; Alvarez *et al.,* 1995 and Mondragon *et al.*, 2002) have examined the effect of oxidising coal at moderate temperatures (from 30°C to 300°C) prior to pyrolysis, and found that a greater degree of oxidation (in terms of either the temperature to which the coal is exposed or the length of time exposed to oxygen at a given temperature), the more 'volatile' the sulphur in the coal when subsequently pyrolysed. Alvarez *et al.* (1995) concluded that oxidation prior to pyrolysis (between 150-270°C), resulting in an increase in oxygen density in the coal structure, lead to a greater loss of organic sulphur compounds during pyrolysis due to a more highly developed pore structure, with greater production of carbonyl sulphide (COS) the result. Mondragon *et al.*, 2002 conducted experiments to examine the effect of coal oxidation on the reaction of oxidised coal with elemental sulphur. Coal samples were oxidised at 30, 50, 80 and 150°C and then reacted with elemental sulphur in a TPP reactor. The H_2S evolved from the re-reaction process was monitored by absorption into sodium hydroxide. H_2S production was found to be highly sensitive to the oxidation temperature, with the samples oxidised at 30°C losing 50-75% of their reactive hydrogen, limiting H_2S formation. Furimsky *et al.* (1991) conducted fast pyrolysis in a fixed bed reactor with sub-bituminous and bituminous coals at 1200K and found that the coal that resulted in the greatest evolution of SO_2 during pyrolysis (nitrogen only) was known to readily chemisorb oxygen from the air. The resultant SO_2 was believed to come from the oxidation of evolved H_2S with this chemisorbed oxygen.

Therefore it is possible that SO_2 may be the result of reaction of oxygen, either inherent in the coal structure or chemisorbed onto the coal surface during storage, with organically bound sulphur during the low temperature stages of TPP through a type of sulphur rearrangement-annealing process. That SO_2 achieves a peak evolving rate of 0.1%min^{-1} much sooner than H_2S, CH_3SH and COS (at 280°C for SO_2 *cf* 370°C for the other species), indicates a higher relative volatility of progenitor species when compared to the latter. For this reason, it is believed that these reactive structures, if the proposed mechanism applies, are likely to be simple thiols (R-SH).

That no SO_2 is detected during the TPP of air-dried Lochiel is believe to relate to its affinity for metallic species that are present, particularly calcium, which result in fixation as either sulphides or sulphates. Lochiel coal, containing an abundance of calcium (as dolomite) means that the structures most likely formed by this reaction are calcium sulphide (eg CaS) and/or calcium sulphate ($CaSO_4$)/calcium sulphite ($CaSO_3$). By removing the metallic ions that readily react with SO_2 (and other sulphur species) via acid-washing, the quantity of SO_2 evolved increases. A potential source of oxygen to facilitate the reactions is the air-drying step after acid-washing during which the acid-washed coal is dried to reduce its moisture content. This may have encouraged chemisorption of oxygen and/or the reaction of inherent oxygen with organic and inorganic sulphur forms.

To attempt to elucidate the products of pyrolysis prior to any possible intra-particle interactions and the speciation of sulphur during TPP, and shed light on the proposed SO_2 formation mechanisms, experiments were also undertaken with acid-washed coal using the particle size fraction less than 0.5mm.

4.4.1 Small particle (<0.5mm)

The TPP evolving rate profile for acid-washed coal of particle diameter less than 0.5mm in diameter (AW<0.5) is shown in Figure 4-4. By examining the profile for smaller particles, the interactions between the evolved gas phase species (in the internal pore network) and the char surface as they make their way out of the pores can be decreased (Zielke *et al.* (1954); Telfer (1999)). This results in a gas phase mix that should be more representative of the primary products, eliminating to an extent the complex intra-particle volatile-char interactions. As performed for the air-dried (AD) and acid-washed (AW) TPP experiments, concentration data results are converted to evolving rate profiles to allow suitable comparison between samples with different sulphur content.

The evolving rate for H_2S in the region less than 300°C is significantly less for the AW<0.5 sample than the AW sample. This difference means that by 300°C, the total conversion to the gas phase for the AW sample approaches 6% while for the AW<0.5 sample, it approaches 8%. Between 300-400°C, the evolving rate for H_2S for the smaller particle size sample (AW<0.5) increases compared to the AW sample reaching a maximum of 2.25%min^{-1}, compared with 2%min^{-1}, and from 400°C to the termination of the experiment at 1200°C, the evolving rates for the two different sample sizes remain relatively similar at less than 0.05%min^{-1}. The evolving rate comparison for COS, by comparing the shape of the curves in **Figure 4-4**, shows that particle size has little effect, and a peak evolving rate of 0.21%min^{-1} *cf* 0.24%min^{-1}.

The quantities of CH_3SH and SO_2 are impacted heavily by particle size. Examining first the profile for CH_3SH, the onset of evolution for the smaller particle sample (AW<0.5) is delayed by some 30°C, and between 300-400°C reaches a peak evolving rate of 0.37%min^{-1}, lower than the larger particle sample of 0.55%min^{-1}). The difference in evolving rate represents a difference in overall conversion to the gas phase of 1.5%, or 65% less relative to the acid-washed sample of smaller size.

However the evolving rate profiles for SO_2 and CH_3SH between AW and AW<0.5 appear to have an inversely proportional relationship. For the AW<0.5 sample, SO_2 reaches a peak evolving rate that is 400% the peak evolving rate for the AW sample of over 0.4%min^{-1}. The SO_2 evolved for the AW<0.5 sample adds 2.3% to total sulphur conversion, whereas the contribution for the AW sample adds only 0.4%.

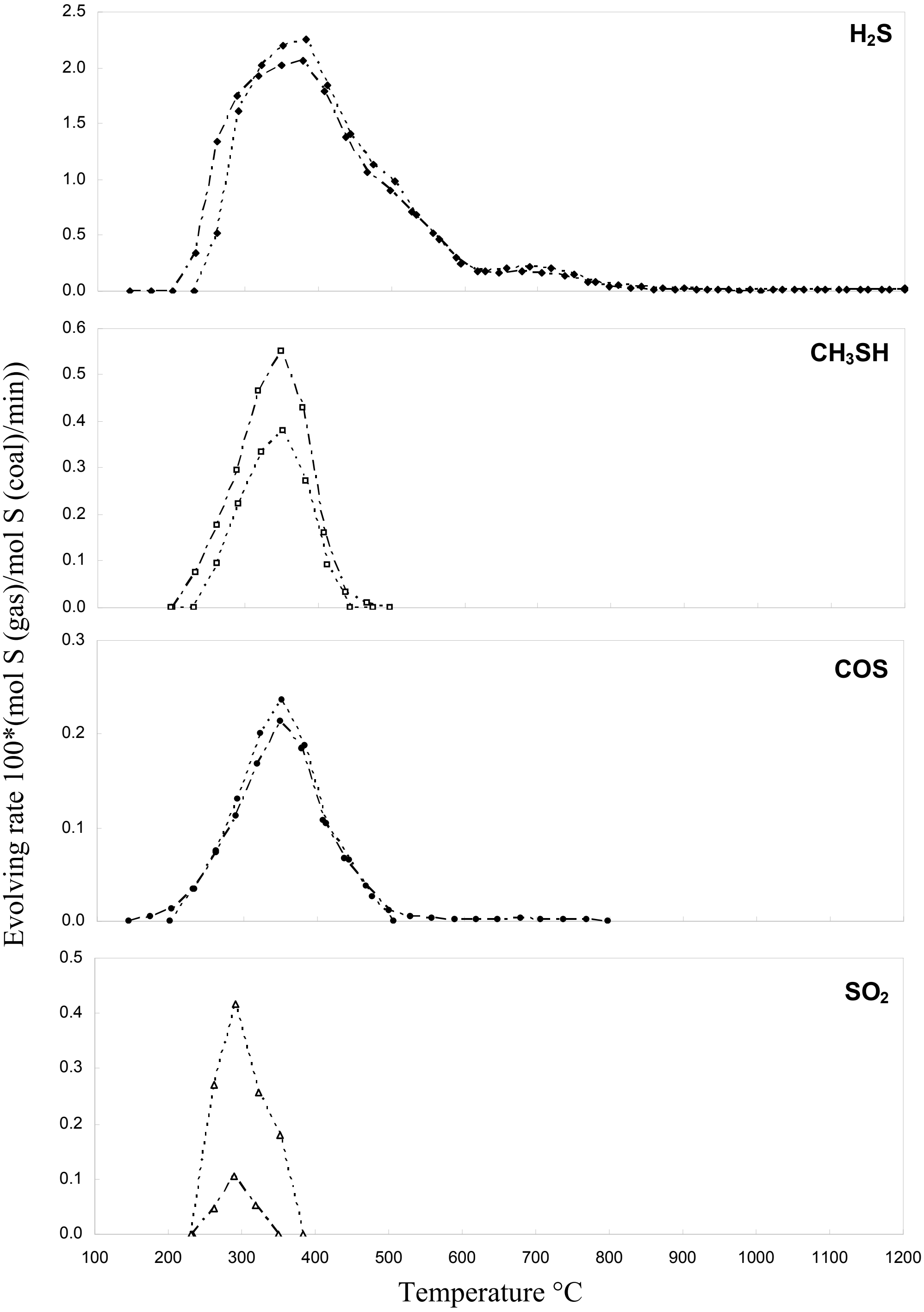


Figure 4-4 Evolving rate of sulphur species as a function of temperature for acid washed Lochiel (–·–··) and acid washed Lochiel less than 0.5mm particles (··········).

Comparing the conversion due to CH_3SH and SO_2 for both sample sizes, the decrease in CH_3SH for the AW<0.5 sample over the AW sample equates to 1.5% of conversion. The corresponding increase in conversion due to SO_2 is 1.9%. It is possible that the evolution of SO_2 and CH_3SH may be linked to similar progenitor species in the coal matrix and that particle size (hence intra-particle interactions) has an impact on the final sulphur speciation (Garcia-Labiano *et al.,* 1995); Miura *et al.,* 2001).

4.5 Comparing Bowmans and Lochiel

Both Lochiel and Bowmans coal have been proposed as feed-stocks for advanced coal fired power stations in South Australia, and, as described in the introduction, are the best suited in terms of the size of their resource and proximity to the national electricity market and major load centres. Bowmans coal has similar sulphur distribution (amongst organic and inorganic forms) and ultimate and proximate analysis, and contains higher absolute sulphur content than Lochiel coal. The mineral matter composition, however, is very different, therefore it is expected that, while the coals may be similar in terms of conversion with temperature behaviour, similar speciation in the gas phase is unlikely.

The TPP evolution profiles for sulphur species detected during heat treatment for Bowmans coal are shown in Figure 4.6, calculated as per the methodology described in previous sections for air-dried (AD) and acid-washed (AW) Lochiel coal. The evolution profiles for individual sulphur species for air-dried Bowmans (BW) coal are superimposed on the profiles for AD, AW and AW<0.5 samples.

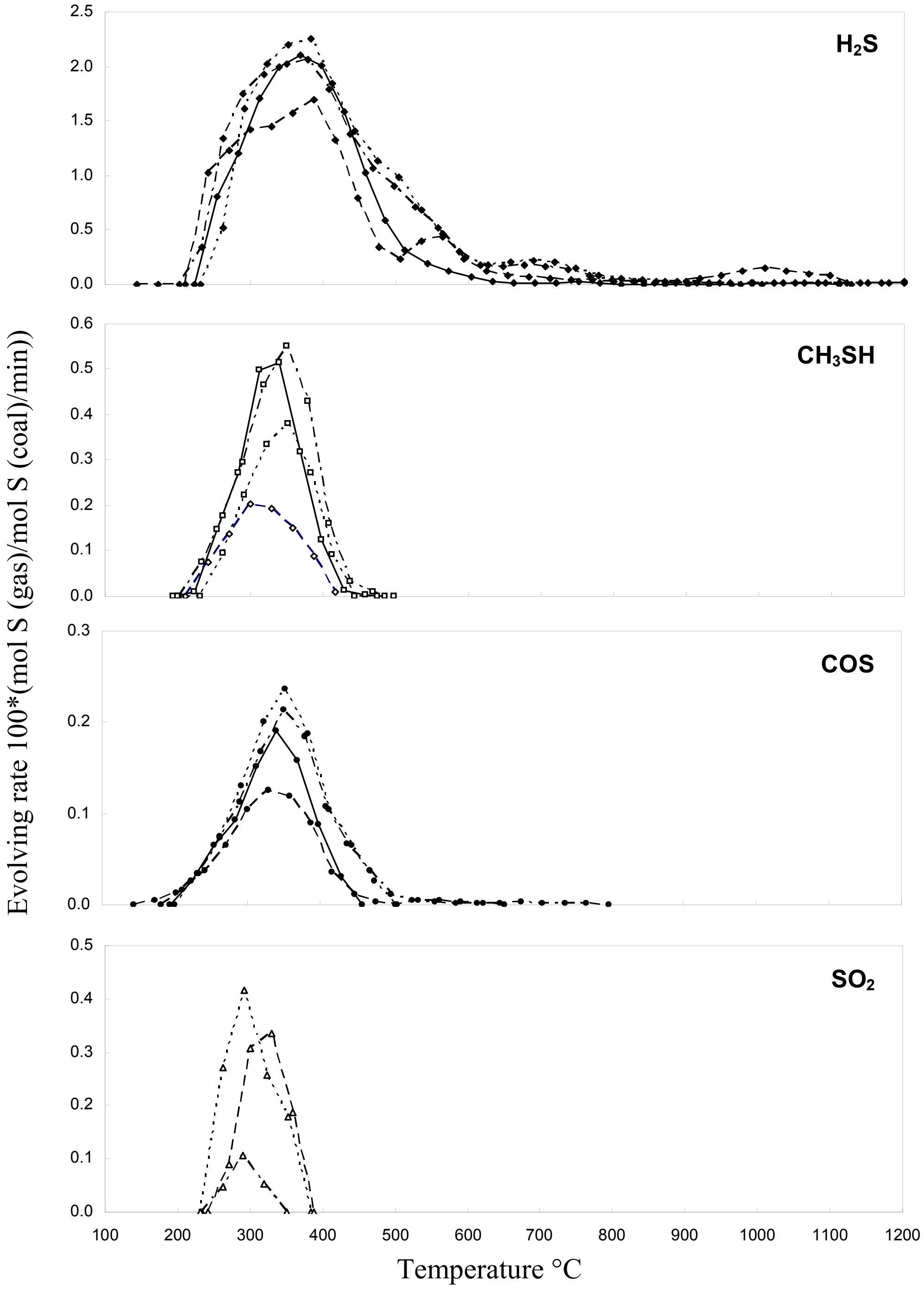


Figure 4-5 Evolving rate of sulphur species as a function of temperature for Lochiel (——), acid washed Lochiel (- · – · ·), acid washed Lochiel less than 0.5mm particles (··········) and Bowmans (– – –) coals.

The evolving rate for Bowmans increases significantly between 200°C and 400°C, to 1.7%min^{-1} at 390°C (*cf* 2.1%min^{-1} at 370°C for Lochiel). At 400°C the total conversion to the gas phase due to H_2S equates to 17%, while by 500°C, this figure is approximately 22%. For Bowmans coal, as opposed to the AW and AW<0.5 Lochiel samples, there is a distinct peak between 500-600°C, that equates to approximately 2% of the total conversion to the gas phase. Also in contrast to the acid-washed Lochiel samples, there is an additional peak from 900-1100°C that represents approximately 1% of the total conversion to the gas phase, at evolving rate of approximately 0.2 %min^{-1}. This markedly different evolving rate profile suggests that the phenomena operating during the TPP of Lochiel coal, including the acid-washed samples, are very different from those which influence that of Bowmans.

The evolving rate for CH_3SH shows a single peak structure in the same temperature range as the AD, AW and AW<0.5 samples, achieving a peak conversion evolving rate of 0.2%min^{-1} at 300°C (*cf* 0.5%min^{-1} at 340°C (AD); 0.55%min^{-1} at 350°C (AW); 0.38%min^{-1} at 350°C (AW<0.5)). The contribution of CH_3SH to the overall conversion to the gas phase for Bowmans coal is approximately 1.2%, less than the contribution to conversion of the Lochiel sample at approximately 1.6%.

The profile for COS shows a single peak structure in the 200-500°C region, with small quantities continuing to be detected out to 600°C, as with the AW sample. The peak evolving rate equates to 0.125%min^{-1} at 330°C, significantly less than the rates achieved for the AD, AW and AW<0.5 samples for Lochiel coal (0.19%min^{-1} at 340°C; 0.21%min^{-1} at 350°C; and 0.24%min^{-1} at 350°C). The additional contribution to conversion from the prolonged evolution out to 600°C represents only 0.03% of the total sulphur conversion to the gas phase.

The BW TPP profile shows a significant contribution to sulphur conversion from SO_2, with a large peak (maximum 0.34%min^{-1}) over the range 250°C to 400°C. Unlike the peak evolving rates for the AW and AW<0.5 profiles, the peak for BW appears to be delayed by approximately 25°C. The evolving rate profile for SO_2 represents 1.8% of the total sulphur conversion to the gas phase.

The evolving rate profile for BW gives insight into the sulphur structures that are present in the coal through comparison with AD. That H_2S evolves at slightly lower temperature and at a faster peak rate for BW over AD suggests that BW has a greater portion of simple sulphur compounds (thiols, R-SH, or aliphatic sulphides R-S-R’) that are easily released from the structure. That there is a distinct secondary peak of evolution at 400°C for BW indicates that there is stronger differentiation between the sulphur types more so than for AD, which has a broad peak over the 200-500°C range. The structures responsible for evolution in this range have previously been assigned to aliphatic sulphides and disulphides (R-S-S-R’) (Telfer, 1999). Thiophenes are very stable and do not readily decompose below 450°C, therefore the peak from 500-600°C for BW is possibly due to the decomposition of thiophenes. Note that while the evolving rate for AD is low in this region, decomposing thiophenes may still be contributing. Telfer (1999) observed the decomposition of sulphates in the 600-800°C region, and also observed an increase in organic sulphur, believed to be the result of the solid state transformation of sulphates to strongly bound organic sulphur species. This would not be observed in the gas phase for the AD sample.

The final peak in the 900-1100°C region is likely to be either the result of the final decomposition of cyclic sulphur structures (such as dibenzothiophene or thionaphthene) (Attar, 1979; Khan, 1989) or the decomposition of metal sulphides, although a number of researchers have shown that sulphides, for example iron sulphide, FeS, only completely decompose at temperatures of around 1700°C (Attar, 1978; Gryglewicz and Jasienko, 1992; Patrick, 1993). Telfer (1999) suggested BW did not form sulphides, at least in forms that were easily detectible using standard wet chemical methods. This is well beyond the practical operating temperature of advanced gasification processes.

That SO_2 is detected for air-dried Bowmans, and not air-dried Lochiel coal, might be due to several reasons. Firstly, SO_2 could be a primary product of pyrolysis for

Bowmans coal and not Lochiel coal, indicating that the sulphur species are bound as a different (oxidised) forms for Bowmans coal and/or in greater abundance than Lochiel. However, as shown by the acid-washing experiments, SO_2 is detected in the absence of mineral matter, and in greater abundance for small size particles (AW<0.5), suggesting that it may be a primary product for both coals. In which case, its detection during the pyrolysis of Bowmans coal and not Lochiel relates to secondary reactions, the most likely of which is with the mineral matter present in the non-treated samples.

A summary of the total conversion to the gas phase during the TPP for the AD, AW, AW<0.5 and BW experiments is presented in**Figure 4-6**, including speciation, while **Figure 4-7** shows the relationship between cumulative sulphur conversion and temperature for the TPP. The plot indicates that conversion is essentially complete for the AD sample by 600°C, while for the AW and AW<0.5, the conversion versus temperature relationship is very similar and continues to increase up to around 800°C. The relationship for BW, however, shows two distinct step changes in sulphur conversion, the first occurring at approximately 550-600°C and the second at 950-1050°C.

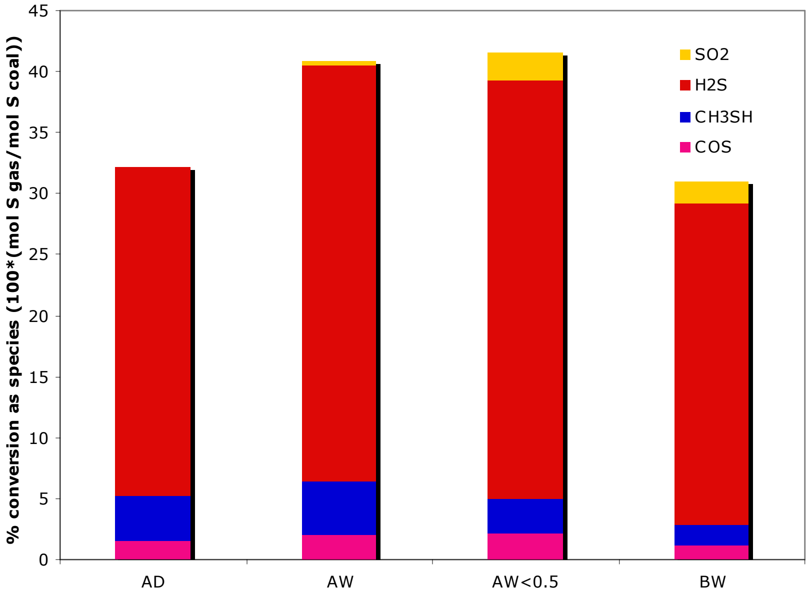


Figure 4-6 Total conversion of sulphur to the gas phase for air dried (AD), acid washed (AW), AW particles less than 0.5mm (AW<0.5) TPP for Lochiel coal, compared to Bowmans (BW) coal.

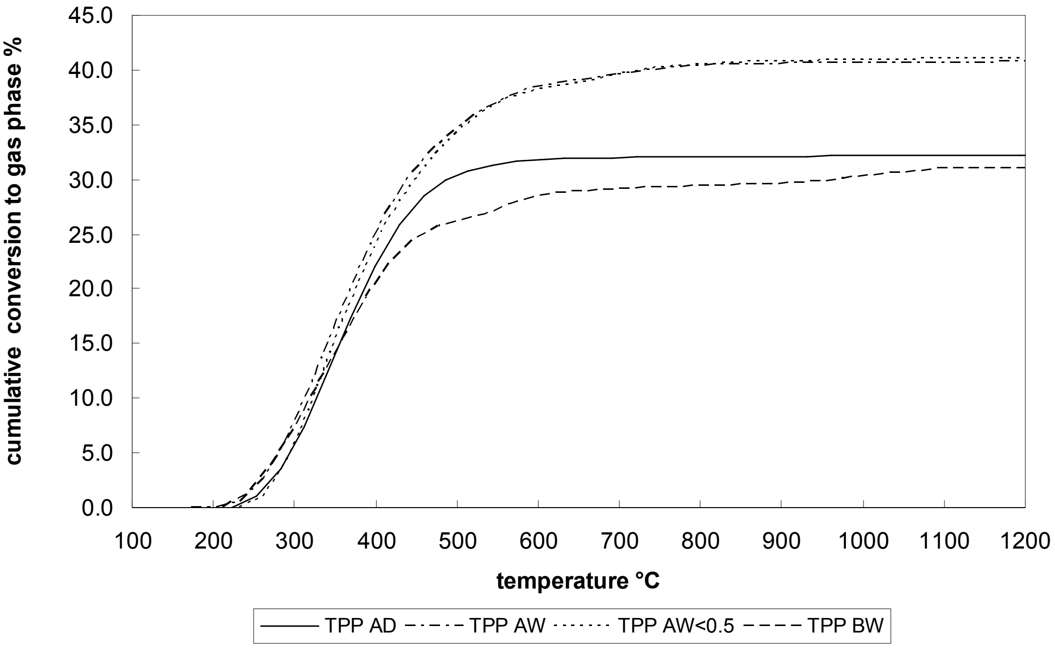


Figure 4-7 Cumulative conversion of sulphur to the gas phase for air dried (AD), acid-washed (AW), AW particles less than 0.5mm (AW<0.5) TPP for Lochiel coal, compared to Bowmans (BW) coal.

4.6 Mineral matter considerations

Mineral matter present in coal is known to have a profound effect on the behaviour of sulphur during pyrolysis of South Australian low rank coals (Telfer, 1999; Ross, 2000; Kosminski, 2001). This section examines the mineral matter content of the resulting chars post TPP at 15Kmin^{-1}. Table 3.1 from Chapter 3 is reproduced as **Table 4-1** below, showing the results of elemental ash analysis for the air-dried coals studies in this chapter.

Table 4-1 Elemental ash analysis of Lochiel, Bowmans and Acid-washed Lochiel coals (air-dried) used in TPP experiments

Component	Description	Lochiel	Bowmans	Acid-washed Lochiel
Elemental ash analysis (%db)	Si	1.62	0.56	1.31
	Al	0.55	0.46	0.27
	Fe	0.43	0.87	0.19
	Ti	0.068	0.005	0.14
	K	0.031	0.025	0.006
	Mg	0.77	0.96	0.05
	Na	0.8	1.82	0.02
	Ca	1.29	0.46	0.13

The difference between the mineral matter compositions for Lochiel and Bowmans coal reveal that Bowmans coal has one third of the calcium of Lochiel, while at the same time having 2.3 times the quantity of sodium. The abundant calcium, found mainly as dolomite, can react with sulphur species, oxidised or reduced, forming sulphates or sulphides respectively.

If SO_2 is formed in the early stages of pyrolysis for air-dried Lochiel coal (as a primary product), it may react with calcium to form sulphates or sulphites. These readily decompose to thermally stable sulphides as pyrolysis progresses, but sulphides do not easily decompose until temperatures over 900°C (Attar, 1978). Sulphate may also convert to organic compounds through the solid-state reaction as suggested by Medvedev and Petropolskaya (1966) and observed by Telfer (1999). Bowmans, however, with much less calcium, does not undergo the same level of reattachment to form sulphates and then thermally stable sulphides, explaining why it might show a greater quantity of SO_2 released to the gas phase.

Table 4-2 presents the results of XRD analysis of the residues removed from the HTF after TPP. For Lochiel coal TPP, sodium, calcium, magnesium and aluminium are dominant metal species remaining post pyrolysis (>60 wt%), and sulphur is found primarily as calcium sulphide (minor phase (5-20 wt%) oldhamite, CaS) For acid-washed Lochiel TPP, trace quantities (<5 wt%) of sulphur are found as sodium sulphate (thenardite, Na_2SO_4) in the acid washed sample. For Bowmans coal, however, sulphur remains as a co-dominant phase as sodium sulphate (thenardite, Na_2SO_4). XRD analysis confirms that, for low heating rate pyrolysis of Lochiel coal, calcium plays an important role in the retention of sulphur as sulphides (CaS), while for Bowmans, sodium plays an important role in retaining sulphur as sulphates (Na_2SO_4) during low heating rate pyrolysis.

Table 4-2 XRD analysis of TPP residues for air-dried Lochiel (AD), acid-washed Lochiel (AW) and air-dried Bowmans (BW) coal

Char type	**Dominant (>60%) or co-dominant (Σ=>60%)**	**Minor (5-20%)**	**Trace (<5%)**	**Possible**
Lochiel (AD)	Cristobalite (SiO_2)	**Oldhamite (CaS)**	Quartz (SiO_2)	**Gypsum ($CaSO_4.2H_2O$)**
Lochiel (AW)	Quartz (SiO_2)	Gehlenite ($Ca_2\,Al_2\,Si\,O_7$) Augite ($Ca(Mg,Fe)Si_2\,O_6$)	Cristobalite (SiO_2) Nepheline ($NaAlSiO_4$) **Thenardite (Na_2SO_4)**	Monticellite ($Ca\,Mg\,Si\,O_4$)
Bowmans (AD)	**Thenardite (Na_2SO_4)** Forsterite ($Mg_2\,Si\,O_4$) Periclase (MgO) Spinel ($Mg\,Al_2\,O_4$)	Cristobalite (SiO_2)	Nepheline ($NaAlSiO_4$)	Gehlenite ($Ca_2\,Al_2\,Si\,O_7$) Monticellite ($Ca\,Mg\,Si\,O_4$) Hematite (Fe_2O_3)

Telfer (1999) performed water and acid-washing followed by ion exchange on Lochiel and Bowmans coal, finding that sodium sulphate exchanged Bowmans coal was unlikely to form sodium sulphides during TPP, instead, the sulphur was believed to undergo solid state transformations to enhance the organic sulphur content of the char. Acid-washed Bowmans coal exchanged with calcium sulphate, however, showed significant transformation to calcium sulphide while solid state transformation to organic sulphur was also observed.

4.7 Summary & Conclusions

Sulphur species are distributed throughout the products of fixed-bed Temperature Programmed Pyrolysis (TPP) in a number of forms. Examining solely the gas phase products of pyrolysis, sulphur evolves rapidly for all coal types and treatments until around 400-500°C, after which time the evolution rate decreases.

The main species detected during TPP of Lochiel and Bowmans coal, including acid-washed Lochiel coal of differing particle size fraction, is hydrogen sulphide (H_2S). While this is to be expected during pyrolysis of all coals containing sulphur, H_2S only constitutes roughly 80% of the gas phase sulphur products, with carbonyl sulphide (COS), methyl mercaptan (CH_3SH) and sulphur dioxide (SO_2) the remaining most abundant species detected. No carbon disulphide (CS_2) or ethyl mercaptan (C_2H_5SH) was detected for any of the coal types or treatment.

A complex interaction of evolving sulphur and sulphur remaining in the char is believed to result in the varying distribution of sulphur among these species, with acid-washing (and the removal of inorganic material responsible for sulphur re-attachment after evolution in the air dried Lochiel sample) resulting in a significant increase in total sulphur conversion. For Lochiel coal, acid-washing saw small amounts of SO_2 detected, which did not occur for the air-dried sample. Conversion of sulphur during TPP of Bowmans coal, however, received a greater contribution from SO_2 than any species other than H_2S, suggesting that the two coals have very different structures and that the effect of the inherent and adventitious mineral matter is significant. This was confirmed by XRD analysis of the residues from these experiments, which showed sulphur preferentially reacting with sodium during TPP for Bowmans coal (forming thenardite, Na_2SO_4) while forming oldhamite (CaS) and possibly gypsum ($CaSO_4.2H_2O$) for Lochiel coal. This corresponds to the results of Telfer (1999) who found that sodium sulphate does not reduce to sodium sulphide during pyrolysis, while calcium sulphate converts to calcium sulphide.

Given the above information, it is essential to understand the effect of heating rate on the evolution of sulphur during pyrolysis, since the industrial scale combustion or gasification processes all carry out pyrolysis at heating rates much faster than that during TPP. The effect of mineral matter, particle size and coal type on the extent of sulphur conversion and its products during fast pyrolysis are all examined in the following chapter.

5 FAST PYROLYSIS: FIXED BED

5.1 Introduction and Objectives

Chapter 4 examined the transformations of sulphur in Lochiel and Bowmans coal under slow heating rate pyrolysis conditions of 15Kmin^{-1}. In this chapter, the transformations of sulphur at much faster heating rate conditions are investigated in a horizontal tube furnace by plunging samples of coal into a preheated furnace with a 5 minute holding time. By examining the final cumulative product concentration of each species, the total mass of sulphur and carbon can be determined, which enables the fate of sulphur in each of the phases – solid, gaseous and tar – to be calculated. The purpose of examining the behaviour of sulphur during fast heating rate pyrolysis is to gain insight into its behaviour in industrial systems where the pyrolysis step typically takes place in situ, that is, in the combustion or gasification chamber, and where directly determining the pyrolysis behaviour is complex and costly.

While there is a body of literature that examines the fate of sulphur during fast heating rate pyrolysis, which is reviewed extensively in Chapter 3, the purpose of this chapter is to determine the relationship between final sulphur conversion and its distribution to final temperature and coal treatment for Lochiel and Bowmans coal.

A simple reaction system is chosen in the form of a horizontal tube furnace, as it has the advantage over a fluidised bed of being able to:

- minimise secondary reactions of volatiles with other volatile species and/or char
- prevent the loss of catalyst/product due to fines carry-over and hence
- more accurately calculate mass balances

The results in this chapter are presented with respect to Lochiel coal's sensitivity toward final pyrolysis temperature; acid-washing and particle size. As with the work presented in Chapter 4, results for Bowmans coal are included by way of comparison.

5.2 Concentration data and conversion calculation

As described in Chapter 3, only concentration data for sulphur species is available from the micro-GC, and a mass balance is calculated from this data as per the calculation methodology outlined in Chapter 4. The MS is used to check the background concentration of oxygen and to validate the methodology, that is, to ensure that the 5 minutes holding time was sufficient time for pyrolysis at the fast heating rate conditions to complete. For each of the experimental temperatures (700, 800, 900, 1000°C) and for each coal (Lochiel and Bowmans) or treatment (acid-washed Lochiel), pyrolysis was completed within the 5 minute time frame, as indicated by the absence of any ionisation products apart from m/z 28 and 14 after 5 minutes (indicating nitrogen, the carrier gas). Concentration results for a typical 800°C experiment using air-dried Lochiel coal are shown in **Table 5-1** from which the total moles of sulphur and carbon released to the gas phase during pyrolysis are calculated, as per the methodology outlined in Chapter 3. No sulphur species other than H_2S, COS and CH_3SH were detected during the fast heating rate experiments.

Table 5-1 Raw product concentration from fast pyrolysis of air-dried Lochiel coal at 800°C, along with normalised concentration.

Species	Concentration (v/v%)	Concentration (Excluding nitrogen)
CH4	0.0401	3.87
CO2	0.1501	14.49
C2H4	0.0021	0.20
C2H6	0.0057	0.55
H2S	0.0350	3.38
COS	0.0020	0.19
C3H6	0.0036	0.35
C3H8	0.0016	0.15
CH3SH	0.0043	0.42
H2	0.4220	40.73
N2	98.987	-
CO	0.3689	35.61
TOTAL v/v%	**100.02**	**99.94**

5.3 Sulphur conversion with coal type and treatment

Figure 5-1 shows the total sulphur conversion to the gas phase for each coal type as a function of the final pyrolysis temperature. Each of the coals shows an increase in total sulphur conversion between the 700°C and 1000°C experiments, however both the AD and BW samples show a decrease in sulphur conversion from 700-800°C, which continues for the AD sample over the 800°C to 900°C range.

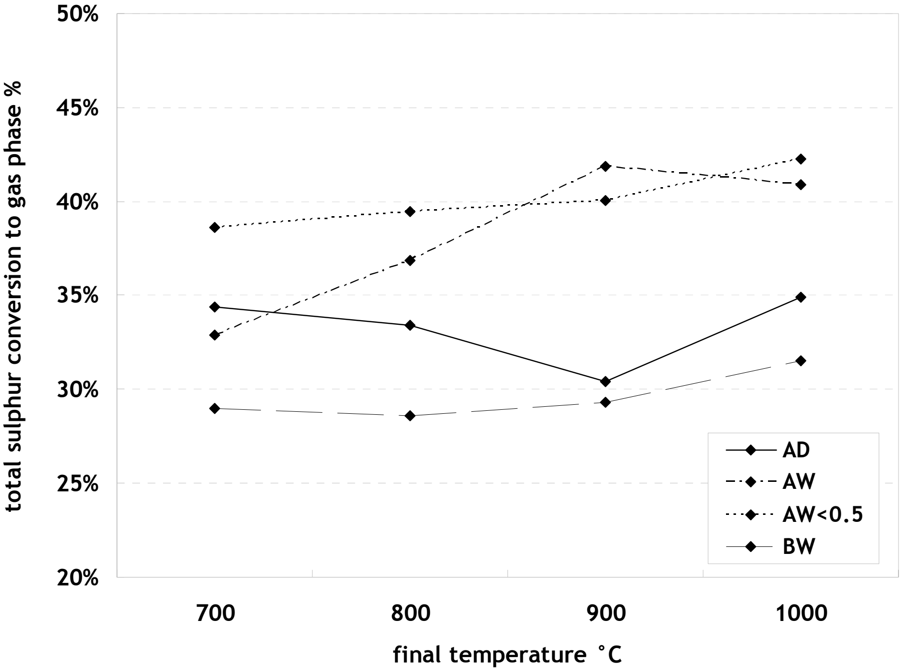


Figure 5-1 Gas phase conversion of sulphur for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures ranging from 700-1000°C.

In absolute terms, the total sulphur conversion to the gas phase at 700°C is lowest for the air-dried Bowmans (BW) sample at 28.95%, which steadily increases to 31.5% at 1000°C. For the air-dried Lochiel (AD) sample, sulphur conversion is 34.3% at 700°C and decreases to 30.4% at 900°C. Sulphur conversion to the gas phase at 700°C is greatest for the acid-washed small particle Lochiel sample (AW<0.5) at 38.6%, increasing to 42.3% at 1000°C, while for the acid-washed Lochiel sample (AW), there is an increase in conversion of 9% from 32.9% to 41.9% between the 700°C and 900°C experiments, diminishing to 40.9% for the 1000°C experiment.

Figure 5-2 through to **Figure 5-4** show the sulphur conversion to the gas phase as a function of the H_2S, COS and CH_3SH products. The conversion to H_2S, as shown in **Figure 5-2**, is the key contributor to the total conversion as shown in **Figure 5-1**.

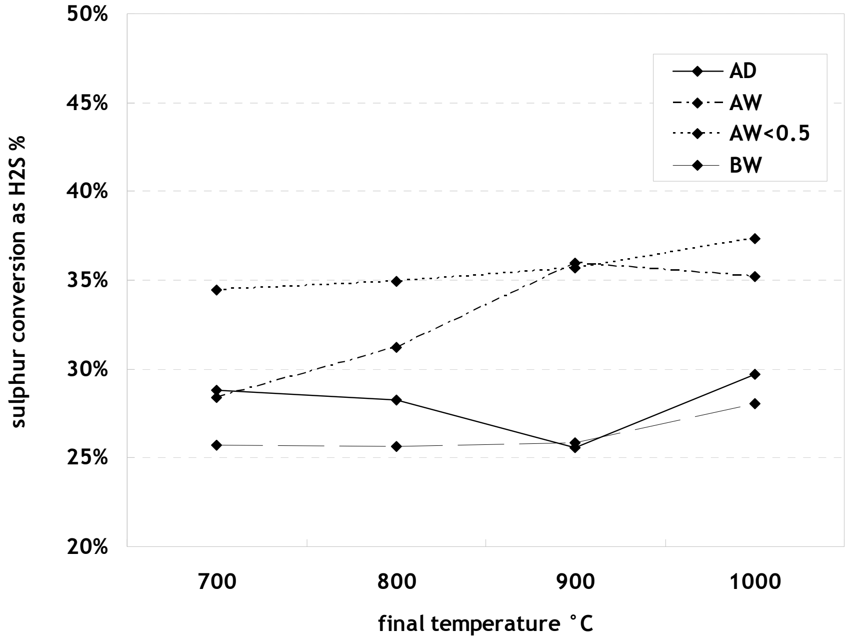


Figure 5-2 Gas phase conversion of sulphur as H_2S for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures ranging from 700-1000°C.

The conversion as H_2S for the AD sample reaches a minimum of 25.5% at 900°C, following conversion values of 28.8% and 28.3% at 700°C and 800°C respectively. At 1000°C, sulphur conversion as H_2S is at its peak over the temperature range in the study at 29.7%. For the AW sample, the H_2S contribution to conversion changes significantly over the range of final temperatures, from 28.4% at 700°C to a maximum of 36.0% at 900°C, and 35.2% at 1000°C. AW<0.5 shows only a slight increase in conversion due to H_2S when moving from 800°C to 900°C, from 34.4% to 35.7%, and reaches a level of 35.2% at 1000°C.

Conversion as COS, as shown in **Figure 5-3**, varies for AD between 1.6-1.8% of the total conversion for all temperatures. For AW, COS contributes 1.8% to conversion at 700°C, a maximum of 2.6% at 900°C and 2.1% at 1000°C, while for AW<0.5 the contribution to conversion remains relatively constant at 2.2-2.3% for each of the experimental temperatures. For the BW sample, conversion at 700°C is 1.8%, slightly lower for the 800°C and 900°C experiments at 1.6% and again, 1.8% for the 1000°C experiment.

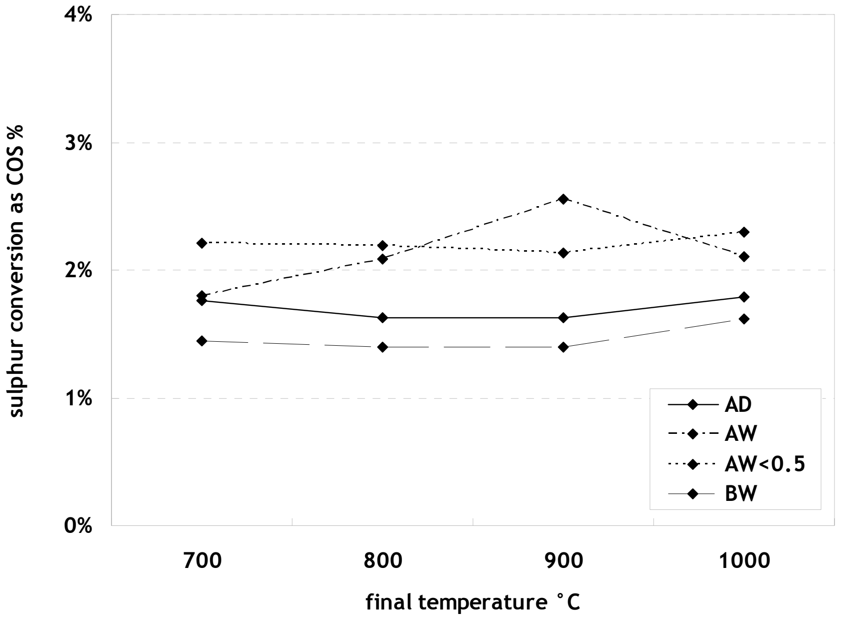


Figure 5-3 Gas phase conversion of sulphur as COS for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures ranging from 700-1000°C.

Results for sulphur conversion as CH_3SH are shown in **Figure 5-4**. For CH_3SH the contribution to conversion is much less consistent than the other species for the different coal types. Its contribution to conversion is greatest for AD, reaching 3.8% at

800°C but only 3.4% at 1000°C. For AW, the conversion due to CH_3SH contributes to 2.7% of the sulphur conversion at 700°C, 3.6% at 800°C and 3.3% at 900°C and 3.3% at 1000°C. The contribution to conversion for CH_3SH for AW<0.5 increases from 2% at 700°C to 2.6% at 1000°C, having steadied at 2.3% and 2.2% for the 800°C and 900°C range. For BW, the CH_3SH contribution to conversion at 700°C and 1000°C is the same at 1.8%, but reaches only 1.5% at 800°C and a achieves a maximum of 2% at 900°C.

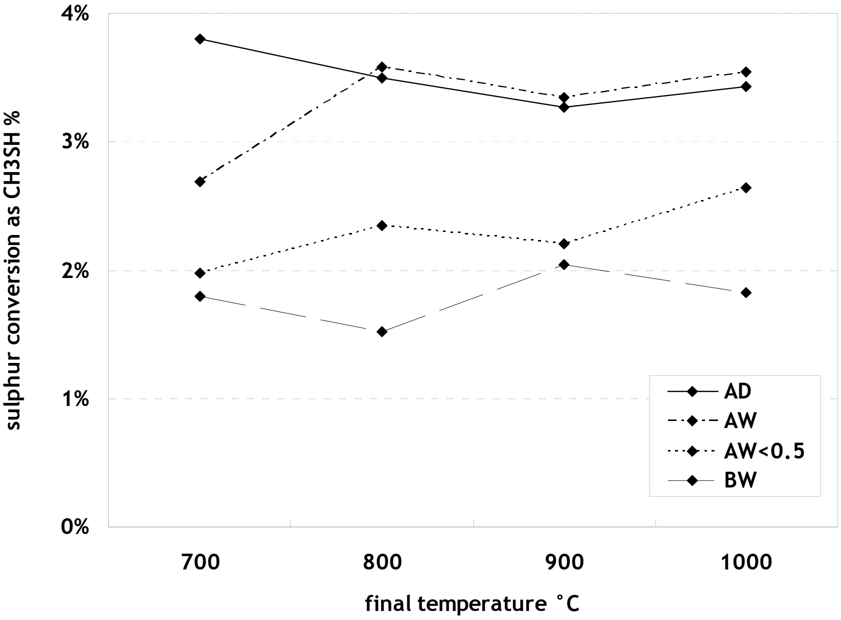


Figure 5-4 Gas phase conversion of sulphur as CH_3SH for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures ranging from 700-1000°C.

Of the inorganic sulphur species that are present in coal - pyrite and sulphate - sulphate is the only one found in abundance in Lochiel coal as determined by the wet chemical methods described in Chapter 3. Literature studies have demonstrated that higher heating rates discourage the transformation of sulphate sulphur to organic sulphur (Telfer, 1999). The results showing the decrease in total sulphur conversion between 700°C to 900°C may be due to the increased heating rate preventing the transformation of sulphate sulphur to organic sulphur (via the solid state reaction as observed by Telfer (1999) and described by Medvedev and Petropolskaya (1966). As Telfer (1999) observed, sulphate sulphur preferentially reduces to sulphides at the higher heating rates, which are not easily released in the 700-900°C temperature range. Sulphides are, however, released at temperatures above 900°C (Attar, 1978). It is believed that the increase in final sulphur conversion noted between 900°C and 1000°C for the AD sample is due to the decomposition of metal sulphide.

The results presented in **Figure 5-1** to **Figure 5-4** show that the effect of acid-washing on the fast pyrolysis sulphur conversion of Lochiel coal is significant, particularly at final pyrolysis temperatures over 800°C, where the difference in total sulphur conversion reaches a maximum of over 10% at the 1000°C final temperature.

At 700°C, there is very little difference between the AD and AW sulphur conversion values, and both coals achieve a maximum sulphur conversion of around 33-35%. This suggests that the phenomenon of back reactions of sulphur with the coal matrix or inorganic species and the intra particle diffusion of those species were controlled. Acid-washing clearly has little effect on the conversion outcome for sulphur at 700°C and this corresponds to the work of Karaca (2003) showing that acid-washing with HCl reduces the release of sulphur from lignite (relative to untreated coal) for temperatures under 700°C. The factors affecting the minor difference are the increased amount of sulphur conversion due to CH_3SH at the expense of H_2S. However, at 800°C, the AW sample sees extra conversion of sulphur as H_2S (3%) and COS (0.5%) while the conversion due to CH_3SH remains the same for both the AD and AW. For final temperature of 900°C, conversion of sulphur as H_2S is now decreased 2.5% for AD (from 800°C) while the total difference in conversion of sulphur as H_2S between AD and AW is now over 10%. At final temperature of 1000°C, the conversion of sulphur as H_2S and COS for the AW sample has dropped slightly from the 900C final temperature experiment, while the increase in sulphur conversion to H_2S and COS for the AD sample have increased.

As discussed in Chapter 4, and referenced to the literature in Chapter 3, the removal of inorganics from coal via acid-washing results in a decrease in sulphur re-attachment reactions via the formation of sulphidic or sulphatic structures, therefore it is not surprising that there is an increase in the degree of sulphur conversion for each of these temperatures for the acid-washed sample.

Examining the differences between AW and AW<0.5 at the final pyrolysis temperature of 700°C, it is clear that the effect of particle size, for the equivalent coal treatment, is important. The total conversion of sulphur to the gas phase is more than 6% greater for the AW<0.5 sample than the AW sample. This is a result in an increase across all the species except for CH_3SH, which contributes only 2% to conversion compared with 2.8% for the AW sample. This suggests that for the 700°C final pyrolysis temperature, for the AW sample, there is still a significant quantity of back reactions occurring that fix sulphur to the organic coal matrix. By reducing the particle size, the intra-particle temperature gradient increases and the intra-particle residence time of the evolved gases and tars decreases. Smaller particles therefore enhance the sulphur evolution at lower temperatures. For the AW sample then, sulphur conversion is heavily dependent on the final temperature, whereas for AD, the presence of metals inhibits the sulphur conversion until the final temperature exceeds 900°C, as evident by the diminishing sulphur conversion up to and including 900°C. This is the reason why, for final temperatures of 800-900°C, the total sulphur conversion and the individual species conversion is relatively constant for the AW<0.5 sample. Only at the final temperature of 1000C does the total conversion of sulphur increase above that of the AW sample, suggesting that there is an organic sulphur species present in the coal which, in the absence of mineral matter and with sufficient temperature to decompose, does not re-react with the organic coal matrix during transport to the bulk fluid phase.

For BW, the sulphur conversion as a function of final temperature remains relatively constant to 900°C, but increases by 3% between 900 and 1000°C. This suggests that the total sulphur conversion to the gas phase for BW is relatively insensitive to the final pyrolysis temperature, and is an important consideration for fluid bed processes where operating temperatures for low rank coals are typically 800-900°C.

It also suggests that Bowmans coal has a vastly different structure to Lochiel coal, and the following section, examining the carbon conversion and the major species contributions to carbon conversion, aims to clarify these differences.

5.4 Carbon conversion with coal type and treatment

Figure 5-5 shows the overall conversion of carbon (as percentage of the prepared coal carbon) to the gas phase for each of the fast heating rate experiments.

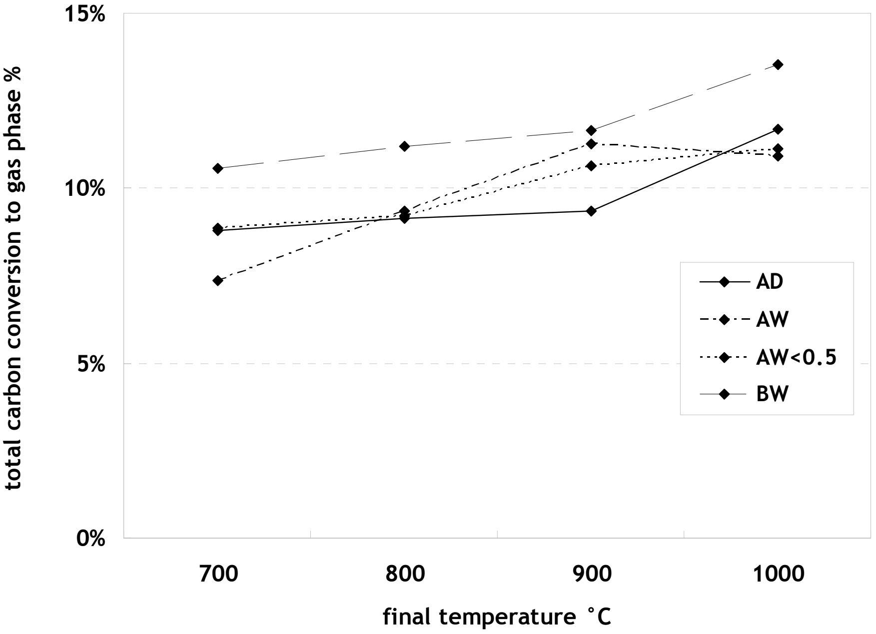


Figure 5-5 Gas phase conversion of carbon for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures from 700-1000°C.

For the AD and BW samples, carbon conversion increases minimally with increasing final pyrolysis temperatures between 700-900°C, from 8.8% to 9.3% for AD and 10.6% to 11.7% for BW. For the 1000°C experiment, however, there is a significant increase in carbon conversion to the gas phase, to 11.7% for AD and 13.5% for BW. Meanwhile the increase in carbon conversion to the gas phase is significant between 700°C and 900°C for AW, from 7.4% to 11.3% before reaching 10.9% at 1000°C while for the AW<0.5 sample, conversion increases from 8.9% at 700°C to 11.1% at 1000°C.

The conversion of carbon to the gas phase due to CO_2 formation is shown in **Figure 5-6**. For the AD sample, the conversion changes little as the final temperature is increased from 700°C to 1000°C, from 2.4% to 2.1%. For AW, at 700°C the conversion due CO_2 is only 1%, increasing to 1.5% by 800°C and 1.9% by 900°C, diminishing only marginally between 900°C and 1000°C to 1.8% while for AW<0.5, the conversion remains relatively constant over the range of pyrolysis temperatures. For BW, the carbon conversion to the gas phase due to CO_2 remains relatively constant for final pyrolysis temperatures between 700-1000°C and also for the TPP experiments, at a figure of 4.2-4.5%.

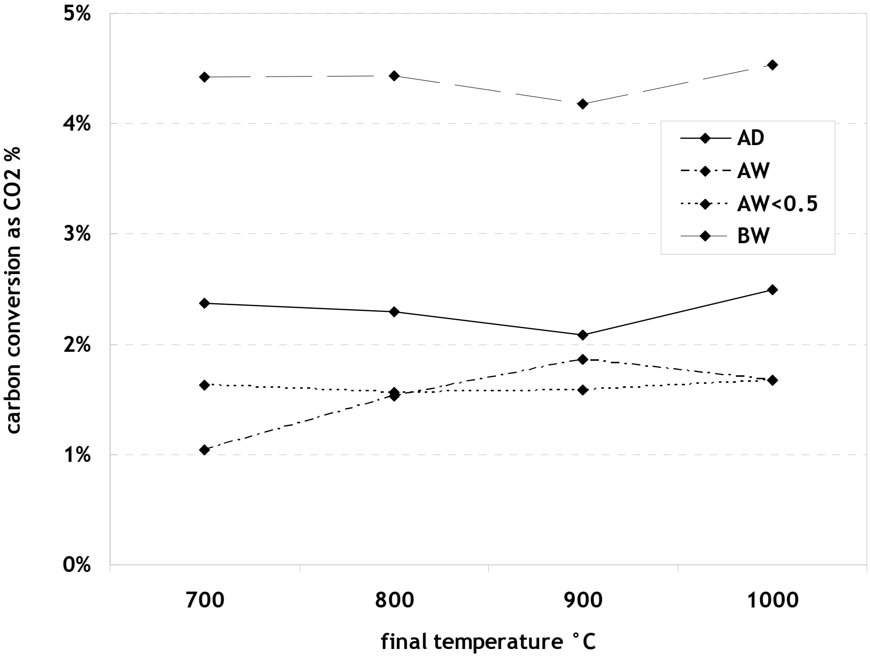


Figure 5-6 Gas phase conversion of carbon as CO_2 for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures from 700-1000°C.

Figure 5-7 shows the conversion to the gas phase due to CO evolution for each of the coals as a function of final pyrolysis temperature. For AD and BW, the conversion due to CO is similar, with 5.3% of conversion due to CO at 700°C, increasing moderately to 6.1% and 6.5% respectively at 900°C before reaching a final value of 8.0% for each of the coals at 1000°C. The increase in carbon conversion to the gas phase is significant between 700°C and 900°C for AW, from 5.0% to 7.8% before reaching 7.5% at 1000°C while for the AW<0.5 sample, conversion increases steadily from 5.9% at 700°C to 7.8% at 1000°C.

The carbon conversion to the gas phase due to higher hydrocarbons, which include CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H_8, is relatively insensitive to the final pyrolysis temperature for each of the coals.

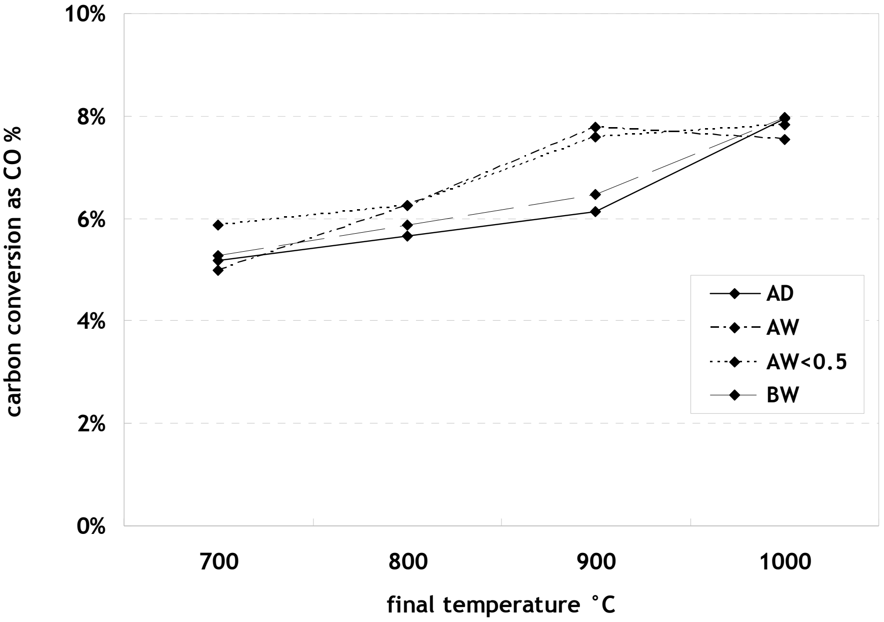


Figure 5-7 Gas phase conversion of carbon as CO for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for pyrolysis at temperatures ranging from 700-1000°C.

Figure 5-8 shows the ratio of the gas phase carbon conversion due to CO (%) to CO_2 for the fast pyrolysis experiments at each of the final temperatures and for the cumulative conversion at those temperatures during TPP. The lower the ratio of CO/CO_2, the lower the conversion of carbon as CO to the gas phase.

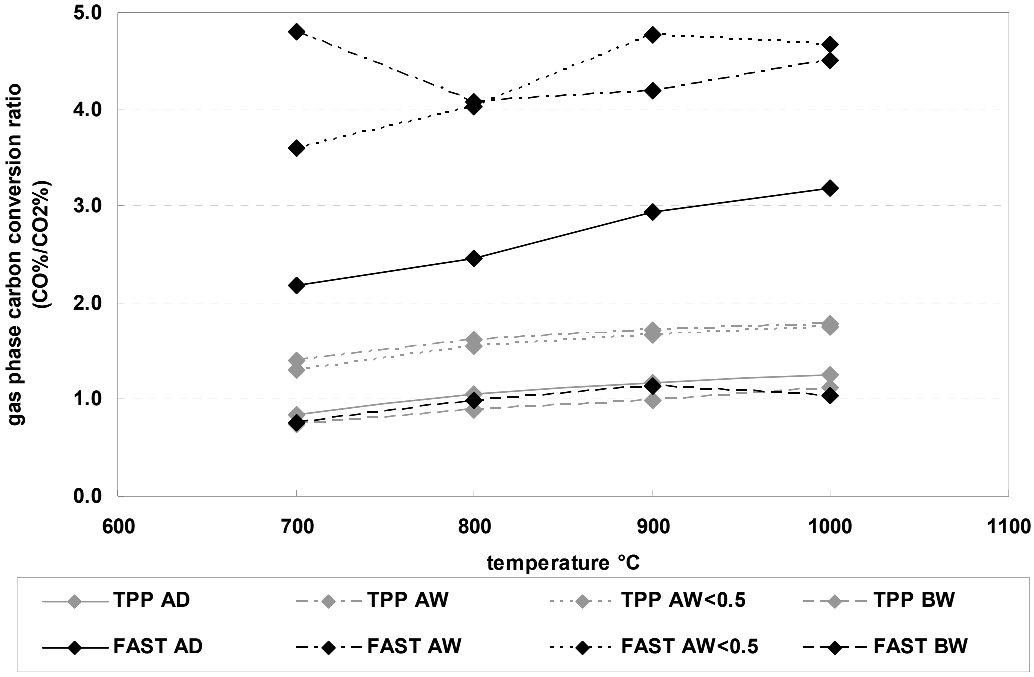


Figure 5-8 Gas phase carbon conversion ratio – the ratio of carbon conversion as CO (%) to carbon conversion as CO_2 (%) for air-dried (AD), acid-washed (AW) and acid-washed less than 0.5mm (AW<0.5) Lochiel coal, along with air-dried Bowmans coal for fast pyrolysis at temperatures ranging from 700-1000°C (FAST) and TPP.

For the Fast AD, AW and AW<0.5, the carbon conversion as CO_2 is significantly less following the fast pyrolysis experiments when compared to the TPP work as evidenced by the low values of CO/CO_2 conversion ratio during the TPP work. CO/CO_2 ratios of between 3.5 and 5 are calculated for fast pyrolysis of AW and AW<0.5, and between 2 – 3 for the AD samples, but the cumulative CO/CO_2 conversion ratios obtained during TPP are between 1-2 for AW and AW<0.5 and around 1 for AD.

For BW, however, the total carbon conversion as CO_2 is approximately equal during both fast pyrolysis and TPP, as evidenced by equivalent CO/CO_2 factors. In addition, the CO/CO_2 conversion ratio being around 1 suggests that the conversion of carbon to the gas phase is almost equally distributed between CO and CO_2 (neglecting the small percentage converted as hydrocarbons).

This difference in the partitioning of carbon as CO and CO_2 during the two different pyrolysis modes confirms that Lochiel and Bowmans coals are fundamentally different in their structure. The difference could be due to several factors that relate to the oxygen content of the original coals and the comparative stability of carbon/oxygen groups, particularly carboxyl (COO^-) groups, caused by the presence and type of mineral matter in the coals (Takarada *et al.,* 1985; Ye *et al.,* 1993). Because Lochiel coal has more calcium than Bowmans, it is possible that since the Ca^{++} ion is divalent and stabilises two COO^- groups, there is less CO_2 released during pyrolysis (Quyn, 2002). This would also explain why there is significantly less CO_2 released during the pyrolysis of acid-washed Lochiel samples, which contain negligible calcium. That there is less CO_2 during fast pyrolysis may suggest that the increased heating rate results in a lesser transformation of calcium (however it is found) to organically bound calcium, resulting in a greater release of CO_2 during pyrolysis.

While a detailed examination of all of these factors is out of the scope of the current study, each may have a significant impact on the determination of the type and nature of the sulphur forms present in the coal, and also how they react during pyrolysis and subsequent gasification.

5.5 The presence of sulphur dioxide

In Chapter 4, the presence of SO_2 during the TPP of acid-washed Lochiel coal at 1-1.7mm and less than 0.5mm particle size, along with Bowmans coal, was postulated to be either:

- A primary product of pyrolysis, not detected during the slow heating rate process with air-dried Lochiel due to its rapid uptake by calcium (4.1.1).

- A product of reactions between sulphur species (either present in the coal structure or already volatilised) and oxygen species (either inherent, due to oxidation of the coal prior to use or chemisorbed oxygen groups, or already volatilised as H_2O, CO_2 or CO).

If SO_2 is a primary product of pyrolysis, it would be expected that the fast heating rate experiments see a greater quantity of SO_2 in the product gas, provided that the SO_2 evolved and did not undergo subsequent re-reaction prior to being cooled and detected in the micro-GC. However, as indicated in the results presented in this chapter, no SO_2 is detected in the gas phase for the fast heating rate experiments undertaken between final temperatures of 700-1000°C.

Evidence of the change in sulphur allotment for different heating rates, and for the position that SO_2 is not a primary product of pyrolysis, is found in the literature in the work of Miura *et al.*, 2001. Flash pyrolysis experiments were undertaken at 3000°C/s for 10 coals (6 Japanese, 3 US and 1 Chinese) with the products containing sulphur determined using gas chromatography. These results were compared to the results of slow heating rate (20°C/min) pyrolysis. It was observed that for the flash pyrolysis experiments, SO_2 was not detected, while abundant CH_3SH and C_2H_5SH (methyl and ethyl mercaptan) were detected. The authors believed that the mercaptan species were primary products of pyrolysis, but that these readily decomposed to H_2S at the slow heating rate, which was oxidised by H_2O and CO_2 to form SO_2. For the coals in this study, which still contain approximately 13% moisture after air drying, there is abundant moisture released during the low temperature stage, when SO_2 is detected in the product gas, and there is also significant CO_2 released at temperatures as low as 200°C for all of the coals. The fast heating rate, by encouraging rapid evolution of H_2O and CO_2, may introduce affect the oxidation of sulphur by these species, as they are produced and rapidly enter the bulk fluid phase, limiting the SO_2 concentration at higher heating rate. The inverse relationship between CH_3SH and SO_2 during TPP for acid-washed particles of differing size has previously been discussed in Chapter 4 and this relationship, after Miura *et al* (2001), may be due to CH_3SH oxidation, owing to a higher portion of H_2O and CO_2, with the additional SO_2 coming from another source, possibly oxidised sulphur species in the coal.

If the theory of Miura et al (2000) is valid for these coals, however, it would be expected that the reaction of H_2S (or other mercaptans) and CO_2 to form SO_2 during TPP would continue until the species were not detected. But SO_2 ceases to be detected well before H_2S and CO_2 reach peak evolution rate. The reason it is detected for Bowmans and not Lochiel coal has previously been attributed (Chapter 4) to the presence of calcium in Lochiel and its rapid uptake of sulphur species. However, if the oxygen concentration as H_2O and CO_2 is the determining factor in SO_2 concentration at slow heating rate, this does not adequately describe why there is an increase in SO_2 conversion when moving to smaller particles for the acid-washed sample. Smaller particles decrease intra particle residence time for gas phase species, therefore, if the sulphur oxidation reaction is mass transfer limited by the concentration of H_2O and CO_2, it would be expected that the smaller particle experiments see a diminished conversion as SO_2, not an increase.

However, Telfer (1999) performed experiments using manufactured coal pellets for Bowmans coal, subjecting them to fast heating rate (in a fluidised-bed) up to temperatures of 800°C, and, taking a cross section of the pellets and obtaining an X-ray map of the surface, indicated that that sulphur appeared to be concentrated at the edge of the particle. This was believed to imply that, after evolution or release of sulphur towards the centre of the coal particle, cyclisation and back reactions of those released species with the rapidly depleting coal structure towards the edge, as it makes its way to the bulk fluid, lead to sulphur fixation. Therefore, it is possible that for the smaller particles at low heating rate, oxidised sulphur species which are formed in the internal pore structure (from reaction of H_2S with inherent or chemisorbed oxygen, or CO_2 and H_2O), rapidly move to the bulk fluid after a lower intra-particle residence time, and consequently do not re-react with the coal matrix (there is negligible mineral matter to react with due to the acid-washing) to the same extent that those same species formed in the larger particle do.

5.6 Tar phase sulphur

Employing the same method as the experiments described in this chapter(albeit with a greater quantity of coal: 0.5g *cf* 0.05g), samples of AD, AW and BW are subjected to fast pyrolysis at 800°C to yield a quantity of char (for further experiments in Chapter 6) and to undertake solid phase analysis to determine the system mass balance. While wet chemical analysis on the 0.05g sample residue was not possible, the residue from the fast pyrolysis of a 0.5g sample was analysed according to the methods described in Chapter 3. Tar yield for the 800°C experiment is then estimated by the difference between the mass of char removed from the fast heating rate experiments (too small for chemical analysis) and the carbon and sulphur analysis from the 0.5g pyrolysis residue used to calculate the carbon and sulphur conversion to tar. The chemical analysis of the char phase removed from the large sample size 800°C fast pyrolysis experiments for air-dried (AD) and acid-washed (AW) Lochiel coal, along with air-dried Bowmans coal (BW) are shown in **Table 5-2**.

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.

Char at 800°C			**Ultimate %db**				**Sulphur form (%S_{total})**		
Char type	Moisture ar%	Ash %db	C	H	N	S	Sulphate	Pyrite	Organic
AD	2.5	22	75.1	1	0.96	3.93	12.21	0.51	87.3
AW	2.1	9.5	86.2	1.2	0.98	1.79	0.56	0.56	98.9
BW	2.3	29	74.1	0.9	0.89	5.24	19.66	0.76	79.6

According to this method of estimation by difference, and based on the data in **Table 5-2**, **Figure 5-9** shows the distribution of coal sulphur for the 800°C fast heating rate pyrolysis experiment for AD, AW and BW.

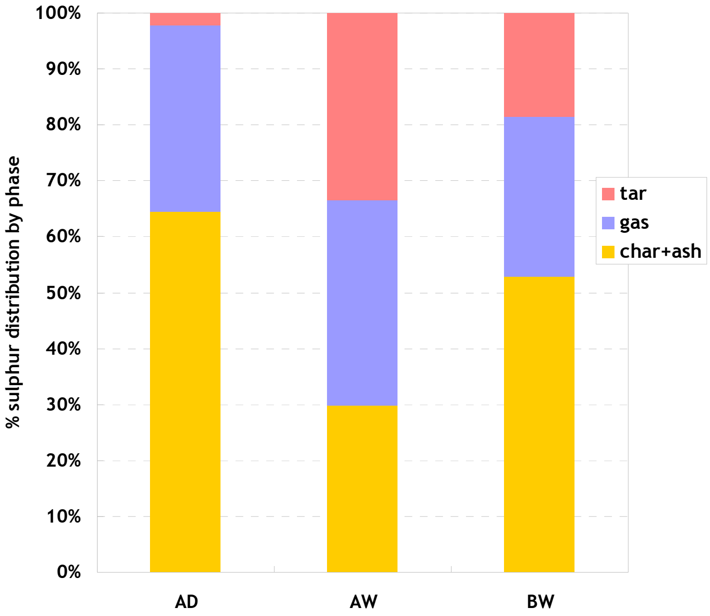


Figure 5-9 Sulphur distribution for air-dried (AD), acid-washed (AW) Lochiel coal and air-dried Bowmans coal fast heating rate pyrolysis at 800°C.

There exists a large differential between the quantity of sulphur estimated to be contained in the tar phase for air-dried Lochiel coal (AD), at just over 2% of total conversion, compared with AW and AW<0.5 Lochiel at 33% and 31% of total conversion respectively. For Bowmans coal, the estimated sulphur conversion to the tar phase equates to 18.5%. This also suggests that for fast heating rate pyrolysis at 800°C final temperature, almost 65% of the sulphur is retained in the solid phase for Lochiel, dropping to only 30% for the acid washed sample. For Bowmans, approximately 53% of the original coal sulphur is retained in the solid phase after 800°C fast pyrolysis. This solid phase consists of both char (amorphous material) and ash. This compares to the work of Telfer (1999) in which the total sulphur retention for Lochiel was 50% and 45% for Bowmans.

Figure 5-10 shows the equivalent carbon distribution between the phases. This does not show a large differential between the quantity of carbon estimated to be contained in the tar phase for air-dried Lochiel coal (AD) when compared with AW, AW<0.5 and BW coal. On the contrary, the estimated total conversion of carbon to the tar phase is greatest for the AD sample at almost 29%, while for the AW and AW<0.5 samples, the tar phase carbon conversion is just over 21%. For BW, the total carbon conversion to the tar phase is estimated at less than 21%. The greater distribution of carbon to the tar phase for Lochiel may assist in explaining why conversion to gas as CO_2 was lower for Lochiel than Bowmans. Given that tar is known to contain large amounts of oxygenated functional groups, a greater carbon conversion to tar may suggest that CO_2 precursors (COO^- groups) are less concentrated in the char and therefore less 'available' to form CO_2 during rapid pyrolysis compared with the lower heating rate. At low heating rate, any tar evolved in the early temperature zone readily re-reacts with the organic carbon matrix in the particle pore network, and subsequently decomposes to form simple compounds.

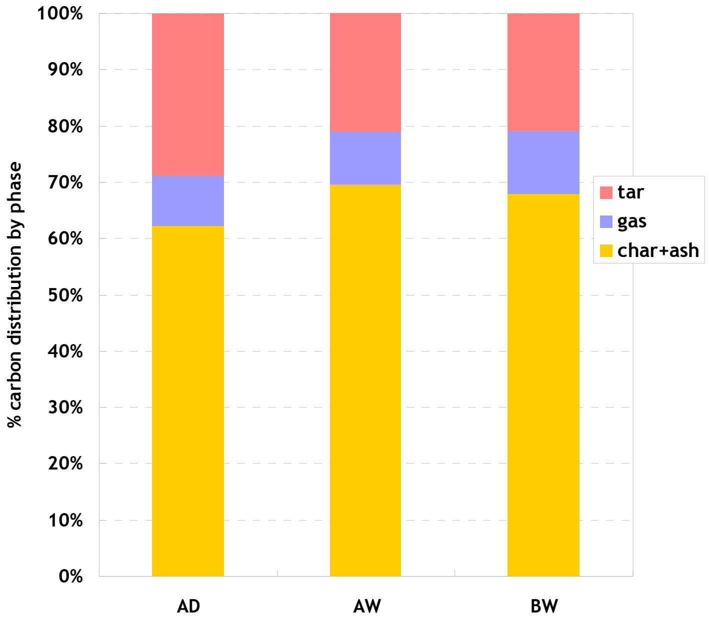


Figure 5-10 Carbon distribution for air-dried (AD), acid-washed (AW) Lochiel coal and air-dried Bowmans coal fast heating rate pyrolysis at 800°C.

For Lochiel coal, the carbon and sulphur distribution indicates that there is very little sulphur in the tar phase, while the quantity of carbon in the tar phase is significant. This differs from the acid-washed and Bowmans samples, which evolve between 33% and 18% of the original sulphur respectively as tar. The total volatiles conversion of sulphur (tar plus gas phase) for AD reaches 35.5%, while AW reaches just over 70%, and BW

47%. Therefore, while it is suggested in Chapter 4 that the sulphur in Lochiel coal is more easily released during pyrolysis than Bowmans coal, based on the higher conversion to gas phase for TPP, the results of this fast heating rate work suggests that it is only true for sulphur conversion to the gas phase alone and that, when the total conversion of sulphur to tar is considered, Bowmans coal contains more volatile sulphur, at least for fast heating rate conditions and terminal temperature of 800°C.

However, it is possible that greater quantities of sulphur and carbon are indeed released to the tar phase but they may easily crack with temperature or undergo secondary reactions with gas phase species, mineral matter and the char itself to form H_2S and other sulphur species.

5.7 Ratio of sulphur to carbon conversion

Given the inherent difficulty in accurately determining sulphur mass balances in large scale apparatus, for the various reasons described in Chapter 2, it is beneficial to relate the conversion of sulphur to the conversion of carbon, being substantially easier to detect and measure accurately.

The key output of the comparison between the sulphur and carbon in the gas phase can be expressed as a ratio of the cumulative conversion of each to the gas phase $(X_s/X_c)_{gas}$. For each of the fast pyrolysis experiments (terminal temperatures 700-1000°C) and for each TPP experiment (by taking the cumulative conversion up to the equivalent fast pyrolysis terminal temperature), the relationship between sulphur and carbon conversion to the gas phase is shown in **Figure 5-11**. It is also represented as a ratio of the sulphur to carbon ratio in the original coal, $(X_s/X_c)_{gas}/(S/C)_{coal}$, in **Figure 5-12**.

Figure 5-11 indicates that there is a slightly decreasing $(X_s/X_c)_{gas}$ ratio with increasing pyrolysis temperature for all coals and for both pyrolysis methods. For the air-dried (AD) Lochiel sample, the $(X_s/X_c)_{gas}$ decreases from approximately 3.9 to approximately 3.3 for both fast pyrolysis and TPP experiments. For the acid washed Lochiel samples (AW), the $(X_s/X_c)_{gas}$ diminishes from approximately 4.5 to 3.9 for both fast pyrolysis and TPP experiments. The major difference in the behaviour between the two heating rates lies with Bowmans coal, which displays significantly higher sulphur to carbon conversion ratio for the slow heating rate compared with the fast heating rate. For the fast pyrolysis experiment, the $(X_s/X_c)_{gas}$ decreases from a value of 2.7 at 700°C to 2.4 at 1000°C whereas for the TPP experiment, the $(X_s/X_c)_{gas}$ decreases from 3.5 at 700°C to 3.1 at 1000°C.

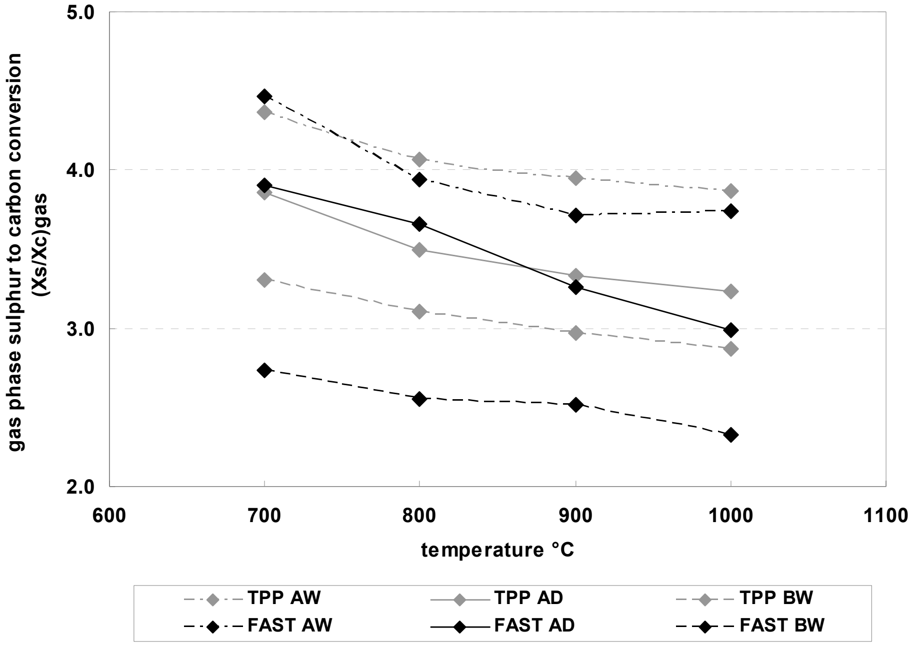


Figure 5-11 Cumulative gas phase conversion ratio for sulphur to carbon conversion as a function of temperature, $(X_s/X_c)_{gas}$, for the TPP and Fast pyrolysis conditions, using air-dried (AD), acid-washed (AW) and air-dried Bowmans (BW) coal.

When comparing the $(X_s/X_c)_{gas}/(S/C)_{coal}$ for each of the samples under either TPP or fast pyrolysis mode, the differences between Lochiel and Bowmans are more pronounced, driven by the higher concentration of sulphur in Bowmans coal. Whereas Lochiel coal shows similar behaviour of sulphur relative to carbon for the different heating rates, and over a range of final temperatures, that the relative sulphur to carbon conversion should increase with decreasing heating rate for Bowmans coal suggests, once again, that the two coals are structurally very different.

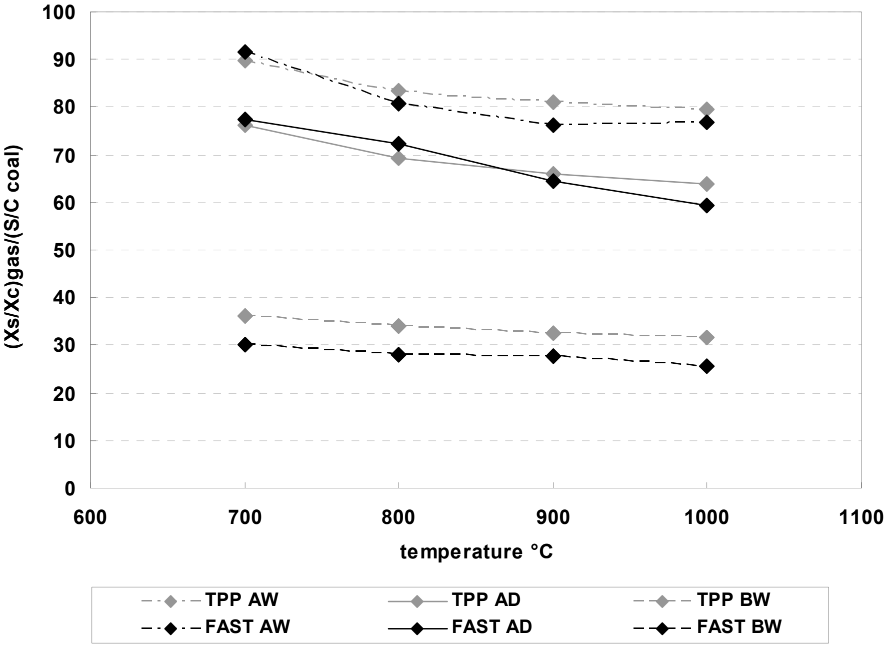


Figure 5-12 Ratio of cumulative gas phase conversion ratio for sulphur to carbon conversion as a function of temperature, $(X_s/X_c)_{gas}$, to the sulphur to carbon % mass content of the coal $(S/C)_{coal}$, for the TPP and Fast pyrolysis conditions, using air-dried (AD), acid-washed (AW), and air-dried Bowmans (BW) coal.

For Bowmans coal, the lower $(X_s/X_c)_{gas}$ for the fast heating rate conditions suggests that carbon preferentially converts to the gas phase, as opposed to sulphur, at faster heating rate pyrolysis conditions. This suggests that a large portion of the sulphur groups in Bowmans coal are prevalent as organic sulphides (R-S-R) or other structures that are less inclined to be released rapidly under conditions of high heating rate. This corresponds with the conclusions of Telfer (1999) that aliphatic sulphides form a greater proportion of the progenitor species for sulphur evolution in Lochiel coal than Bowmans coal.

Based on these results, and those from section 5.6 where the conversion of tar phase sulphur and carbon were estimated, it is possible to derive a dimensionless ratio, $(X_s/X_c)_{vol}$ representing the total conversion of sulphur to volatiles (gas and tar phase) to the corresponding conversion of carbon to volatiles for fast pyrolysis at 800°C. This is shown in **Figure 5-13**.

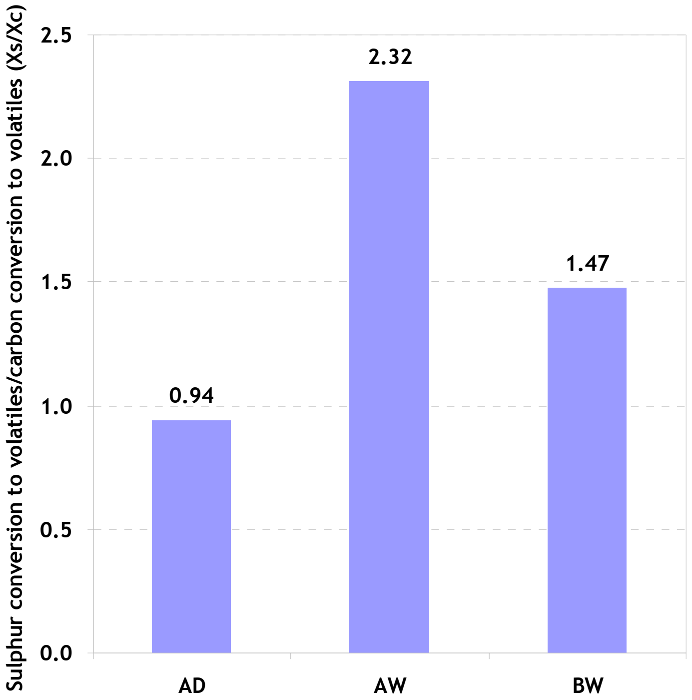


Figure 5-13 Ratio of cumulative sulphur conversion to volatiles per carbon conversion to volatiles $(X_s/X_c)_{vol}$ to the sulphur to carbon % mass content of the coal (S/C coal) for 800°C fast pyrolysis for air-dried Lochiel (AD), acid-washed Lochiel (AW) and air-dried Bowmans (BW) coals.

Figure 5-13 indicates that for air-dried Lochiel coal, sulphur and carbon are almost equally converted to volatiles for fast pyrolysis at 800°C, with an $(X_s/X_c)_{vol}$ ratio of 0.94. Bowmans coal, however, has an $(X_s/X_c)_{vol}$ ratio of 1.47, implying that, for fast pyrolysis at 800°C, conversion of sulphur is 50% greater than the conversion of carbon to the volatile phase than carbon. For the acid-washed coal sample, the $(X_s/X_c)_{vol}$ ratio is significantly greater than for the air-dried sample at 2.32. This result implies that the total conversion of sulphur to volatiles in the absence of mineral matter is more than double the conversion of carbon.

5.8 Mineral matter considerations

In order to assess the mineralogical characteristics of the residue remaining after fast pyrolysis, and to examine the final state of sulphur in the char (in crystalline phase), XRD analysis is undertaken for the char created at 800°C. The results are shown in **Table 5-3**.

Calcium-sulphur complexes are interpreted as anhydrite ($CaSO_4$) and oldhamite (CaS) in minor phase for Lochiel char and as trace in Bowmans char. This corresponds to **Figure 5-14** and suggests that calcium selectively discourages sulphur evolution by the formation of calcium sulphates and sulphides, and was previously observed by Kosminski (2001) for these coals in reducing environments.

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

Char (800°C)	**Dominant (>60%)**	**Minor (5-20%)**	**Trace (<5%)**	**Possible**
Lochiel (AD)	amorphous	Quartz (SiO_2) **Anhydrite ($CaSO_4$)** **Oldhamite (CaS)**	Halite (NaCl)	Periclase (MgO) Monticellite ($CaMgSiO_4$)
Lochiel (AW)	amorphous	**Possible pyrite ($Fe_{0.96}S$)**	Anatase (TiO_2)	
Bowmans (BW)	amorphous	Quartz (SiO_2) Halite (NaCl)	**Anhydrite ($CaSO_4$)** **Oldhamite (CaS)**	Periclase (MgO) Monticellite ($CaMgSiO_4$)

That there is more anhydrite and oldhamite remaining post pyrolysis for Lochiel coal when compared with Bowmans coal is not surprising given that Lochiel coal contains three times the calcium. For acid-washed (AW) Lochiel, the possible presence of pyrite in the acid-washed sample is anomalous, given that pyrite was believed to constitute less than 0.5% db of the total sulphur in the acid-washed coal sample. That no pyrite is evident in the Bowmans analysis is also interesting, given that there was pyrite detected using wet chemical methods. It is likely that this discrepancy relates to the limitations of the wet chemical methods in accurately determining pyrite, as outlined in the literature review.

Using the wet chemical analysis results for inorganic content, the effect of specific mineral matter species on sulphur and carbon evolution can be quantified. **Figure 5-14** shows the ratio of sulphur to carbon conversion to volatiles, $(X_s/X_c)_{vol}$, for each of the coal samples, plotted as a function of their dry basis inorganic contents.

Only three inorganic species appear to correlate with the ratio of sulphur to carbon conversion to volatiles: potassium, aluminium and calcium. The $(X_S/X_C)_{vol}$ ratio is only slightly dependent on the potassium content, and its relationship to aluminium content is only moderate. Its relationship to calcium, however, is much more pronounced and the plot of $(X_s/X_c)_{vol}$ to calcium content (% wt db) shows a distinct logarithmic relationship:

$$\mathbf{(X_s/X_c)_{vol} = -0.6*\ln(Ca)+1.1} \qquad \text{Eq 5-1}$$

where X_S is the total conversion of sulphur to volatiles, X_C the total conversion of carbon to volatiles, Ca the calcium percentage weight content of either AD, AW or BW on a dry basis. Again, this observation corresponds to a number of studies suggesting that the presence of calcium impacts the release of sulphur from coal (Attar, 1978), and these coals in particular (McCullough, 2007; Kosminksi and Manzoori, 1990)

This correlation, of course, attempts to relate calcium content of the original coals to the quantum of sulphur and carbon released during pyrolysis across the different coals and treatments. Care should be taken then in attempting to apply this correlation to coals with calcium content less than 0.13%wt dry basis given the exponential dependence on sulphur to carbon conversion to volatiles for coals with no mineral matter content.

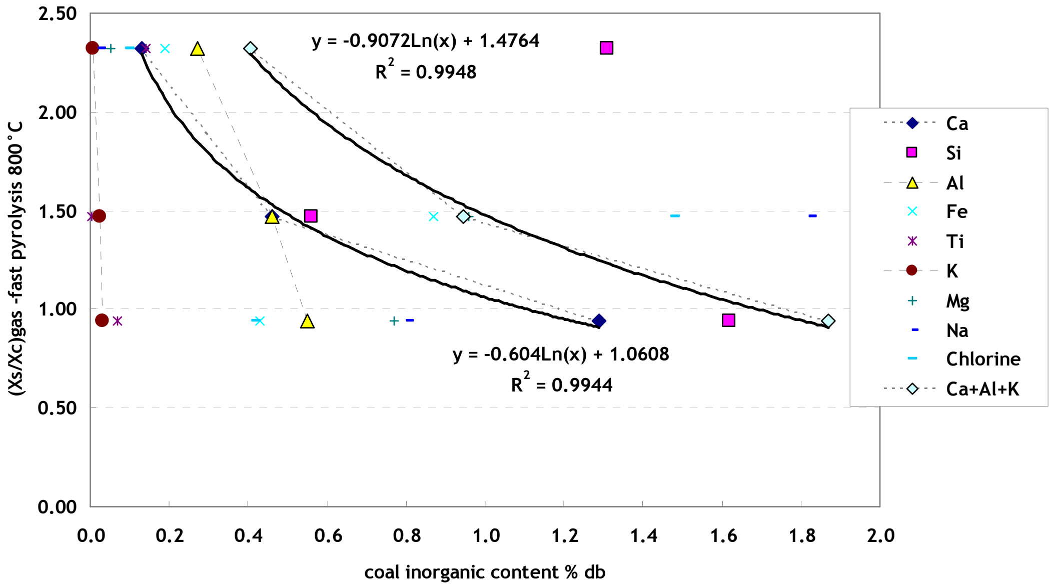


Figure 5-14 Relationship between sulphur to carbon conversion to volatiles ratio $(X_s/X_c)_{vol}$ to inorganic species content (%db) for air-dried (AD) and acid-washed (AW) Lochiel coal, along with Bowmans coal.

5.9 Summary and conclusions

While Chapter 4 showed that sulphur is distributed throughout the products of fixed-bed Temperature Programmed Pyrolysis (TPP) in a number of gas phase species, this chapter investigated the effect of a much faster heating rate on that distribution.

Under the fast pyrolysis conditions investigated, no SO_2 was detected for any of the coal types or treatment, while H_2S constitutes a much greater proportion of the gas phase products than COS or CH_3SH – the only other species detected. This corresponds to the findings of Miura *et al.* (2001) who proposed that SO_2 (detected at slow heating rates but not fast for the same coal) was a product of the reaction of mercaptan with H_2O or CO_2 during pyrolysis, and not a primary product.

As the final pyrolysis temperature increases, the effect of mineral matter and particle size are more pronounced for Lochiel coal, with acid-washed having very little impact on the total carbon conversion for Lochiel coal pyrolysed at 700°C. At 900°C, however, the additional sulphur conversion achieved through acid-washing was 10% more than the conversion of coal sulphur for the air-dried sample. For the acid-washed Lochiel sample of smaller particle size, however, the conversion at 700°C exceeded both the air-dried and acid-washed samples by more than 5%, remaining relatively constant for both the 800°C and 900°C final temperature experiments. This indicates that particle size, hence intra-particle reaction and redistribution of sulphur, and not mineral matter, are the dominant factors in determining the sulphur allotment at lower temperatures. This has implications for industrial plant where standard operating temperatures for these coals would be in the order of 800°C.

The move to faster heating rates is also shown to affect the absolute gas phase conversion and relative distribution of carbon among CO_2, CO and other compounds (up to C3 hydrocarbons and including COS and CH_3SH). Conversion to the gas phase due to CO_2 is a factor of two times that achieved at the slower heating rate for air-dried and acid-washed Lochiel coal. However, for Bowmans, conversion to the gas phase due to CO_2 was unchanged when moving from slow to fast heating rate, and only increasing CO concentration with final temperature contributed to a greater overall carbon conversion to the gas phase for the fast heating rate experiments over TPP. One factor believed responsible for this behaviour is the calcium content of the initial coal which, being found in much greater concentration in the AD sample, is believed to stabilise the COO^- groups, restricting the evolution of CO_2.

The evidence presented in this chapter points to the need for two different structural models for Lochiel and Bowmans coal, particularly with respect to the organic sulphur portion of each coal. Their behaviour during steam gasification should therefore be different with respect to their reactivities and the rates at which sulphur is gasified. The next chapter, by reviewing the behaviour of Lochiel and Bowmans char and the corresponding sulphur interactions under steam gasification in a fixed bed, aims to examine whether this is indeed the case and detail the steam gasification kinetics for both coals.

6 FIXED-BED STEAM GASIFICATION

6.1 Introduction and Objectives

Several studies have been undertaken previously looking at the behaviour of Lochiel and Bowmans coal during steam gasification and a large body of work examining the fixed-bed steam and carbon dioxide gasification behaviour of Lochiel coal exists in the work of Kosminski (2001) and McCullough (2007). Ye (1994) has previously examined the steam and CO_2 gasification behaviour of Bowmans coal. Both of these studies paid particular attention to the solid phase transformations of inorganic matter. The reactivity of lignite, being strongly affected by the presence of inorganic species, has been the focus of several other studies examining the catalytic effect of these species with respect to coal gasification (Takarada *et al.* 1986, 1987, 1991; Yamashita *et al.,* 1991), and sodium is considered a leading catalyst. In all these studies, however, the gas phase product mixture received little or no attention, as the analytical methods used to examine reactivity and the catalytic effects of inorganics have all been based on the char removed either during or after reaction has occurred. In effect, the literature has focussed on the behaviour of the coal and char, with little attention paid to the species present in the syngas. The syngas composition is critical from a commercial point of view given that the sales value of syngas is determined by its calorific value and the presence of pollutants has a significant impact on plant capital requirements by virtue of the scrubbing processes required prior to sale or combustion.

This chapter examines the conversion of coal sulphur under steam gasification conditions to provide a basis for fluidised-bed studies of the sulphur and carbon steam gasification kinetics for SA low rank coals. The objectives of this chapter are to report on sulphur and carbon gasification kinetics in a steam/nitrogen mixture and to characterise the sulphur and carbon species distribution among the various gas phase products.

6.2 Experimental justification

Literature studies have previously demonstrated that the gasification rate of low-rank coals at temperatures up to 900°C for gasification with carbon dioxide or steam is reaction-rate controlled, that is, independent of diffusion rates for mass transfer between coal and gas (Riley and Judd, 1987; Kwon *et al.*, 1988; Ye, 1994; Kosminski, 2001). For this reason, the simplicity of a fixed-bed system was chosen. Fixed-beds also:

- allow for an easily controllable heating environment;
- eliminate the issue of mixing in fluidised-beds, particularly channelling of fluidising medium;
- eliminate the carry over of fines and loss of catalyst; and
- reduce mass losses via tars and fines adhering to large internal surface areas (usually associated with fluidised-bed systems) during the pyrolysis stage of gasification.

The initial step in designing these experiments is to generate char that closely resembles that created in a fluidised-bed system. This is carried out in the HTF as described in the experimental section (Chapter 3), at 800°C and with a 5 minute holding time, and as previously outlined in Chapter 5 when calculating tar yields. The ability to quench the reaction as quickly as possible is absolutely necessary to avoid secondary reactions during the quench process following the formation of the char. The composition of the chars developed for these experiments, along with their XRD analysis, is shown in **Table 6-1** and **Table 6-2** (as previously presented in Chapter 5).

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.

Char at 800°C			**Ultimate %db**				**Sulphur form (%S_{total})**		
Char type	Moisture ar%	Ash %db	C	H	N	S	Sulphate	Pyrite	Organic
AD	2.5	22	75.1	1.0	0.96	3.93	12.2	0.51	87.3
AW	2.1	9.5	86.2	1.2	0.98	1.79	0.56	0.56	98.9
BW	2.3	29	74.1	0.9	0.89	5.24	19.7	0.76	79.6

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.

Char 800°C	**Minor (5-20%)**	**Trace (<5%)**	**Possible**
AD	Quartz (SiO_2) **Anhydrite ($CaSO_4$)** **Oldhamite (CaS)**	Halite (NaCl)	Periclase (MgO) Monticellite ($CaMgSiO_4$)
AW	**Possible pyrite ($Fe_{0.96}S$)**	Anatase (TiO_2)	
BW	Quartz (SiO_2) Halite (NaCl)	**Anhydrite ($CaSO_4$)** **Oldhamite (CaS)**	Periclase (MgO) Monticellite ($CaMgSiO_4$)

For these experiments, a steam composition of 25% v/v is chosen, as this represents a compromise between the steam volume composition indicative of industrial scale fluidised-bed gasification processes and the provision of sufficient carrier gas flow to enable a dry gas sample for analysis.

The delivery of a dry sample to the micro-GC is essential, and, in order not to condense moisture (and remove H_2S from the product gas) a Perma Pure drier is employed at the reactor exit. The drier contains a proprietary membrane that allows only water vapour (and not acid-gases such as H_2S) to pass across it, driven by a moisture gradient between the product gas and the drying medium (in this case UHP nitrogen), without removing acid gases in the condensable phase.

6.3 Conversion of carbon and sulphur

Gas phase data is collected during the experiment for carbonaceous species up to C3 and for sulphur species as H_2S. No species other than H_2S are detected for the experiments using Lochiel coal and only trace amounts of COS are detected for the experiments using Bowmans coal (and then, only at 850°C). The gasification experiments are terminated when no further carbon is detected in the product gas as CO_2 or CO.

6.3.1 Calculation methodology

A sample concentration profile from (AD) Lochiel char for gasification undertaken at 800°C is shown in **Figure 6-1**.

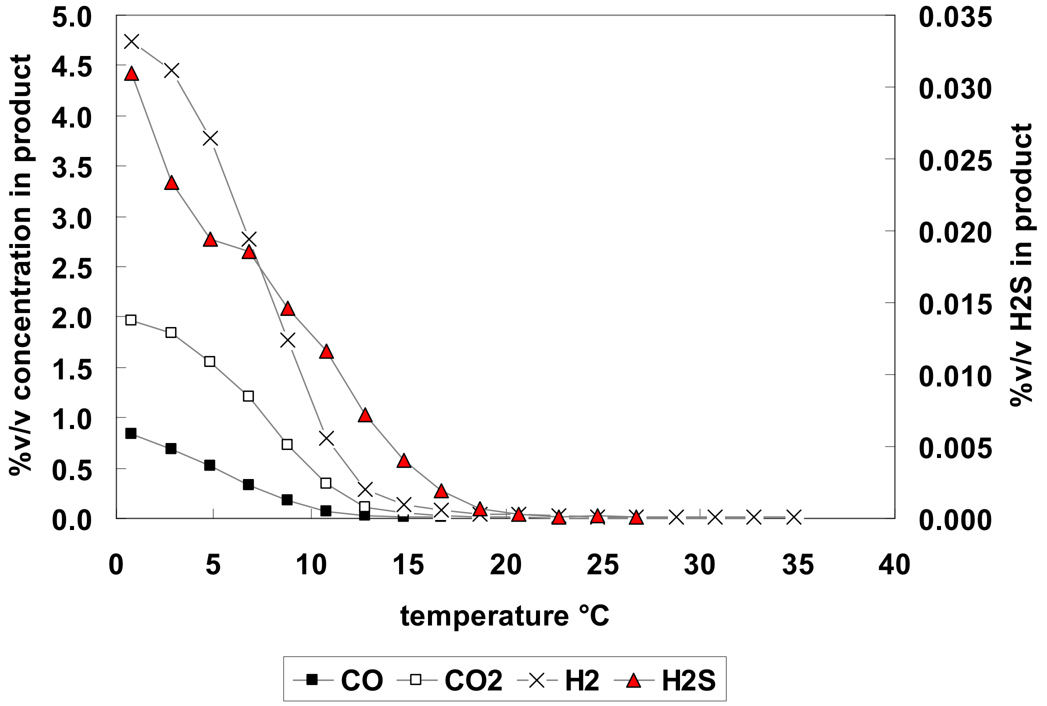


Figure 6-1 %v/v (dry basis) concentration profile for product gas from steam (25%v/v) fixed-bed gasification of air-dried (AD) Lochiel char at 800°C.

Following the calculation methodology from chapter 4, the total mass flow out of the system is calculated by integrating the concentration curves for each species, for a given flow rate (constant) of nitrogen carrier gas, enabling curves of cumulative conversion to be plotted (since there is no tar, only gas phase products), as a function of time. These are shown in **Figure 6-2** for Lochiel char carbon species, and **Figure 6-3** for sulphur. Conversion is defined as the ratio of the mass of species (carbon or sulphur) evolved to the gas phase to the initial species content in the char.

6.3.2 Conversion versus time calculation

Results presented in **Figure 6-2** show the relationship of carbon conversion due to gasification with time for the AD sample. For the 850°C experiments a 95% carbon conversion is achieved after 10 minutes, while for the 800°C experiment the final carbon conversion is 75%. For the 750°C experiment, conversion reaches only 25% after 10 minutes. In each case, approximately 100% conversion of the carbon in the sample is achieved, but this only after 20 minutes for 850°C gasification, 30 minutes for 800°C and 80 minutes for 750°C. An appropriate comparison measure is the comparison of the time taken to achieve 50% conversion (absolute), t*, as this metric can also be used to evaluate the suitability of a given kinetic model if required. The time taken to achieve 50% conversion for the 750°C, 800°C and 850°C gasification experiments is approximately 17, 7 and 4 minutes respectively.

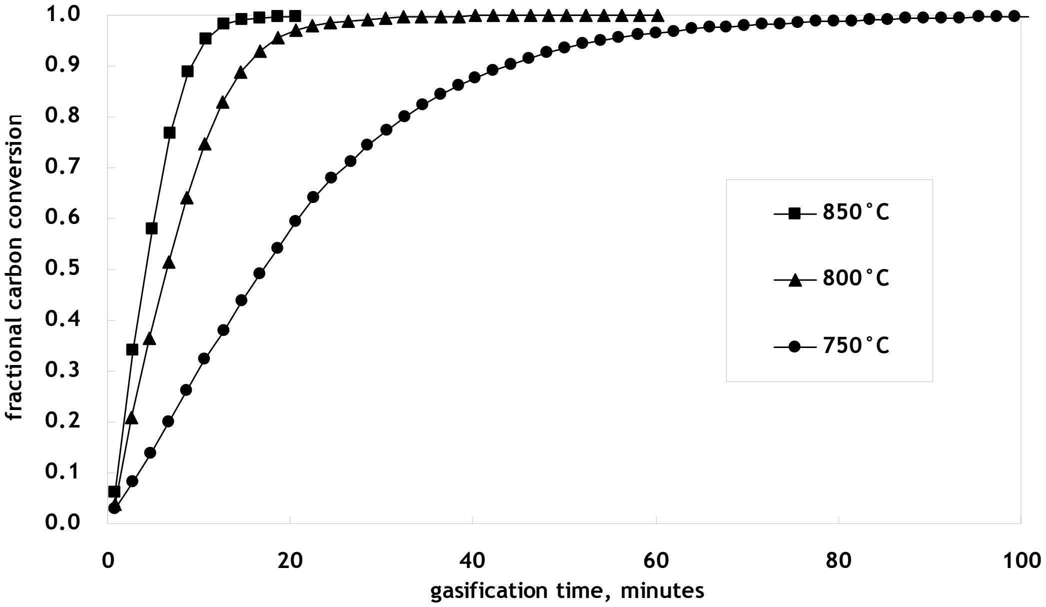


Figure 6-2 Carbon conversion profile for air-dried (AD) Lochiel char, steam gasification (25% v/v) at 750°C, 800°C and 850°C temperature.

AD sulphur conversion as a function of time is shown in **Figure 6-3**. The maximum sulphur conversion achieved is 52%, 61% and 74% at 750°C, 800°C and 850°C respectively. The time to 50% conversion, of approximately 68, 15 and 8 minutes respectively, is not an appropriate measure of reactivity given that sulphur conversion doesn't approach completion for these conditions. There is also a clear lag time between the commencement of the 750°C experiment and the onset of sulphur release of approximately 5 minutes.

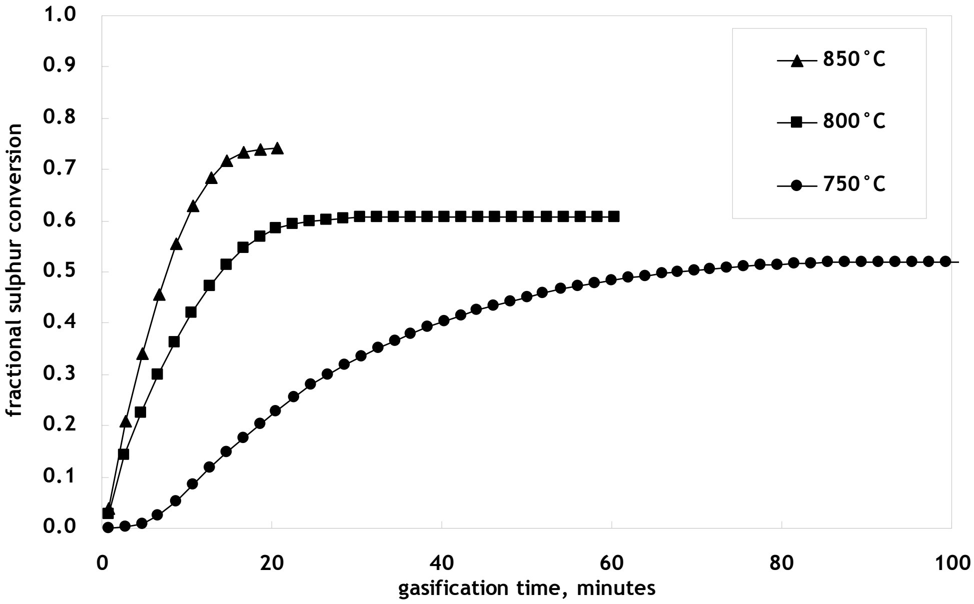


Figure 6-3 Sulphur conversion profile for air-dried (AD) Lochiel char, steam gasification (25% v/v) at 750°C, 800°C and 850°C temperature.

For AW, **Figure 6-4** and **Figure 6-5** show the relationships for carbon and sulphur conversion. At 750°C, the gasification rate is very slow, such that concentration data can not be obtained for the flow rate of carrier gas, hence only 800°C and 850°C curves are included. There is little difference between the final conversion figures achieved for both carbon and sulphur, only differences in the rate at which these species are gasified. For the carbon conversion plot in **Figure 6-4**, the total time to achieve 50% conversion was approximately 37 and 14 minutes for the 800°C and 850°C experiments respectively, while for the sulphur conversion curve (**Figure 6-5**), the time taken to achieve 50% conversion was approximately 60 and 24 minutes for the 800°C and 850°C experiments respectively. The maximum sulphur conversion achieved for both of these experiments is approximately 80%. In addition, there is a conversion lag time of approximately 8 and 15 minutes for the 850°C and 800°C experiments respectively.

When comparing the time taken to achieve a given conversion for the acid-washed char compared to the non treated sample, the rate of conversion is highly sensitive to the gasification temperature.

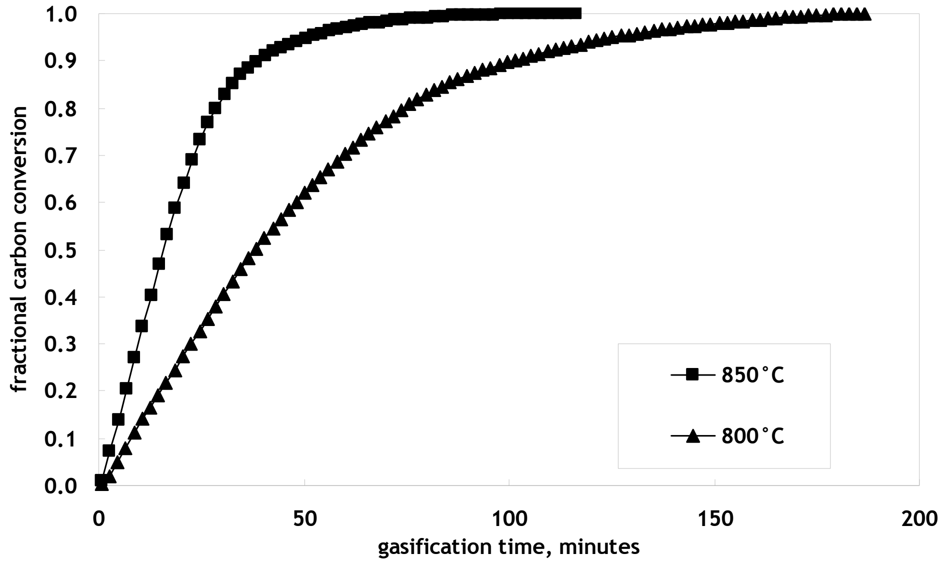


Figure 6-4 Carbon conversion profile for acid-washed (AW) Lochiel char, steam gasification (25% v/v) at 800°C and 850°C gasification temperature.

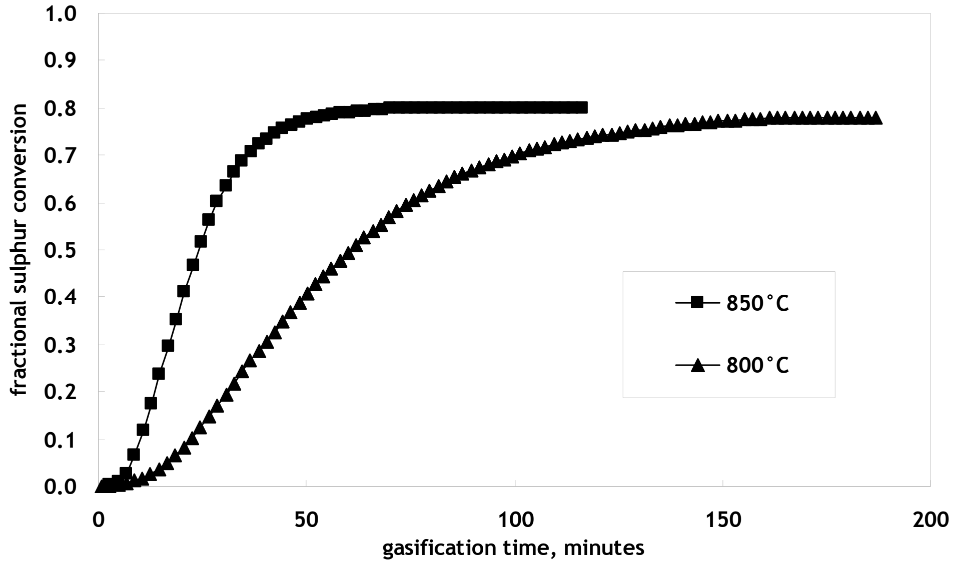


Figure 6-5 Sulphur conversion profile for acid-washed (AW) Lochiel char, steam gasification (25% v/v) at 800°C and 850°C gasification temperature.

For Bowmans coal, the time taken to achieve 50% conversion is shown in **Figure 6-6**. The rate of gasification over the investigated temperature range is similar to Lochiel.

For the 750°C, 800°C and 850°C experiments, the time taken to achieve 50% conversion equates to approximately 11, 8, and 4 minutes respectively.

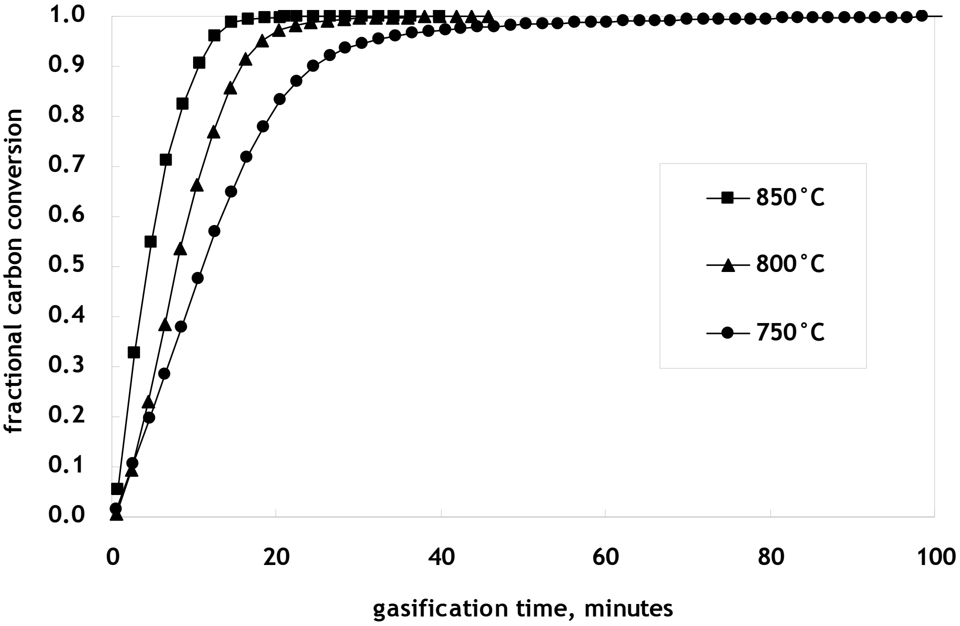


Figure 6-6 Carbon conversion profile for air-dried Bowmans (BW) char, steam gasification (25% v/v) at 750°C, 800°C and 850°C temperature.

For sulphur in the char, however, as shown in **Figure 6-7**, the time to achieve 50% sulphur conversion for BW is approximately 18, 12 and 8 minutes for the 750°C, 800°C and 850°C experiments respectively, implying a much faster sulphur gasification rate than AD or AW. Bowmans char also sees a greater final sulphur conversion for each temperature - 97% and 98% for the 800°C and 850°C experiments, and 76% for the 750°C experiment.

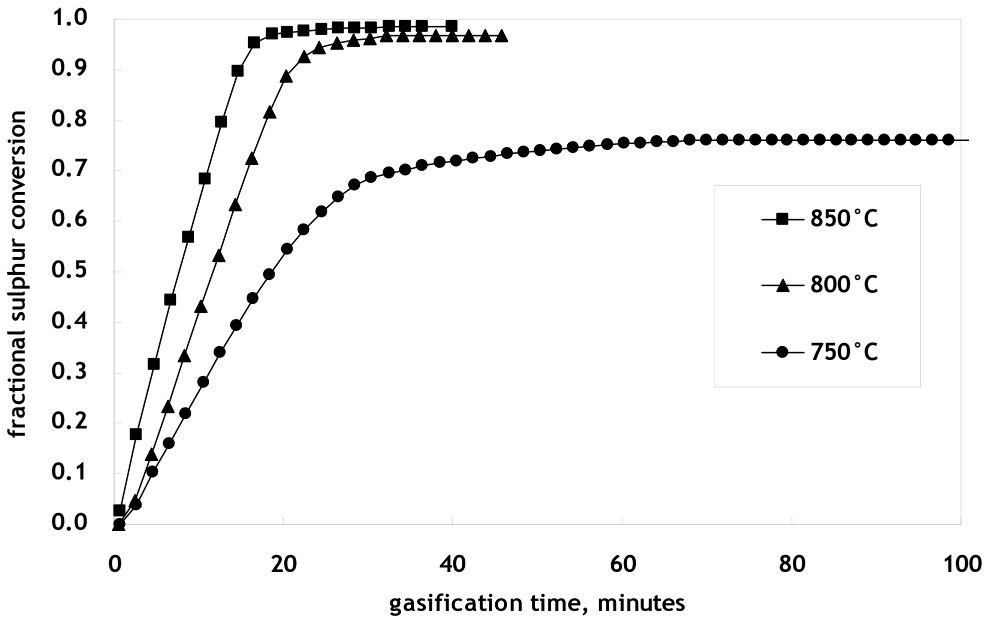


Figure 6-7 Sulphur conversion profile for air-dried Bowmans (BW) char, steam gasification (25% v/v) at 750°C, 800°C and 850°C gasification temperature.

Figure 6-8 shows the maximum sulphur conversion achieved for each of the temperatures, for each of the chars. For Lochiel char, sulphate and pyrite content constitute 12.2% and 0.5% of the total sulphur in the char, a total of 12.7% as inorganics. For AD char gasification, there is a 10.2% difference between the sulphur conversion at 750°C and 800°C, with an increase from 800°C and 850°C of approximately 12.2%. This constitutes a total increase in conversion between 750°C and 850°C of 22.4%, significantly greater than the total inorganic sulphur content of 12.7%.

For Bowmans char gasification there is an increase in conversion of 20.8% between steam gasification at 750°C and 800°C, while the difference between 800°C and 850°C is only 1.6%. Referring to **Table 5-2** showing the sulphur form analysis of the initial char, sulphate sulphur constitutes 19.66%, while pyrite sulphur constitutes 0.76%, that is, the total inorganic sulphur in the Bowmans char is 20.4%. Therefore, the increase in conversion between 750°C and 800°C may be due mainly to the reaction of inorganic constituents such as sulphates and sulphides, along with a small increase in the amount of organic sulphur evolved.

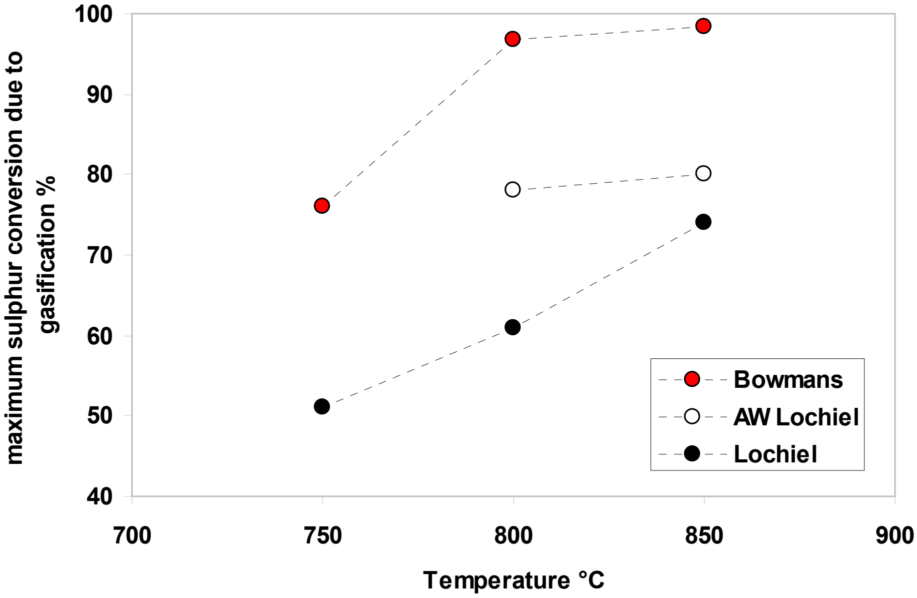


Figure 6-8 Maximum sulphur conversion for steam (25% v/v) gasification for air-dried (AD) Lochiel, acid-washed (AW) Lochiel and air-dried Bowmans (BW), for 750°C (where available), 800°C and 850°C gasification temperature.

For AW, the result suggests that, in the absence of mineral matter, the total sulphur conversion achievable is about 80% over the 800-850°C range. This means that approximately 20% of sulphur in the char (of which 99% was originally organic in form) forms mostly inorganic sulphur species (since some ash remained following ash treatment) rather than stable organic compounds given carbon conversion reashes over 99%. These sulphur containing compounds are not easily released even at these temperatures.

6.3.3 Summary of results for conversion versus time

Table 6-3 through to **Table 6-5** present a summary of the work described thus far in this chapter according to the key parameters of time to 50% conversion (t*) and maximum conversion (X_{max}) for each of the coals and each reaction temperature.

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.

Char 750°C	$t^*_{\text{carbon, C}}$	$X_{\text{max, C}}$	$t^*_{\text{sulphur, S}}$	$X_{\text{max, S}}$
AD	17	100	68	52
AW	-	-	-	-
BW	11	100	18	76

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.

Char 800°C	$t^*_{\text{carbon, C}}$	$X_{\text{max, C}}$	$t^*_{\text{sulphur, S}}$	$X_{\text{max, S}}$
AD	7	100	15	61
AW	37	100	60	78
BW	8	100	12	97

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.

Char 850°C	$t^*_{\text{carbon, C}}$	$X_{\text{max, C}}$	$t^*_{\text{sulphur, S}}$	$X_{\text{max, S}}$
AD	4	100	8	74
AW	14	100	24	80
BW	4	100	8	98

Comparing the results for the acid-washed and air-dried Lochiel samples indicates that the time to 50% conversion for carbon is increased by a factor of five on removal of the inorganic species, while for sulphur conversion, the time taken to achieve 50%

increases by a factor of 7 for the 850°C experiment, and approximately a factor of 12 for the 800°C. In terms of the differences between the air-dried and the acid-washed coals, the catalytic nature of the inorganic species and its importance to the ability to gasify Lochiel coal are apparent. For carbon, the major catalytic species sodium, which for Lochiel coal, is present in a concentration of approximately 0.8%db, and for Bowmans coal 1.8%.

Results of XRD analysis of the ash residue from gasification at 800°C are shown in **Table 6-6**. Insufficient residue was recovered following the gasification of the AW samples to enable XRD to be performed.

Table 6-6 XRD analysis of 800°C steam gasification residue for Lochiel and Bowmans char.

Char type	**Dominant (>60%)**	**Minor (5-20%)**	**Trace (<5%)**	**Possible**
Lochiel (AD)	Quartz (SiO_2)		Nepheline ($NaAlSiO_4$) Gehlenite ($Ca_2Al_2SiO_7$) Hematite (Fe_2O_3) **Anhydrite ($CaSO_4$)** Cristobalite (SiO_2)	Forsterite (Mg_2SiO_4) Monticellite ($CaMgSiO_4$) Larnite (Ca_2SiO_4)
Bowmans (AD)	Periclase (MgO) Magnetite (Fe_3O_4)	Nepheline ($NaAlSiO_4$)	Hematite (Fe_2O_3) Cristobalite (SiO_2) **Thenardite (Na_2SO_4)**	**Niningerite (MgS)**

For Lochiel char, XRD analysis of the residue indicates that while the parent char (XRD found in **Table 6-2**) contains sulphur species (minor phase, 5-20% wt) as anhydrite ($CaSO_4$) and oldhamite (CaS), the residue from steam gasification at 800°C (**Table 6-6**) contains only trace quantities of anhydrite (trace phase <5% wt). For Bowmans ash, sulphur is found in trace quantities (<5%) as thenardite (Na_2SO_4) and possibly as niningerite (MgS).

Regarding the level of sodium in the char prior to gasification, **Table 6-2** indicates the presence of halite (NaCl) as a trace phase (5%) for Lochiel char, and a minor phase (5-20%) for Bowmans char. For sulphur, on the other hand, the removal of calcium through acid washing, (calcium being shown to facilitate the uptake and retention of sulphur as calcium sulphate or sulphide in Chapters 4 & 5) does not enhance the release of sulphur during gasification. This suggests that the removal or release of sulphur from Lochiel char during gasification is linked to the rate of carbon gasification, more so than the inorganic content. Over 80% of the sulphur in Lochiel coal is organic in nature, and following the char making process, total organic sulphur approaches 90%. Therefore, the release of sulphur during gasification is likely to be dependent on the rate at which the strongly bound sulphur species that remain after pyrolysis competitively react either with H_2O or with the organic coal matrix.

The differences between the carbon and sulphur conversion of Lochiel and Bowmans are significant for the 750°C temperature experiments. The time for 50% carbon conversion is approximately twice as long for Lochiel char than for Bowmans. While the initial sulphur contents are similar, the difference in their mineral matter compositions suggests that the gasification rate of these chars at 750°C is highly dependent on the sodium content.

For the time to achieve 50% conversion of sulphur, the main difference is the 750°C experiment, where the time taken to achieve 50% sulphur conversion is approximately three time longer for the Lochiel char. If the conversion of sulphur in the char was proportional to the conversion of carbon, the difference in 50% sulphur conversion time between the two chars would be 20 minutes for Bowmans and 30 minutes for Lochiel, as opposed to 55 minutes. Therefore, the conversion of sulphur cannot be entirely related to the presence of sodium and its catalytic effect on carbon conversion at temperatures of around 750°C.

By examining the XRD analysis in Table 6.2, clear differences in the mineral matter content between the two chars in terms of the sulphur species are evident. For Lochiel char, Anhydrite ($CaSO_4$) and Oldhamite (CaS) are a minor phase (5-20%), while they are only found in trace quantities (<5%) for Bowmans coal. According to the wet chemical analysis shown in Table 6.1, however, the percentage of sulphate in the Lochiel char is considerably lower (12.2 % of the total sulphur) when compared with Bowmans char (19.7% of the total sulphur), highlighting the differences that can occur between analysis methods, as mentioned in the literature review. Wet chemical methods for sulphur determination are based on the following three assumptions that do not always apply for char samples due to the changes that occur in the structure during pyrolysis:

- Sulphur determined in the HCl extract represents sulphate sulphur
- Fe determined in a HNO_3 digest of the HCl insoluble matter represents FeS_2 (pyrite) in the sample and pyritic sulphur was calculated from this Fe value
- Inorganic sulphur is the sum of the sulphate and pyritic sulphur and its subtraction from the determined total sulphur represents organic sulphur

Therefore it is possible that pyrite, as determined in the char via wet chemical analysis, may in fact be an iron complex that is HCl insoluble, but nevertheless digested with HNO_3, giving a Fe concentration in the extract that is incorrectly assigned as pyrite. Therefore, while the two methods are not quantitatively comparable, they are still useful in deriving the qualitative conclusions about the key drivers of gasification rate.

6.4 Correlating sulphur to carbon conversion

Consistent with the approach in Chapters 4 and 5, the following section aims to develop a relationship between sulphur and carbon conversion in order to simplify the prediction of sulphur conversion in gasification systems. **Figure 6-9** through to **Figure 6-11** show the relationship between sulphur conversion and carbon conversion obtained for this work, and are based on data presented in **Figure 6-2** through to **Figure 6-7**.

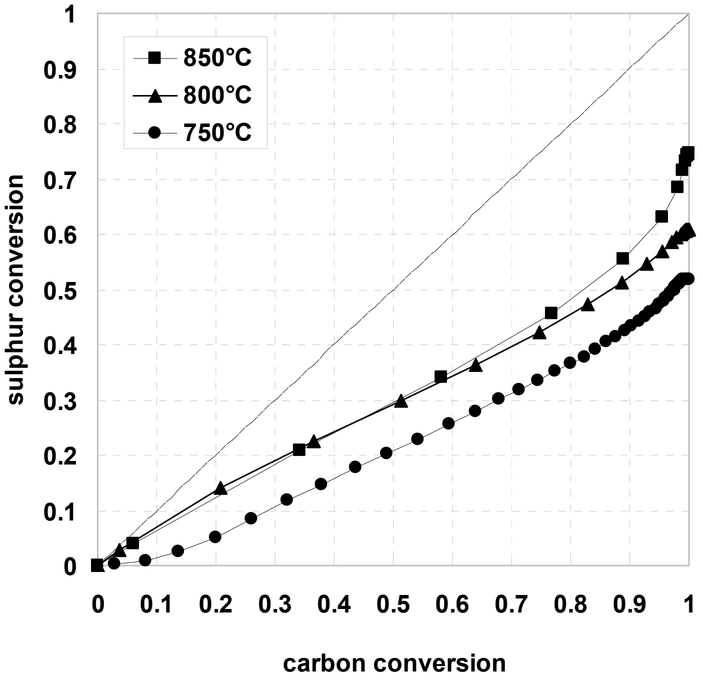


Figure 6-9 Cumulative sulphur conversion fraction as a function of carbon conversion fraction for air-dried (AD) Lochiel coal gasification in 25% steam at 750°C, 800°C and 850°C

For Lochiel char gasification, shown in **Figure 6-9**, the sulphur to carbon conversion relationship is very similar for the 800°C and 850°C data sets up to 80% carbon conversion, at which point sulphur conversion reaches approximately 45%. At 750°C, however, sulphur conversion lags carbon conversion for up to 10% carbon conversion, thereafter following a line of slope 0.6 (similar to the 800/850°C data)to reach approximately 37% at carbon conversion of 80%.

For the acid-washed gasification experiments at 800°C and 850°C, results shown in **Figure 6-10** indicate that there is negligible difference in the sulphur conversion to carbon conversion relationship for carbon conversion up to 80%. As with the Lochiel char gasification experiment at 750°C, the sulphur conversion lags the carbon conversion until between 10 and 20% carbon conversion, increasing linearly thereafter at slope of 1 to achieve a sulphur conversion of 60% at carbon conversion of 80% for both temperatures.

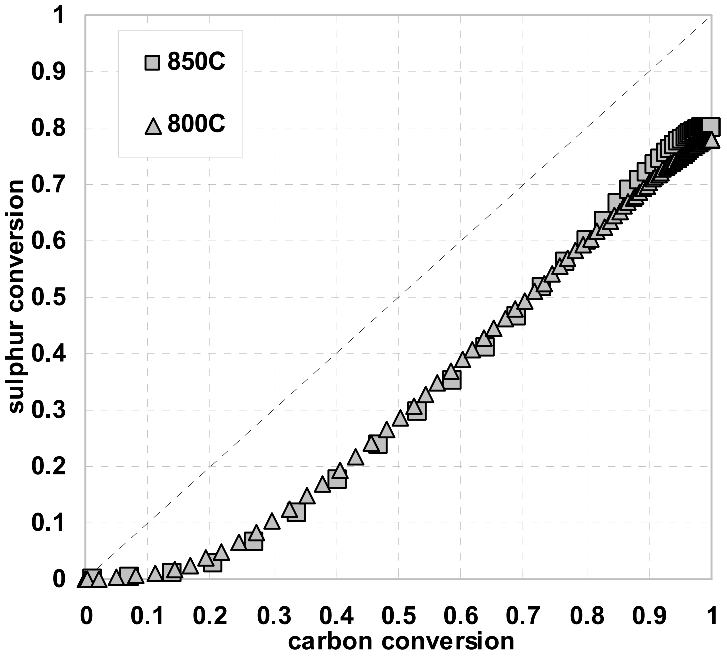


Figure 6-10 Cumulative sulphur conversion fraction as a function of carbon conversion fraction for acid-washed (AW) Lochiel coal gasification in 25% steam at 800°C and 850°C

A common feature of the AW (800°C and 850°C) and AD (750°C) experiments is the lag between sulphur and carbon for up to 30% carbon conversion.

Results for Bowmans coal, shown in **Figure 6-11**, indicate that for 750°C, 800°C and 850°C gasification experiments, the relationship between sulphur and carbon conversion increases until 70-80% carbon conversion at a point where sulphur conversion reaches between 45-55%. After 80% carbon conversion, while the 800-850°C experiments approach almost complete conversion for both sulphur and carbon, sulphur conversion reaches a maximum of 75% for the 750°C experiment.

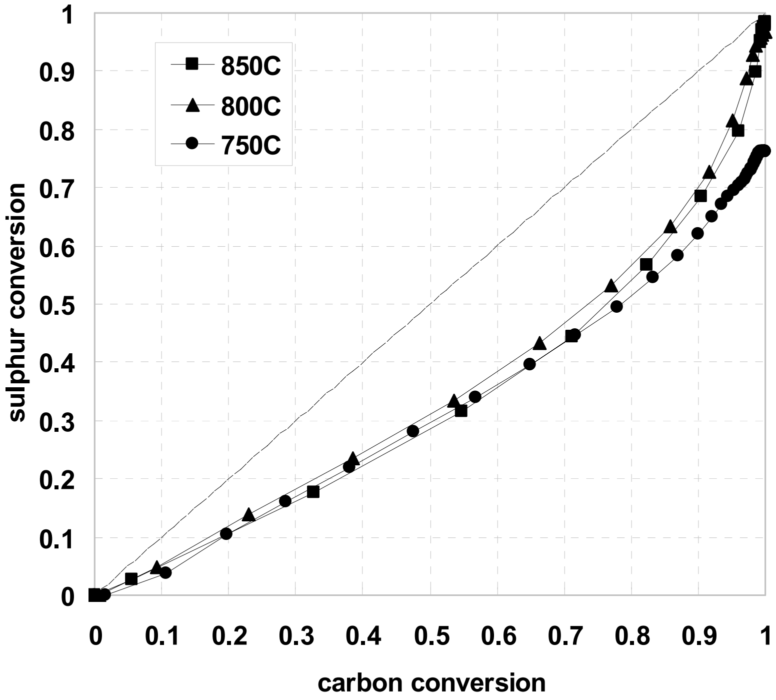


Figure 6-11 Cumulative sulphur conversion fraction as a function of carbon conversion fraction for air-dried Bowmans (BW) coal gasification in 25% steam at 750°C, 800°C and 850°C

As established in the literature, and shown in Chapters 4 and 5, the pyrolysis step prior to gasification enriches the char with organic sulphur. Several studies have shown that the formation of stable sulphur compounds, that are organic in nature, often makes it difficult to completely remove sulphur from the char during gasification and combustion. These compounds are typically cyclical in nature with the sulphur species resonance stabilised in the benzene ring structures that characterise them. That the conversion of sulphur lags the conversion of carbon for the AW char at both 800 and 850°C, as well as the AD char gasification at 750°C, suggests that there is a mechanism which sees carbon preferentially (over sulphur) react with steam in the early phases of gasification. For the 750°C gasification experiment, it is believed that sulphur, having formed stong organic bonds to the carbon matrix during the char making process (at 800°C), is involved in rearrangement reactions which see it convert to metal sulphide (most likely calcium sulphide). Even for the AW char, which contains more than 99% of its sulphur in the organic form, there is still approximately 10% (dry basis) ash contained on an ultimate analysis. The initial 'lagging' of sulphur conversion is potentially the result of the same rearrangement reaction, producing metal sulphides that are not easily reduced and indeed, are retained in the residue of gasification. Given that the X_s/X_c ratio is 1 from $X_c = 0.2$ to 1.0, the release of the organic form in the initial $0<X_c<0.2$ region, if released in the same 1:1 ratio and completely re-attached, would see 20% of the original sulphur potentially forming sulphides (or other metal sulphur complexes) that correspond to the sulphur calculated to remain in the residue (at $X_c = 1.0$)

Therefore while the assumption of equal conversion rates for sulphur and carbon that is employed in gasification models found in the literature (Ma, 1989; Yan *et al.* 1999) may apply to AW char (for $X_c > 0.2$), the presence of mineral matter in the AD and BW samples means it is not appropriate for low rank coal chars reacted under typical gasification conditions.

By plotting the experimental data for Bowmans char (750°C<T<850°C) and Lochiel char (800°C<T<850°C) on the same graph (**Figure 6-12**), there is an obvious linear relationship between sulphur and carbon conversion for the two coals up to conversions of approximately 80%. This is typically the carbon conversion obtainable in fluidised-bed gasification processes.

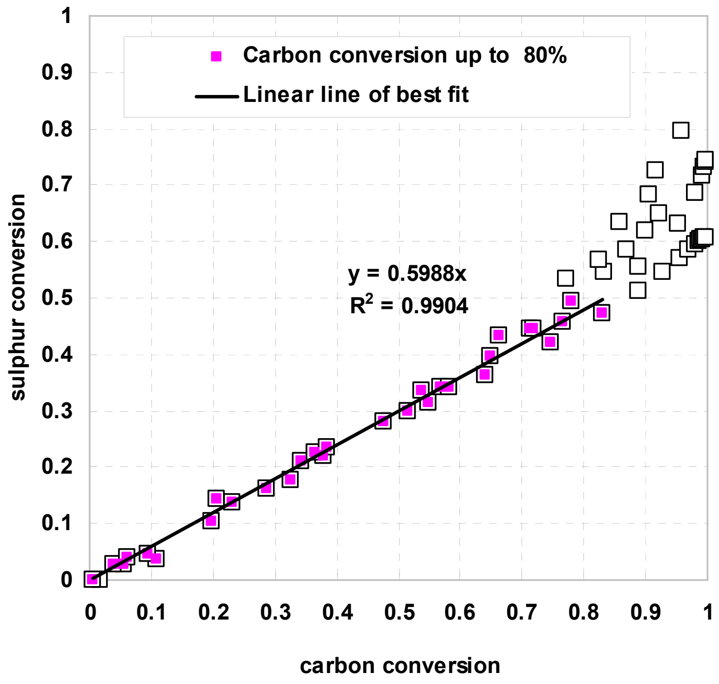


Figure 6-12 Cumulative sulphur conversion fraction as a function of carbon conversion fraction for air-dried Lochiel (AD) and Bowmans (BW) coal gasification in 25% steam at 750°C (BW only), 800°C and 850°C.

The empirical relationship obtained by the linear line of best fit equates to:

$$\mathbf{X_s = 0.6*X_c} \qquad \text{Eq 6-1}$$

for Bowmans char 750°C<T<850°C and Lochiel char 800°C<T<850°C and Xc<0.8 where Xs is the cumulative fractional sulphur conversion due to gasification, based on the cumulative fractional carbon conversion due to gasification.

This relationship does not hold, however, for the acid washed coal samples, which follow a different trend, being slow to evolve sulphur in the early stages of carbon conversion, nor does Lochiel gasification at 750°C, follow this relationship.

6.5 Kinetic Modelling

6.5.1 Background

Kinetic models of the gasification process attempt to characterise the mechanism of the chemical processes involved by relating operating parameters such as temperature, residence-time, species concentration and conversion to the overall char reaction rate. These studies are generally regarded as *macroscopic* or *global* kinetic studies, while accounting for changes in pore structure, catalyitic impurities and the influence of diffusion is the study of *intrinsic* kinetics (Steinfeld *et al.*, 1989).

A global reaction rate for coal can be expressed by measuring the reactivity of the coal as a function of the weight of the char sample, W, or the carbon content of a particular species, eg carbon. In which case the gasification rate, r, relative to the rate of change of the sample weight, can be expressed as:

$$\mathbf{r = (1/W)\ dW/dt = (1/(1-X))dX/dt} \text{ in units of time}^{-1}. \qquad \text{Eq 6-2}$$

The simplest models to describe the gasification process are the Homogeneous and the Shrinking Core (SC) models. Both have been used widely to describe the coal gasification process and previous studies employing South Australian lignite have found little difference between the two in describing the steam and carbon dioxide gasification processes up to 850°C (Ye, 1994; Kosminski, 2001). Previous work has assumed that the overall gasification rate is dominated by the chemical reaction rate and that the physical structure of the coal and mass transfer processes are of little importance under the conditions studied.

The homogeneous model assumes that solid-gas reactions occur throughout the particle uniformly and that, as the reaction progresses, the particle size remains relatively constant and density decreases. Assuming that the carbon-gas reactions occur at the active carbon sites and that these sites are uniformly distributed throughout the coal particle, Kwon et al. (1988) showed that a mass balance on a particle under these conditions reduces to:

$$\mathbf{-\ln(1-X) = kP_A^n t} \qquad \text{Eq 6-3}$$

where k is the reaction rate coefficient, P_A is the partial pressure of the reactant gas, X is the fractional carbon conversion and n is the order of reaction.

In accordance with the Arrhenius equation, the determination of the reaction rate coefficient k then allows for the evaluation of the coal activation energy:

$$\mathbf{k=k_0\exp(-E_a/RT)} \text{ or} \qquad \text{Eq 6-4}$$

$$\mathbf{\ln k = \ln A-E_a/RT} \qquad \text{Eq 6-5}$$

where E_a is the activation energy, T, temperature, A the pre-exponential factor and R the gas constant.

The shrinking-core model assumes that the reaction takes place at the exterior surface of the particle and that a reaction front moves radially inwards. As this reaction front recedes the total conversion of carbon by the reactant gas occurs, and an ash layer is formed in its place. Kwon *et al.* (1988) showed that a mass balance on a particle under these conditions reduces to:

$$\mathbf{1-(1-X)^{1/3}= t/\tau_c} \qquad \text{Eq 6-6}$$

where $\tau_c = (R_o.\rho_p)/(k_sP_A^n)$, for **chemical reaction control**

$$\mathbf{1-3(1-X)^{2/3} + 2(1-X) = t/\tau_c} \qquad \text{Eq 6-7}$$

where $\tau_c = (R^2_o.\rho_p)/(6bDP_A)$, for **ash diffusion control**

$$\mathbf{X = t/\tau_c} \qquad \text{Eq 6-8}$$

where $\tau_c = (R_o.\rho_p)/(3bk_sP_A)$, for **film diffusion control** where R_0 is the initial particle radius, ρ_P is the initial particle density, k_s is the surface reaction rate constant, P_A is the partial pressure of reactant gas, X is the fractional carbon conversion, n is the order of reaction and b the stoichiometric coefficient. The time constant, τ_c, represents the time for complete conversion, the value of which is very difficult to measure accurately. Therefore, in evaluating the suitability of either of these kinetic models to describe the reactivity, a dimensionless reaction time is employed

$$\mathbf{t^* = t/\tau_{0.5}} \qquad \text{Eq 6-9}$$

where $\tau_{0.5}$ is the time required to achieve 50% conversion.

Kwon *et al.* (1989) studied the steam gasification kinetics of lignites and found that both the Homogeneous and Shrinking-Core models describe steam gasification well at low temperatures (700°C), while at higher temperatures, under the assumption of reaction rate control, the S-C model predicted the data better. Observations by Kosminski (2001) of char particles removed during fixed-bed steam and CO_2 gasification of Lochiel coal using SEM, however, did not indicate ash formed on the char surface. Instead, ash was found to be distributed uniformly within the whole volume of char. On the basis of those observations, Kosminksi (2001) considered the homogeneous model more suitable for defining the rate-controlling factor for char gasification, noting that with increasing temperature and reaction time, the number of macropores within the char particles increased.

In light of this, the following sections examine the suitability of the homogeneous (1st order) model in describing the carbon conversion for Lochiel and Bowmans coal.

6.5.2 Carbon kinetics

Figure 6-13 to **Figure 6-16** show the suitability of the homogeneous (1st order) model in predicting carbon conversion up to 80%. The linear plots were extrapolated to the time axis to obtain the value of any induction period.

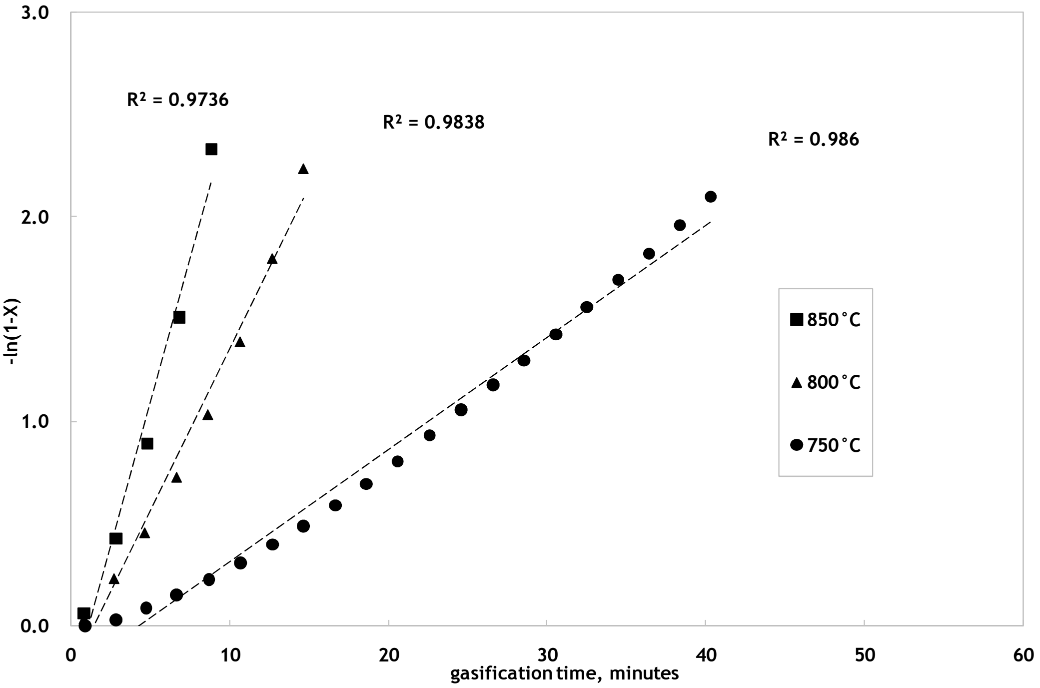


Figure 6-13 Comparison of homogeneous model predictions for carbon conversion with experimental data for air-dried (AD) Lochiel char gasification.

Goyal *et al.* (1989) previously observed that an initial slow rate of reaction for the bituminous coal char gasification may have been due to uncertainty about the temperature of the char during the initial period of the experiments. While the experiments undertaken in this work were assumed to be isothermal, and no deviation from the HTF reaction temperature was observed (controlled by a thermocouple on the outside of the ceramic tube containing the reactor) it is possible that the induction times quantified below were due to the reactor quenched when steam was introduced.

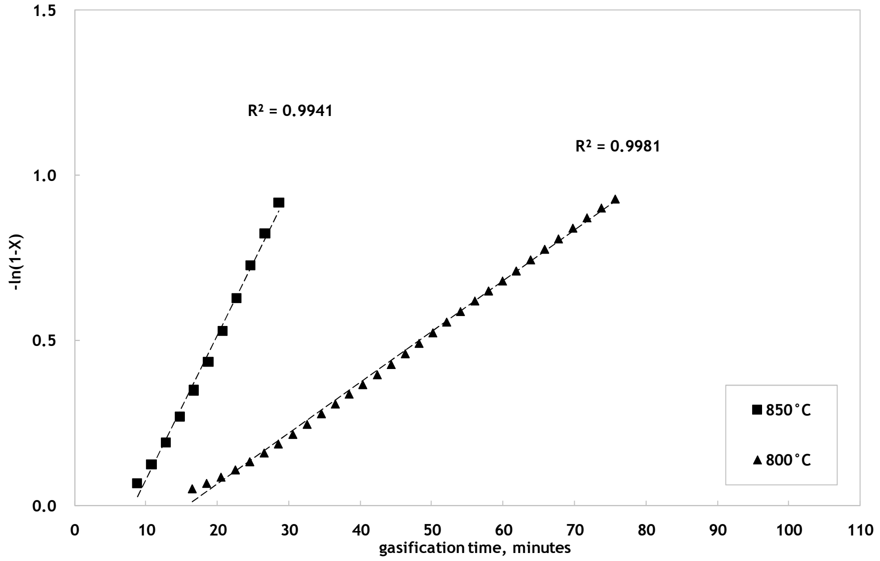


Figure 6-14 Comparison of homogeneous model predictions for carbon conversion with experimental data for acid-washed (AW) Lochiel char gasification (excluding dataprior to 10 minutes at 850°C and 15 minutes at 800°C to calculate induction time)

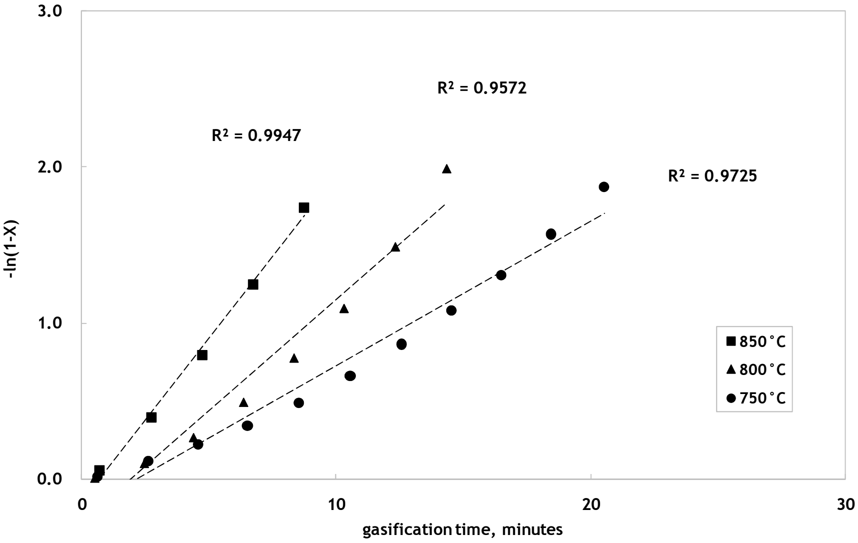


Figure 6-15 Comparison of homogeneous model predictions for carbon conversion with experimental data for air-dried Bowmans (BW) char gasification.

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.

Char	Temperature	k (min^{-1})	Induction time t_0
Lochiel	750°C	0.13	4.2
	800°C	0.36	1.4
	850ºC	0.64	1.1
Bowmans	750°C	0.21	2.2
	800°C	0.33	1.9
	850ºC	0.48	0.7
AW Lochiel	800°C	0.035	15.8
	850ºC	0.10	8.2

Calculation of the activation energy is undertaken by taking the slope of the straight line relationship between the inverse temperature (Kelvin) and the reaction rate constant k (min^{-1}). The reaction rate constant, k, is calculated according to equation 6.2 where the reaction order is set to 0.6 (based on Mann *et al.* 2004 and Yerbury *et al.* 2004) and the partial pressure of reactant 0.25 (25% v/v steam). The pre-exponential factor A is calculated as the exponent of the y intercept of the straight line relationship between the inverse temperature and reaction rate constant. Strictly speaking, it is only possible to calculate the activation energy as the slope of this line when induction time is zero, but assuming that the induction time is caused by the quenching of the reaction during introduction of steam, and that the subsequent rate of gasification is representative of the actual gasification rate in the absence of an induction period, enables activation energies to be calculated.

Arrhenius plots for the conversion obtained during steam gasification experiments are shown in **Figure 6-16** for Lochiel and Bowmans chars respectively, and the calculated activation energies listed in **Table 6-8**.

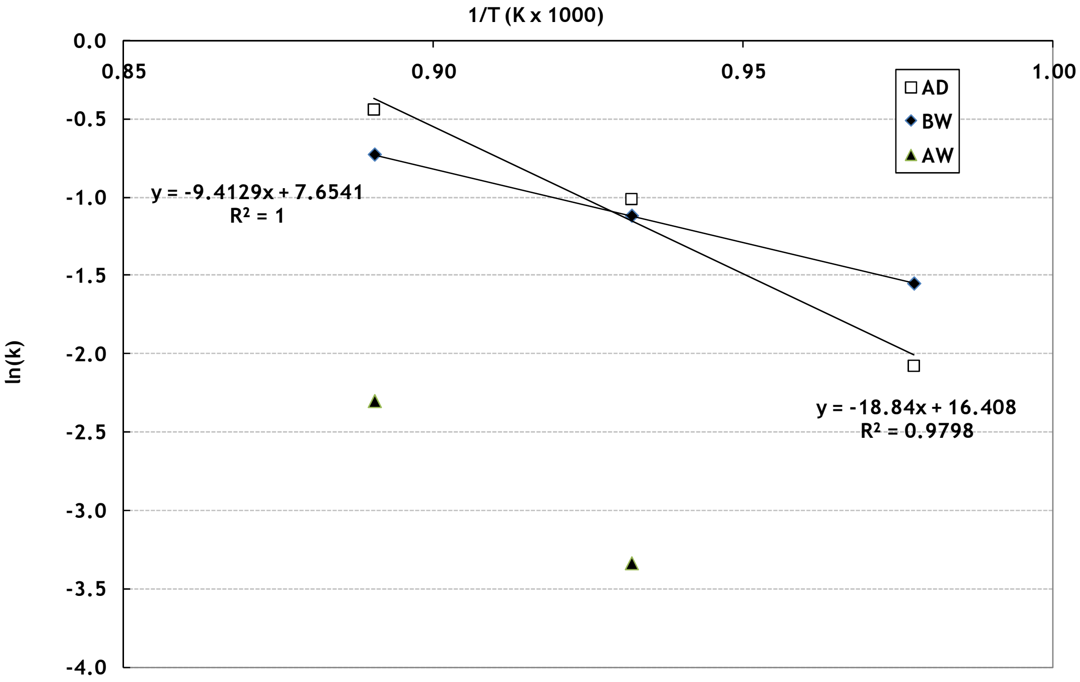


Figure 6-16 Arrhenius plot for carbon gasification of Lochiel (AD), Bowmans (BW) and acid-washed Lochiel (AW) char with 25% steam.

Table 6-8 Comparison of activation energies (kJmol^{-1}) and pre-exponential factors (min^{-1}) for the homogeneous model

Char	**Activation energy kJmol^{-1}**	**Pre-exponential factor, A min^{-1}**
Lochiel	156.6	1.34E+07
Bowmans	78.3	2.11E+03

6.5.3 Comparison to literature

Kosminski (2001) evaluated the gasification rate of Lochiel char in 100% steam, examining the effect of sodium bonding and silica and kaolin concentration on the gasification rate. Using a batch of low-mineral Lochiel coal, air-dried to less than 15% moisture, sodium, silica and kaolin were loaded at pre-determined concentrations, and the steam gasification kinetics evaluated in a fixed bed (horizontal tube furnace) by examining the solid phase carbon conversion. Reaction temperatures were 650°C, 750°C and 850°C. The results are summarised in **Table 6-9**.

Table 6-9 Activation energies (kJmol^{-1}) as evaluated by Kosminski (2001) for low mineral Lochiel coal impregnated with sodium, silica and kaolin.

Coal designation	Sodium (organically bound) % wt	Sodium (as NaCl) % wt	Silica % wt	Kaolin % wt	Activation Energy kJmol^{-1}
NA1	1				148.1
NA1S	1		10		161.6
NA1K	1			10	162.4
NC1		1			230.0
NC1S		1	10		236.7
NC1K		1		10	232.3

The figure for activation energy of Lochiel char gasification, obtained from this work, of 156kJmol^{-1} (homogeneous model) compares well to this range of data, particularly the NA1sample, that is, organic sodium loaded char. There are no other literature studies of the steam gasification of Lochiel coal to report on, although one exists for gasification in CO_2 (Poeze & Zhang, 1999).

In terms of Bowmans steam gasification kinetics, only the data of Ye (1994) is available for comparison. Like the study of Kosminski (2001), steam gasification was carried out in 100% steam, although in a single particle fluidised bed reactor, with solid phase analysis enabling the determination of carbon conversion with time. The experiments of Ye (1994) were conducted in a 100% steam environment and for temperatures of 710°C, 765°C and 810°C. The activation energy for Bowmans coal was determined at 133kJmol^{-1} compared with 78kJmol^{-1} in this work. The significant difference between this work and the work of Ye *et al.* (1998) is the input material – this work examined the gasification rate of char, not coal. Ye (1994) specifically used wet, as-received coal, with a moisture content of 57%, and the coal was stored in the absence of air to prevent any oxidation prior to utilisation. It has previously been proposed that the presence of SO_2 during the devolatilisation of both Lochiel and Bowmans coal was due to oxidation prior to utilisation with chemisorbed oxygen, from the air-drying and storage stages, which has the effect, under gasification conditions, of increasing the rate of gasification due to the abundant oxygen functional groups that have formed.

In addition, the reaction temperatures chosen for the work of Ye (1994) included a temperature of 710°C. The catalytic effect of sodium at 710°C is not as strong as at the higher temperatures of this work, therefore when this point is excluded from the data of Ye (1994) to perform the calculation of activation energy, a figure of 107kJmol^{-1}, is obtained, still over 30% greater than this work.

Also accounting for an increase in the calculated activation energy may be the effect of the fluidised-bed experimental system used by Ye *et al.* (1998). This apparatus consisted of a fluidised-bed of sand in which a single particle was held for a specific period of time. The result of the particularly ‘violent’ pyrolysis step may have been a loss of significant quantity of sodium catalyst with ash carry over. With no recycle loop, this catalyst is not able to transform into the organically bound sodium form necessary to catalyse the reaction. Such a reaction system could have also resulted in loss of catalyst via reaction with silica in the sand bed. In both cases, with less of the original catalyst present to facilitate faster steam gasification reaction rates, the effect is to lower the reaction rate constants, particularly for the lower temperature experiments when catalytic activity of sodium is pronounced, and this can significantly lower the activation energy.

The data presented here will be used to evaluate the fluidised-bed behaviour of these coals in Chapter 7.

6.6 Summary & Conclusions

Under the fixed bed steam gasification conditions described in this chapter, only H_2S was detected as a product of gasification. The total conversion of suphur to the gas phase was found to vary depending on the temperature at which the gasification was carried out, and differed between coal treatment and type.

Bowmans char saw the highest conversion of sulphur to H_2S, but only for the 800C and 850C experiments (at over 95%) while steam gasification of Lochiel at 750C saw only 50% of the total sulphur in the char removed. The total removal of sulphur for Lochiel correlated directly with gasification temperature, but even at 850C, only 75% of the original sulphur in the char had converted to H_2S. Acid–washed Lochiel char, being very slow to gasify, saw total conversion of approximately 80% for experiments undertaken at 800C and 850C, while no data could be obtained for the 750C experiment as the gasification rate was too slow, and the concentrations of product gas too low, to enable accurate mass balance closure.

The rates of reaction for carbon and sulphur and final sulphur conversion depend heavily on the temperature being greater than or equal to 800°C. By excluding data less than 800°C, Lochiel and Bowmans exhibit similar behaviour in terms of gasification rates and activation energies, which suggest that for temperatures less than 800°C, these parameters are dependent on the presence of catalyst, in this case believed to be sodium. Above 800°C, the gasification rates appear independent of coal type (and potentially, sodium concentration).

The activation energy obtained for Lochiel char steam gasification compares well with the work of Kosminksi (2001) which examined the steam gasification kinetics in a 100% steam environment for organic sodium loaded char, but for Bowmans char, the activation energy compares less favourably. The main reason for this difference is believed to be the calculation methodology as applied in the literature, as discussed in the text.

The empirical relationships that are developed in this chapter enable the prediction of the sulphur conversion for any given carbon conversion. For Lochiel and Bowmans char, between 750-850°C (excluding 750°C for Lochiel char), cumulative sulphur conversion is approximately 60% of the carbon conversion (up to cumulative carbon conversion of 80%), irrespective of coal type. For the case where mineral matter is removed (acid-washed Lochiel) sulphur conversion is approximately 50% of carbon conversion, but this only holds for carbon conversion greater than 20% (and less than 80%). It is believed that, as gasification progresses, sulphur species become more strongly bound to the organic coal matrix, and are not removed at the same rate as carbon, until they react with mineral matter to form calcium sulphates and sulphides that are retained in the ash. The lack of calcium in Bowmans coal relative to Lochiel is the primary reason for the high final sulphur conversion figures during gasification of Bowmans coal.

The fixed-bed steam gasification work examined in this chapter provides a basis for proceeding with kinetic studies in the fluidised-bed environment. The work undertaken has enabled the development of:

- activation energies for carbon steam gasification kinetics for Lochiel and Bowmans char;
- relationships between the gas phase sulphur conversion and gas phase carbon conversion for these coals in the temperature range 750°C to 850°C and
- principles surrounding sulphur interactions with mineral matter.

Understanding how the move to laboratory scale fluidised-bed environment impacts the gasification behaviour of sulphur in Lochiel and Bowmans coal is critical to developing the confidence to scale up to large pilot and demonstration tests, and is the subject of the following chapter.

7 ATMOSPHERIC PRESSURE FLUIDISED-BED PYROLYSIS & GASIFICATION

7.1 Introduction and Objectives

This chapter examines the conversion of sulphur during pyrolysis and steam gasification utilising a laboratory-scale 50mm internal-diameter fluidised-bed operated in batch feeding mode.

Fluidised-bed systems are believed to have distinct advantages over fixed-bed systems in their ability to mix reactants well (steam and coal), achieve high heating rates for pyrolysis and achieve high carbon conversion efficiencies during either combustion or gasification processes. As previously described, however, there are limitations to the fluidised-bed system in conducting fundamental kinetic studies, including the difficulty in closing elemental mass balances due to fines carry over; the adherence of sulphur species to internal surfaces; and intra-bed temperature and mass transfer gradients (due to agglomeration and defluidisation or channelling of fluidising medium).

The need for experimental data under fluidised-bed conditions, however, as highlighted in both the literature review and in the previous results chapters, is imperative to evaluate the potential to move to industrial scale equipment for gasification. This chapter attempts to examine the sulphur and carbon conversion during pyrolysis and gasification under the same temperature and steam conditions used in the fixed-bed work of Chapters 5 and 6.

The first part of this chapter outlines the results of fluidised-bed pyrolysis, determined by analysing the first 10 minutes of gas production from the reaction vessel after the addition of coal. A comparison of these results, and those from Chapter 4 (TPP) and Chapter 5 (Fast pyrolysis) is undertaken to compare the effect of reaction system on both the conversion of carbon and sulphur and product distribution of each species. The first 10 minutes of gas production is also examined where pyrolysis is carried out with 25%v/v steam in nitrogen, that is, the same medium used during gasification.

The second part of this chapter outlines the carbon gasification kinetics in steam and nitrogen for both coals with and without the presence of steam in the pyrolysis step. These results are directly compared to those of Chapter 6, in order to elucidate the impact of the fludised-bed system on the kinetic parameters observed in the fixed-bed.

7.2 Fluidised-bed pyrolysis

As previously described in the experimental section, product gases from the 50mm gasifier exit the freeboard and are drawn under vacuum to the analysis system. For the first 10 minutes of the experiment, while pyrolysis is occurring, this stream is collected in Teflon bags, the concentration of which is later analysed using the micro GC. Based on the concentration data from the micro-GC (taken every 1.6 minutes) and the bulk concentration of the first 10 minutes of pyrolysis as measured by the bags, a total molar flow of sulphur and other species is calculated, using the methodology outlined in Chapter 5 and Chapter 6, and this curve integrated to yield conversion versus time data.

7.2.1 Air-dried Lochiel pyrolysis in nitrogen

A typical concentration profile for the first 10 minutes of fluidised-bed pyrolysis in nitrogen for Lochiel coal is shown in **Figure 7-1**.

Once these concentrations are converted to molar flows of species, an estimate of conversion of carbon and sulphur to the gas phase is calculated as described in previous chapters. Sulphur conversion to gas phase, as calculated using this method, is within range of the conversion as calculated by the yield of product in teflon bags. Each experiment utilises the double sampling method to confirm the integration method for the first 10 minute period. Concentration data is recorded for up to C3 hydrocarbons, along with H_2S, COS and CH_3SH for sulphur. No SO_2 was detected.

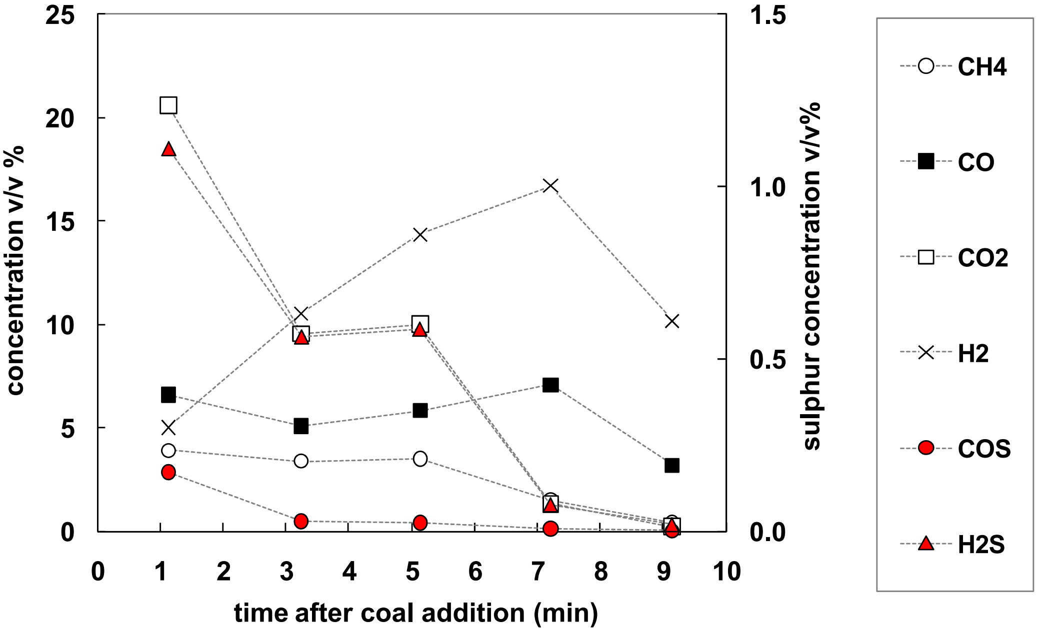


Figure 7-1 Species concentration for carbon (CO_2, CO and CH_4), hydrogen (H_2) and sulphur (H_2S and COS) for fluidised-bed pyrolysis (nitrogen atmosphere) of air-dried Lochiel coal at 800°C.

According to **Figure 7-1** the instantaneous concentration of CO_2 is over 20% at 1.25 minutes after coal addition while CO and H_2 reach approximately 7% and 5% respectively at this time. While CO and CH_4 appear to remain relatively constant for the first 5 minutes of pyrolysis, CO_2 diminishes rapidly to less than 2% by 7 minutes while hydrogen increases to a peak of over 15% by that time. Given that the CO_2 and CH_4 concentrations approach zero by 10 minutes, the assumption of complete pyrolysis in that time is considered valid.

The H_2S concentration is measured at just over 1% v/v at 1.25 minutes after coal addition, and diminishes rapidly until the end of pyrolysis. COS, meanwhile, is detected at a concentration of about 0.2% v/v after 1.25 minute, but diminishes after about 3 minutes of pyrolysis.

The conversion of sulphur to the gas phase during fluidised-bed pyrolysis is shown in **Figure 7-2**, indicating that when compared with the fast pyrolysis and TPP results that have been presented in Chapters 4 and 5, the sulphur conversion is greatest for the fluidised-bed experiments. The total sulphur conversion, at 35.5% of the original sulphur in the coal, approximates the estimated total conversion of sulphur to volatiles (both gas and tar phase) as calculated by difference for the fixed-bed fast pyrolysis experiments, as reported in Chapter 5. This is termed 'volatile sulphur' in **Figure 7-2**.

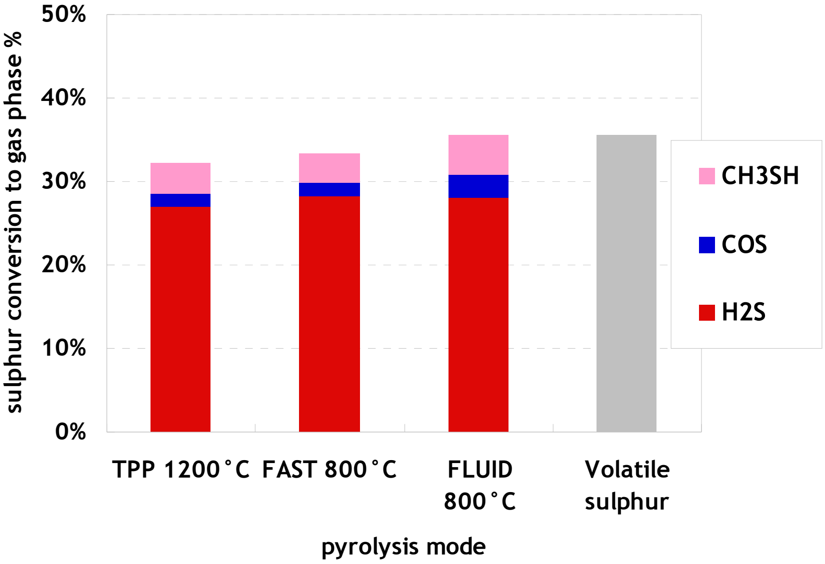


Figure 7-2 Sulphur conversion to the gas phase for each pyrolysis mode for air-dried Lochiel coal. Volatile sulphur represents the predicted total gas and tar phase evolution at 800°C.

Figure 7-3 shows the relative contribution to volatiles for each of the species, indicating that the fluidised-bed process results in a greater portion of sulphur converted to the gas phase as COS and CH_3SH at 7.6% and 13.4% of the total sulphur conversion respectively. For the TPP and fast pyrolysis modes, the percentage of total sulphur conversion is 4.8% and 4.9% for COS and 11.4% and 10.5% for CH_3SH respectively. H_2S contribution to conversion drops to under 80% of the total sulphur conversion to the gas phase for the fluidised-bed process, from approximately 84% and 85% from the TPP and fast mode experiments respectively.

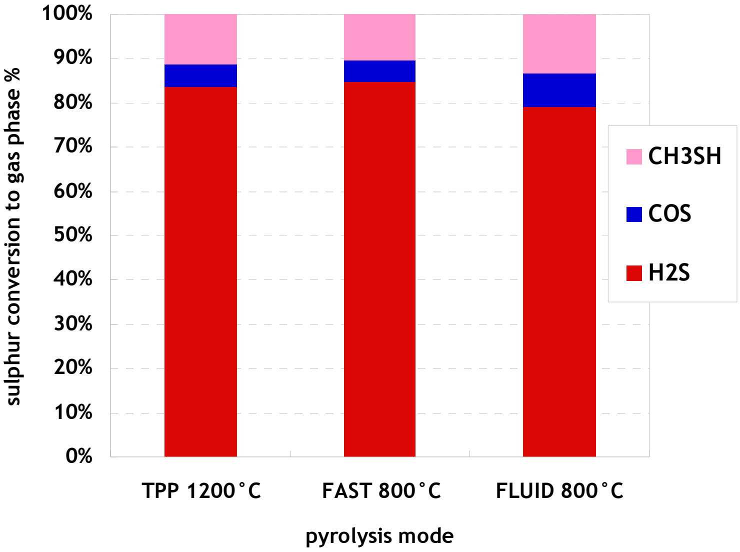


Figure 7-3 Normalised sulphur conversion to the gas phase for each pyrolysis mode for air-dried Lochiel coal.

Figure 7-4 presents the carbon conversion during fluidised-bed pyrolysis, showing a marked increase over the conversion to the gas phase for the fast and TPP pyrolysis mode experiments, from 10% to 20%. This compares with the estimated total volatile carbon (both gas and tar phase) of close to 40% as predicted by difference for the fast pyrolysis experiment in Chapter 5. This is termed 'volatile carbon'. The bulk of this increase in volatile carbon comes from CO_2 and 'other' hydrocarbons.

The carbon containing product distribution changes dramatically when moving from the TPP/fast-pyrolysis mode to the fluidised-bed (**Figure 7-5**). The percentage of total carbon conversion due to 'other' species, that is, C1-C3 hydrocarbons, along with carbon containing sulphur species COS and CH_3SH, contributes 25% to the overall carbon conversion to the gas phase, compared with just 12% for the TPP and fast pyrolysis modes. Conversion to the gas phase for CO decreases for the fluidised-bed process, while conversion to the gas phase due to CO_2 increases.

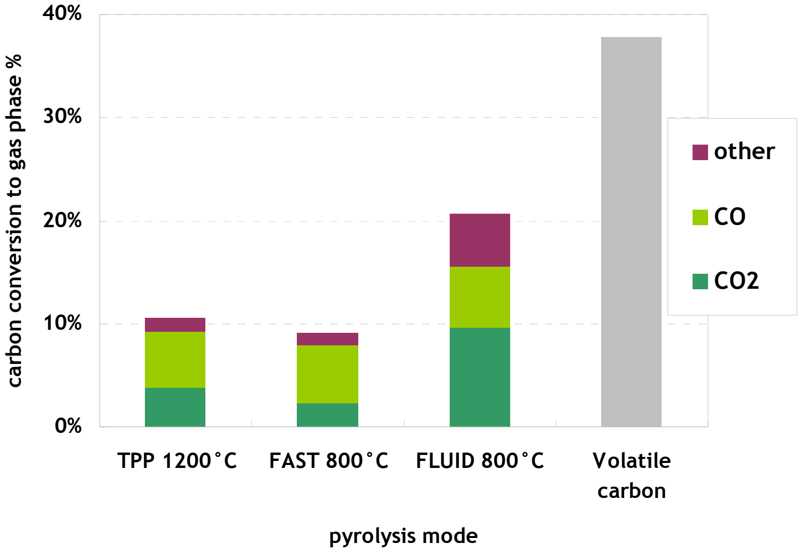


Figure 7-4 Carbon conversion to the gas phase for each pyrolysis mode for air-dried Lochiel coal. Other represents C1-C3 hydrocarbons and COS. Volatile carbon represents predicted total gas and tar evolution at 800°C.

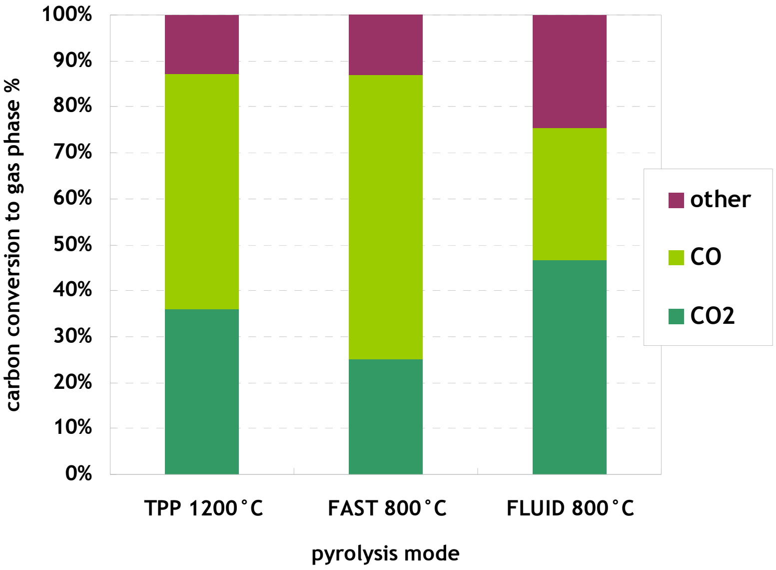


Figure 7-5 Normalised carbon conversion to the gas phase for each pyrolysis mode for air-dried Lochiel coal. Other represents C1-C3 hydrocarbons and COS.

The breakdown of product distribution for the ‘other’ carbon groups is shown in **Figure 7-6**. for TPP and fast pyrolysis, total carbon conversion due to these species is 1.5 and 1.1% respectively, whereas for the fluid-bed, it equates to just over 5%. The single greatest contribution to increasing conversion due to carbon species other than CO_2 and CO is methane, CH_4, while the propylene (C_3H_6) and ethylene (C_2H_4) species also increase significantly in absolute contribution to gas phase carbon conversion.

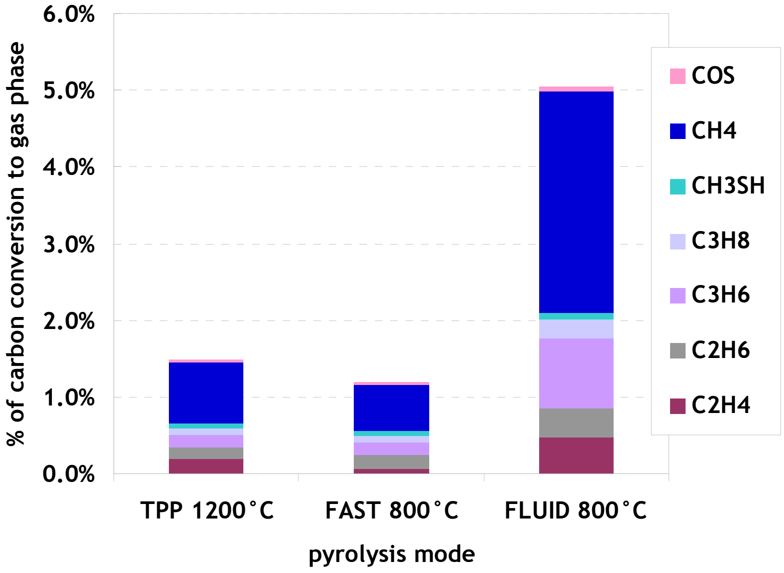


Figure 7-6 Carbon conversion (as hydrocarbons and COS/CH_3SH) to the gas phase for each pyrolysis mode for air-dried Lochiel coal.

When examining the normalised carbon conversion due to ‘other’ species in **Figure 7-7** significant changes in relative contribution to gas phase carbon conversion comes from an increase in C_3H_6, from 10.3% for the TPP experiment, to 13.8% for the fast pyrolysis mode and to 18.1% of total carbon conversion to the gas phase for the fluidised-bed pyrolysis experiment. This is at the expense of diminished CH_3SH and C_2H_6.

The results described in this chapter so far, showing increased carbon and sulphur conversion for the move to the fluidised-bed environment, are believed to reflect the more rapid mixing of hot nitrogen carrier gas with coal particles, resulting in a substantial increase in heating rate that causes a violent breakdown in the carbon matrix during the first 10 minutes after addition of coal to the bed. This results in the detection of more complex sulphur species such as COS, CH_3SH and other hydrocarbons (including CH_4) which, at lower heating rate, rapidly undergo secondary decomposition or reaction to give simpler sulphur and carbon groups such as H_2S, CO and CO_2.

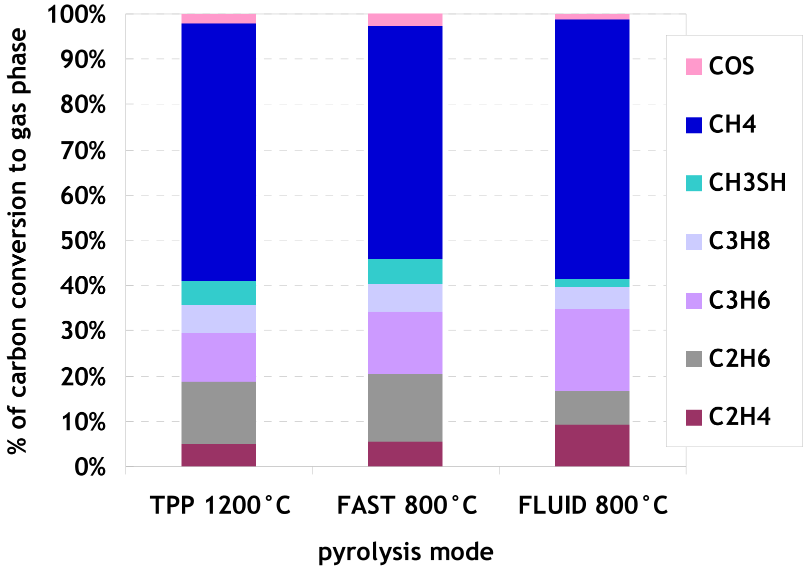


Figure 7-7 Relative carbon conversion (as hydrocarbons and COS/CH_3SH) to the gas phase for each pyrolysis mode for air-dried Lochiel coal.

For sulphur, the total conversion to the gas phase during the fluidised-bed process equates to the predicted total conversion to volatiles (both gas and tar phase, as estimated by difference in Chapter 5) lending credence to the method used to calculate the tar fraction 'by-difference'. It suggests that the slight increase in conversion to the gas phase for sulphur is the result of sulphur in the evolved tar undergoing secondary decomposition reactions. This corresponds to the observations of Telfer (1999) that Lochiel coal contains an abundance of less complex sulphur compounds which undergo rapid devolatilisation and results in the formation of metal sulphides, as opposed to Bowmans coal for which devolatilisation was less pronounced in the lower temperature regions and which saw no formation of metal sulphides.

For carbon, conversion to the gas phase almost doubles for the fluidised-bed over the fast and TPP experiments, suggesting that there is a significant quantity of carbon found in the tar which undergoes secondary decomposition reactions. This is supported by the higher contribution to conversion from 'other' species, particularly methane, and also an increase in contribution to gas phase conversion from CO_2 (the tar phase is likely to contain abundant oxygen as reported in the literature review). That the total conversion from fluidised-bed pyrolysis does not match the total carbon conversion to volatiles as calculated by difference in Chapter 5 indicates that there is probably a significant quantity of tar phase carbon that is not cracked in the fluidised-bed process for Lochiel coal, and is either elutriated from the apparatus or adheres to the internal surfaces of the free-board and gas sample lines (where temperatures are maintained at approximately 580°C and 200°C respectively).

Adherence to internal surfaces by tar condensation is observed during the pyrolysis stage of all steam gasification experiments on the sight-glass situated at the top of the reactor. Vision is limited through the site glass for the first 10 minutes of pyrolysis, although it improves after the addition of steam and is completely removed by 30 minutes. Given that literature studies suggest the bulk of tar phase evolution occurs between 500°C to 600°C (Solomon *et al.,* 1992), the condensation of tars in the freeboard section (held at 580°C gas temperature) and their subsequent reaction with steam, is likely to be contributing to conversion during the first 30 minutes of all experiments. This must be considered when examining the relationships between conversion and time for each of the fluidised-bed experiments.

7.2.2 Air-dried Bowmans pyrolysis in nitrogen

Using the same method described above for Lochiel coal, this section examines the conversion of Bowmans coal during nitrogen pyrolysis followed by gasification in 25% v/v steam. The conversion of sulphur to the gas phase during fluidised-bed pyrolysis for Bowmans coal is shown in **Figure 7-8**, indicating that sulphur conversion during pyrolysis is greatest in the fluidised-bed reactor. This corresponds to the observed result for Lochiel coal. The sulphur conversion, at 33% of the original sulphur in the coal, is significantly less than the estimated total conversion of sulphur to volatiles (both gas and tar phase, 48%) as calculated by difference for the fixed-bed fast pyrolysis experiments in Chapter 5 (termed ‘volatile sulphur’ in **Figure 7-8**).

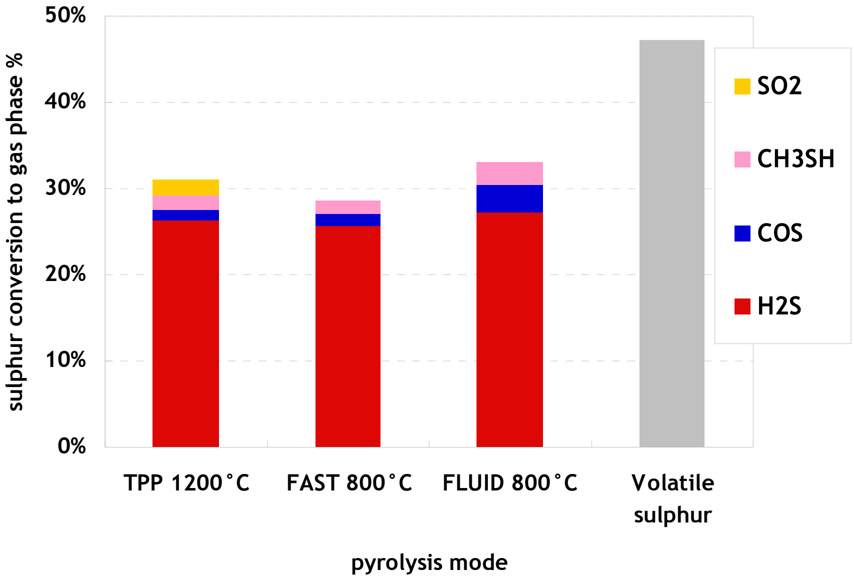


Figure 7-8 Sulphur conversion to the gas phase for each pyrolysis mode for air-dried Bowmans coal. Volatile sulphur represents the predicted total gas and tar phase evolution at 800°C.

COS is observed to increase in contribution to the gas phase conversion of sulphur from 1.2% to 1.4% when moving from TPP to fast pyrolysis environment, and then to 3.3% in the fluid-bed while CH_3SH decreases from 1.7% for the TPP experiment to 1.5% for the fast pyrolysis experiment before increasing up to 2.5% for the fluidised-bed experiment. There is no SO_2 detected during the fluidised-bed pyrolysis mode. The significant difference in conversion of sulphur to the gas phase between fluid and other modes of pyrolysis is believed to be an indication of Bowmans coal containing a greater abundance of more complex sulphur (eg thiophenes), which may be stabilised during TPP and are therefore not released. This again, confirms the work of Telfer (1999), regarding the differences between Bowmans and Lochiel coal.

In terms of speciation, there is more COS and CH_3SH for the fluidised-bed pyrolysis experiment than the TPP and fast experiments. **Figure 7-9** shows the relative concentration of sulphur species. Similar conclusions can be drawn regarding this speciation as per Lochiel coal, that is, the fluid-bed yields less simple sulphur (H_2S).

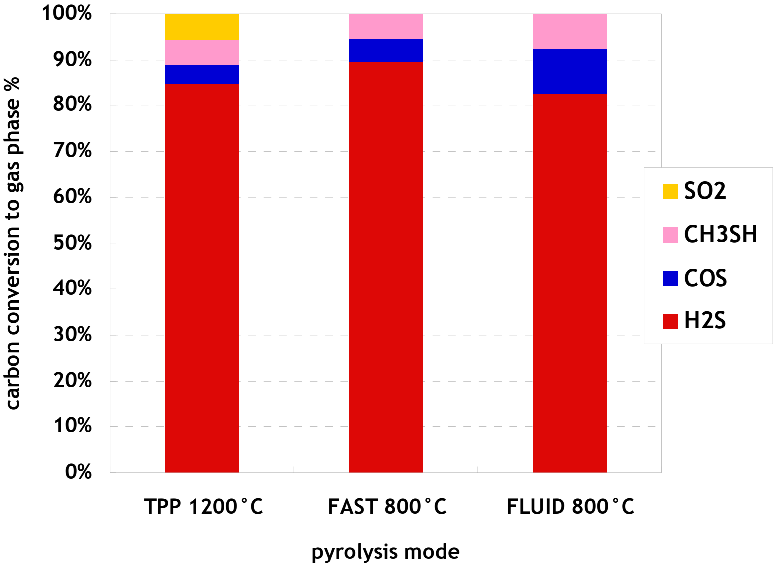


Figure 7-9 Relative sulphur conversion to the gas phase for each pyrolysis mode for air-dried Bowmans coal. Volatile sulphur represents the predicted total gas and tar phase evolution at 800°C.

Figure 7-10 shows results of carbon conversion during fluidised-bed pyrolysis. Total carbon conversion to the gas phase increases from 13.5% and 11.2% for the TPP and fast pyrolysis experiments respectively to 18.2% for the fluidised-bed mode. This compares with the estimated total volatile carbon (both gas and tar phase) of 32% as predicted by difference for fast pyrolysis in Chapter 5. Exhibiting similar behaviour to Lochiel, the bulk of the increase in carbon conversion for Bowmans comes from CO_2 and ‘other’ species, while the actual contribution due to CO decreases.

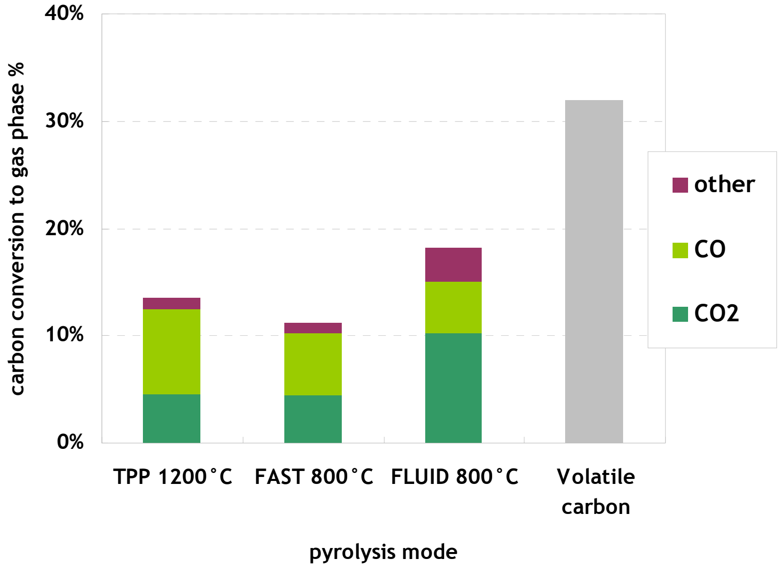


Figure 7-10 Carbon conversion to the gas phase for each pyrolysis mode for air-dried Bowmans coal. Volatile carbon represents the predicted total gas and tar phase evolution at 800°C.

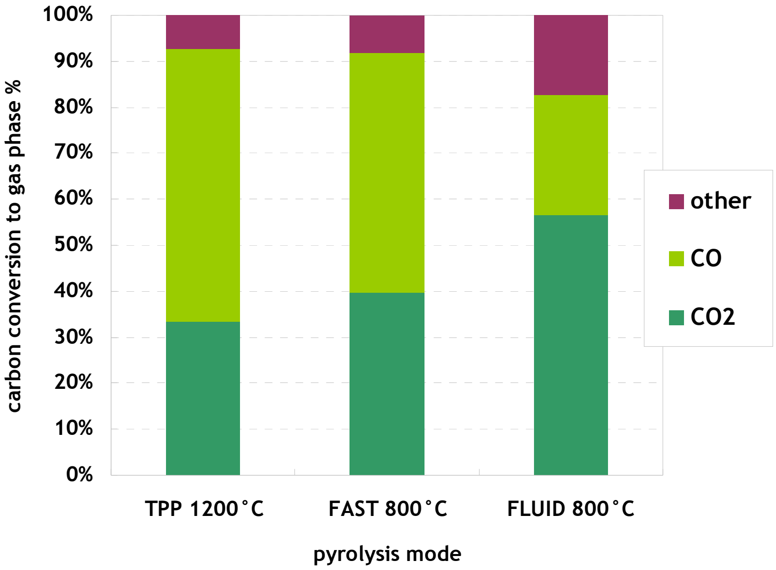


Figure 7-11 Relative carbon conversion to the gas phase for each pyrolysis mode for air-dried Bowmans coal. Volatile carbon represents the predicted total gas and tar phase evolution at 800°C.

The relative contributions to carbon conversion, as shown in **Figure 7-11**, change dramatically by moving from TPP and Fast Pyrolysis to the fluidised-bed environment. The relative concentrations indicate that the contribution to gas phase conversion from ‘other’ carbon containing species and CO_2 increases with increasing heating rate, while the contribution from CO decreases. Over 55% of the gas phase conversion of carbon during fluidised-bed pyrolysis comes from the contribution of CO_2.

By examining the ‘other’ species distribution, shown in **Figure 7-12**, the contribution of CH_4 is clearly the single biggest factor in this increase in gas phase conversion due to carbon species other than CO_2 and CO, equating to almost 1.6% of the gas phase carbon conversion during the fluidised-bed process. Absolute conversion contribution due to CH_3SH increases from 0.6%/0.5% v/v for TPP/Fast Pyrolysis to 0.9% v/v for the fluidised-bed, while the contribution to the other hydrocarbons and COS doubles with the increasingly violent pyrolysis conditions, from 0.04%/0.05% v/v for TPP/Fast Pyrolysis respectively to 0.11% v/v for the fluidised-bed.

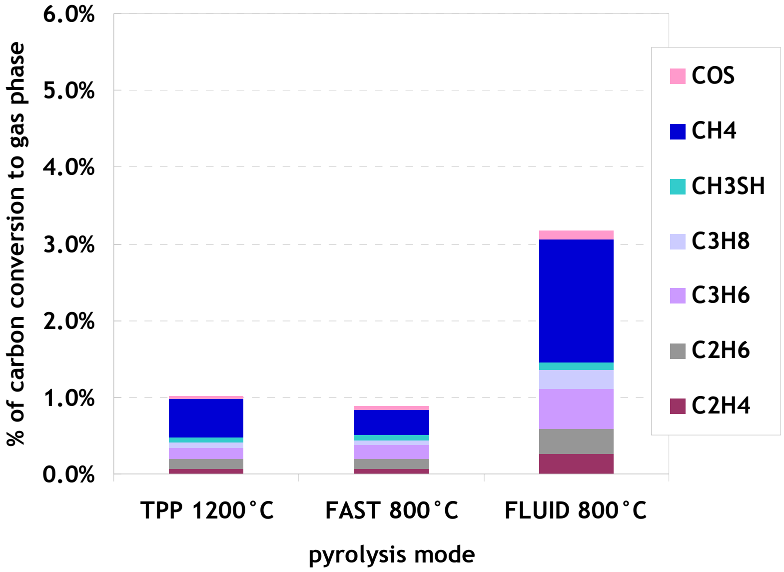


Figure 7-12 Carbon conversion (as hydrocarbons and COS) to the gas phase for each pyrolysis mode for air-dried Bowmans coal.

The relative contribution to gas phase carbon conversion from other species is shown in **Figure 7-13**, indicating little difference between the fluidised-bed and TPP mode. The fast pyrolysis mode, however, shows a greater relative contribution from C_3H_6 primarily (21.4% of the total 'other' carbon conversion), at the expense of CH_4 (37.4%, relative).

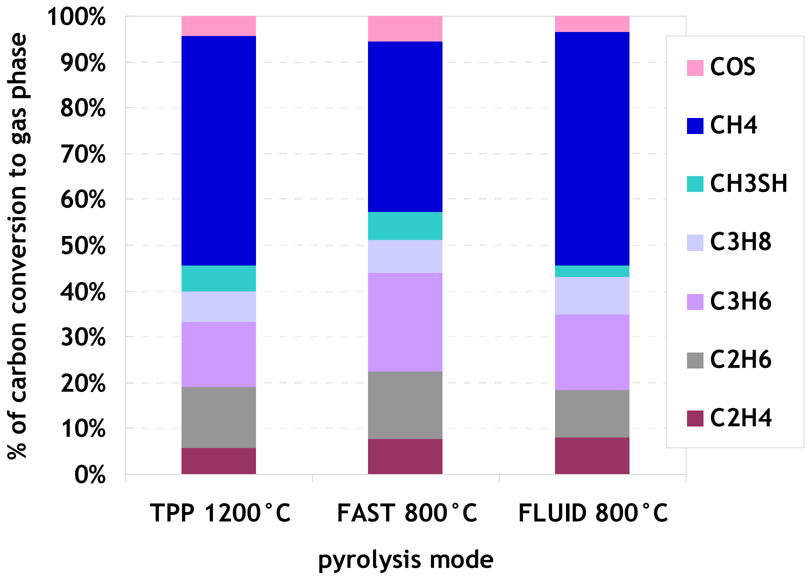


Figure 7-13 Relative carbon conversion (as hydrocarbons and COS) to the gas phase for each pyrolysis mode for air-dried Bowmans coal.

7.2.3 Comparing Lochiel and Bowmans

Table 7-1 to **Table 7-3** display the absolute conversion figures for sulphur and carbon for each of the species detected and for both coals, during fluidised-bed pyrolysis, and are drawn from the Figures presented earlier in this chapter. The "Total Volatile" figures represent the total conversion of sulphur and carbon to volatiles (both tar and carbon) calculated by difference (from Chapter 5).

The difference between the 'predicted' and actual sulphur conversion to the gas phase for Lochiel coal is negligible at 0.05% of total sulphur conversion, while for Bowmans this equates to 14.1%. For carbon conversion, on the other hand, the difference is approximately 17.2% for Lochiel coal and 13.8% for Bowmans. The difference between the two coals for sulphur conversion is believed to relate to the distribution of sulphur (and indeed, carbon) in the tar phase, as discussed earlier in this chapter.

Table 7-1 Absolute sulphur conversion to gas phase during fluidised-bed pyrolysis of air-dried Lochiel and Bowmans coals.

species	Lochiel	Bowmans
H2S	28.05%	27.26%
COS	2.71%	3.26%
CH3SH	4.74%	2.51%
Total	**35.50%**	**33.03%**
Total Volatile	35.55%	47.16%

Table 7-2 Absolute carbon conversion to gas phase during fluidised-bed pyrolysis of air-dried Lochiel and Bowmans coals.

species	Lochiel	Bowmans
CO2	9.63%	10.28%
CO	5.95%	4.71%
other	5.05%	3.18%
Total	**20.62%**	**18.16%**
Total Volatile	37.79%	31.98%

Table 7-3 Absolute carbon conversion to gas phase during fluidised-bed pyrolysis of air-dried Lochiel and Bowmans coals, as ‘other’ species

species	Lochiel	Bowmans
C2H4	0.47%	0.25%
C2H6	0.38%	0.34%
C3H6	0.92%	0.52%
C3H8	0.25%	0.25%
CH3SH	0.09%	0.09%
CH4	2.89%	1.61%
COS	0.05%	0.11%
Total	**5.05%**	**3.18%**

Results in Chapter 5 show that there is an estimated 18% of total sulphur in coal distributed to the tar phase during fast pyrolysis experiments for Bowmans coal, and less than 3% for Lochiel coal. This suggests that more of the sulphur found in Lochiel coal is comparatively ‘simple’ in nature when compared to Bowmans coal, therefore more easily volatilised. That there is only a small increase in sulphur conversion with the move to the fluidised-bed environment for air-dried Bowmans coal suggests that the faster heating rate and more violent nature of the reaction zone environment has little effect on the distribution of sulphur to the volatile (including the tar) phase. Therefore the tar phase sulphur is relatively ‘stable’ and not easily decomposed in a fluidised-bed environment (over a simple fixed-bed). That the increase in conversion of sulphur resulting from the move to fluidised-bed mode (in absolute terms) is primarily due to COS (and to a lesser extent H_2S) may indicate that the tar phase sulphur is bound intimately to carbon associated with oxygen groups. This suggests that COS is likely the result of decomposing carbon-oxygen structures that are bound to sulphur or react with it in the tar phase.

For carbon conversion, a similar argument can be made for both coals, that is, there are large quantities of carbon evolved in the tar phase, given the significant differences between the fixed (for varying heating rates) and fluidised apparatus. These condense and adhere to the internal surfaces in the fluidised-bed apparatus, and undergo decomposition and secondary reactions with gas phase species along with reducing reactions with the steam in the fluidising medium once pyrolysis is completed.

7.2.4 Effect of atmosphere during fluidised-bed pyrolysis

This section examines the effect of steam addition during pyrolysis. Unfortunately it is not possible to obtain gas phase data for sulphur species concentration during steam pyrolysis, or steam gasification, due to the complex downstream clean up system that must be employed to remove particulates and prevent contamination of the micro-GC. In a large scale facility, the gas is either quenched using a direct contact water spray quench or water-cooled in a shell and tube heat exchanger arrangement. In both cases, the condensation of moisture strips sulphur compounds from the product gas as H_2S

dissolves in the condensate. Product gas cooling equipment is, in fact, one of the most expensive items of capital expenditure in a modern IGCC plant and removal of all sulphur is essential before introducing syngas into the gas turbine, given that acid gases in the fuel before combustion leads to corrosion damage (and blade failure) during operation.

Concentration data is recorded for up to C3 hydrocarbons for pyrolysis of air-dried Lochiel coal in 25% v/v steam in nitrogen. Results are shown in **Figure 7-14**.

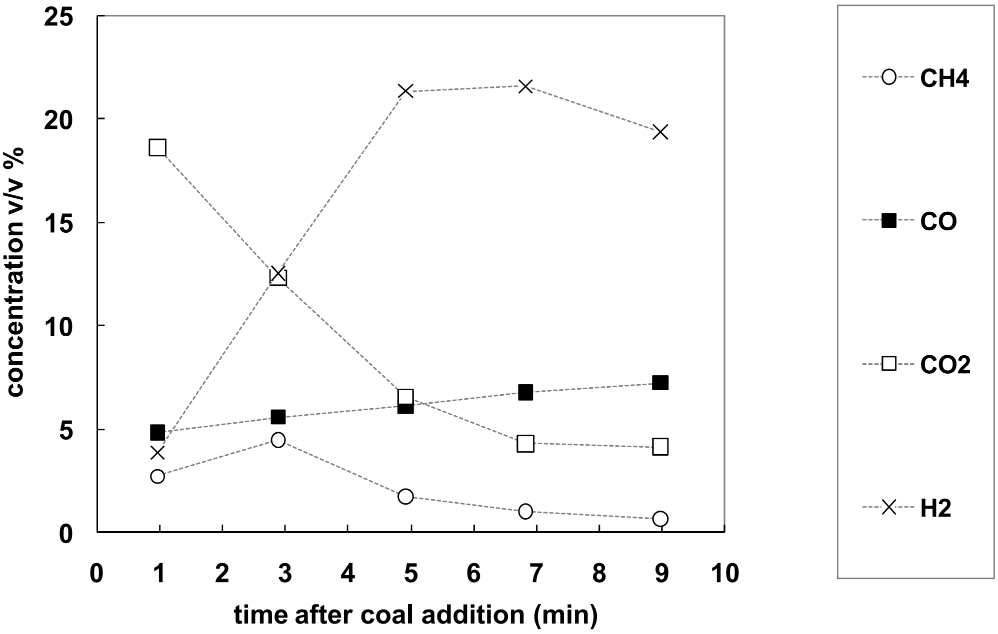


Figure 7-14 Species concentration for carbon (CO_2, CO and CH_4) and hydrogen (H_2) for fluidised-bed pyrolysis (25% v/v steam in nitrogen atmosphere) of air-dried Lochiel coal at 800°C.

According to **Figure 7-14** the concentration of CO_2 1 minute after coal addition is about 18.5%, while CO and H_2 reach approximately 5% and 4% respectively. CO concentration increases over the first 10 minutes while CO_2 diminishes to around 4.3% after 7 minutes. Hydrogen increases to a peak of over 20% after 5 minutes. CH_4 peaks at 4.5% after about 3 minutes before decreasing to around 0.7% after 9 minutes.

The difference in carbon conversion to the gas phase between pyrolysis in pure nitrogen (N_2) and 25%v/v steam in nitrogen (N_2/Steam) is shown in **Figure 7-15**.

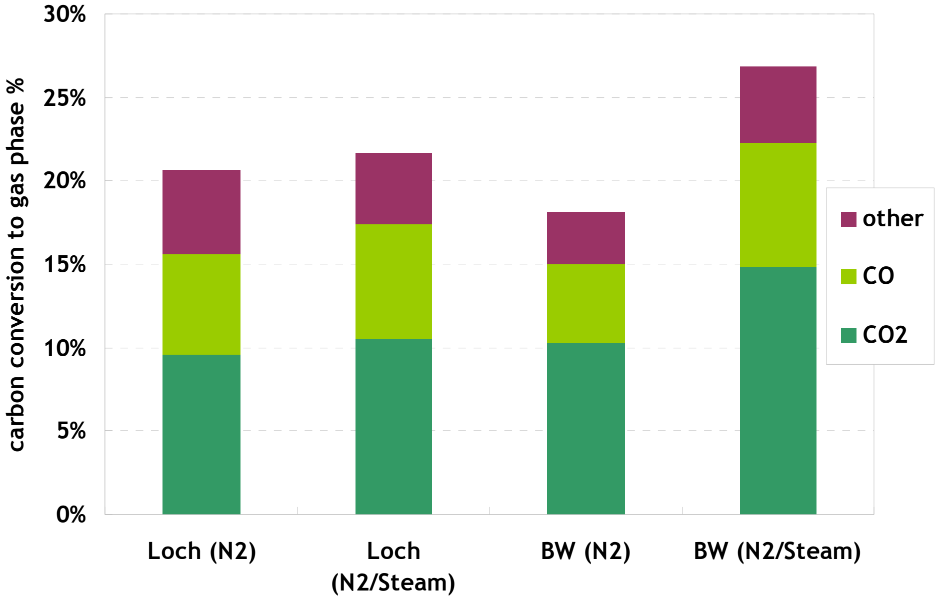


Figure 7-15 Carbon conversion to the gas phase during fluidised-bed pyrolysis of air-dried Lochiel (Loch) and Bowmans (BW) coals in nitrogen (N_2) and nitrogen-steam (N_2/steam) atmospheres at 800°C

Carbon conversion to the gas phase as CO_2 and CO increases when moving to a steam/nitrogen environment from pure nitrogen for both Lochiel and Bowmans coal. Results for conversion to the gas phase as 'other' species (up to C3 hydrocarbons excluding trace COS and CH_3SH) decreases for Lochiel and increases for Bowmans. Bowmans experiences a significant increase in absolute carbon conversion to the gas phase from 18.2% to 26.8% while Lochiel only increases from 20.6% to 21.7%. The most significant increase in carbon conversion when moving to the steam/nitrogen pyrolysis environment comes from CO_2 for Bowmans coal, which increases in contribution to conversion from 10.3% to 14.9%

While the absolute quantity of 'other' carbon species increased for Bowmans coal with the shift to steam/nitrogen pyrolysis from nitrogen only (from 3.2% to 4.6%), the relative contribution to the ‘other’ species that indicates there are negligible differences between the steam and nitrogen environment.

The increase in carbon conversion to the gas phase may be the result of the reaction of evolved tar with steam. The total volatile carbon released during fixed-bed pyrolysis in nitrogen has been estimated at 38% Lochiel and 32% for Bowmans. If the increase in gas phase conversion is due solely to an increase in tar cracking, then this leaves 5.2% of the carbon for Bowmans coal evolved as tar (given the 8.7% increase in carbon conversion from 18.2% to 26.8%), while 16.3% of carbon remains as tar for Lochiel (after carbon conversion increased only slightly from 20.6% to 21.7% with the introduction of steam during pyrolysis). This may suggest that the Lochiel tar phase is less reactive than the Bowmans tar phase towards steam.

The most important consideration in examining the differences between pyrolysis in nitrogen and pyrolysis in steam is how different environments affect the subsequent gasification reactivity. This is examined in the next section.

7.3 Fluidised-bed steam gasification

For each experiment described in section 7.2, steam gasification is either commenced at 10 minutes (following pyrolysis in nitrogen) or continued (for pyrolysis in 25% v/v steam). Having made the chars for steam gasification tests in-situ, the following section details the investigation of the behaviour of sulphur and carbon during prolonged reaction in the 25% v/v steam environment.

The temperature history profile of the reactor is shown in **Figure 7-16** for the Lochiel 800°C fluidised-bed pyrolysis experiment, and included is the temperature profile for the subsequent steam gasification period. Thermocouple locations are described in Chapter 3. The reaction zone takes approximately 5 minutes to reach the desired reaction temperature (according to thermocouple data) following delivery of the batch of coal at ambient temperature to the hot vessel.

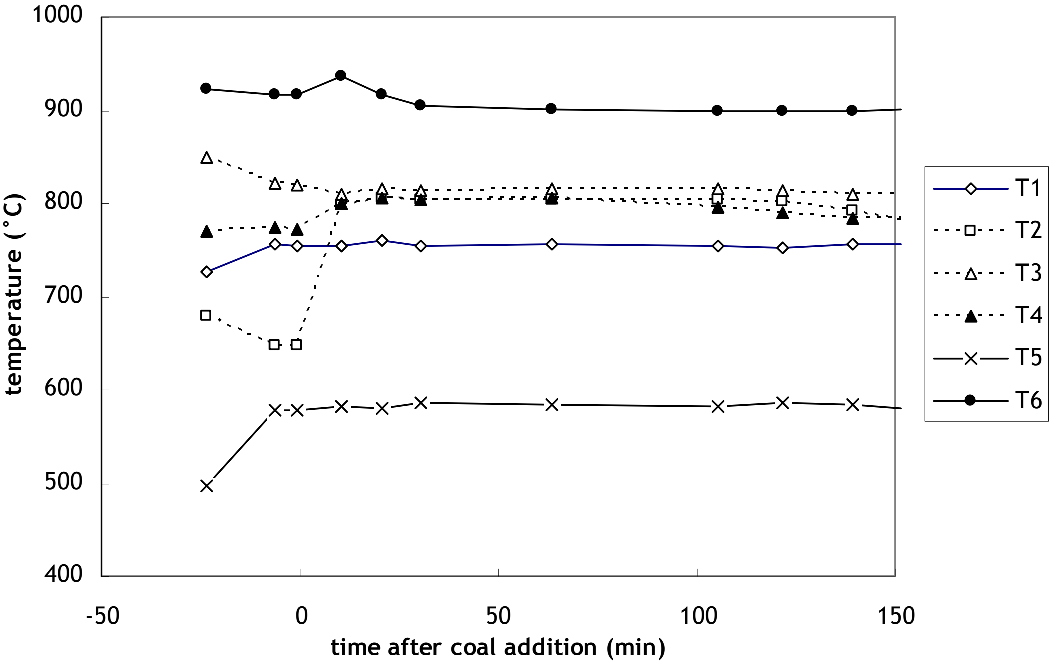


Figure 7-16 Fluidised-bed reactor temperature profiles for the fluidised bed pyrolysis (0-10minutes) and subsequent steam gasification (>10minutes) of air-dried Lochiel coal.

From 0-60 minutes the average reaction zone temperature was 807°C, and from 60 minutes onwards, the temperature in the reaction zone destabilised, with the top (T4) and bottom (T2) of the bed decreasing in temperature from approximately 800°C to 780°C and 790°C respectively, while the centre of the bed diminished only slightly to 810°C (from ~814°C). This digression of reaction zone temperature is believed to be the result of the fluid-bed being significantly depleted of coal, with the centre (T3) and top (T4) thermo-couples completely exposed to the fluidising medium and the subsequently higher flow rate of fluidising medium through the remaining ash enriched bed material (approximately 15g were removed on cool down, which with 11g of fines from the ash can, give a total mass conversion of over 90%). This was confirmed by monitoring the bed intermittently via a site glass at the top of the reaction vessel.

Carbonaceous species up to C3 were detected and analysed. The gasification experiments was terminated when no further carbon is detected in the product gas (as

CO_2 or CO), and this was accompanied by a significant temperature gradient across the reaction zone. Concentration profiles from air-dried (AD) Lochiel gasification undertaken at 800°C are shown in **Figure 7-17**. Results are presented for gasification following pyrolysis in nitrogen only (solid lines) and gasification following pyrolysis in steam (25% v/v) and nitrogen (dashed lines).

Figure 7-17 indicates that gasification following pyrolysis in the steam/nitrogen atmosphere results in a more rapid decrease in concentration as the experiment progresses for all species: hydrogen, carbon dioxide and carbon monoxide. Methane and other hydrocarbon are not detected in appreciable quantities after the initial 10 minutes pyrolysis stage.

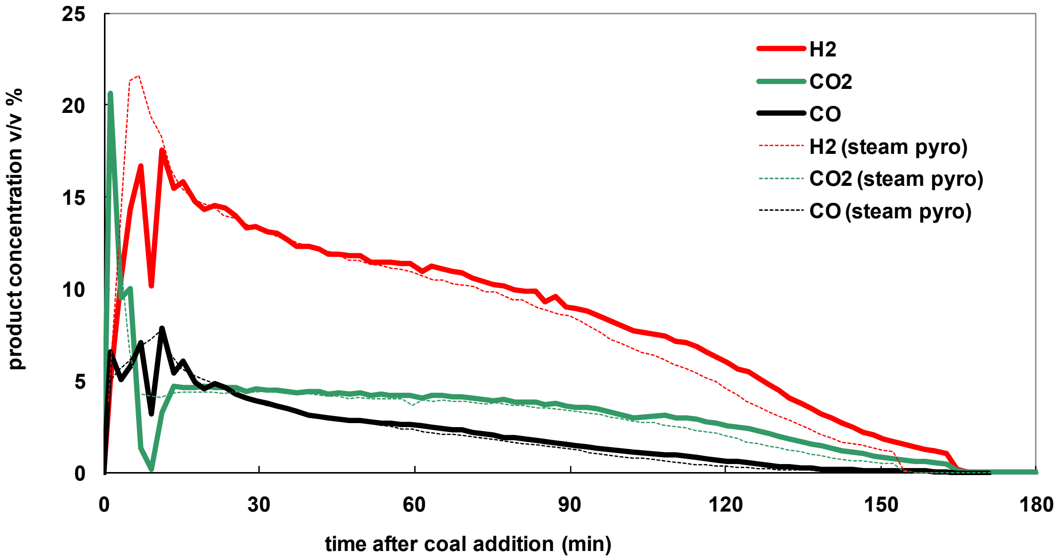


Figure 7-17 Concentration of major product gases and nitrogen carrier gas for fluidised-bed pyrolysis and gasification of air-dried Lochiel coal at 800°C. Solid lines indicate that pyrolysis was conducted in the absence of steam whereas dashed lines represent N_2/steam pyrolysis results.

For nitrogen pyrolysis, hydrogen is detected at a maximum concentration of 16.7% after 7.2 minutes, while for steam-nitrogen pyrolysis, it is detected at 21.6% after 6.8 minutes. In the case of nitrogen pyrolysis, hydrogen concentration diminishes prior to the addition of steam, after which point it increases to achieve its maximum before continuing to diminish until the termination of the experiment.

For carbon dioxide, a maximum concentration of 20.6% is detected at the first sample interval at just over 1 minute after coal addition during nitrogen pyrolysis. This diminishes to 0.2% by about 9 minutes. For the combined pyrolysis mode, a maximum concentration of 18.6% is detected after 1 minute. In both cases, a steady state concentration of approximately 4.5% is achieved from approximately 15 minutes after coal addition, and this diminishes gradually until the termination of the experiment.

For carbon monoxide, the separate pyrolysis-gasification experiment sees a maximum concentration of 7.1% after 7 minutes, while the combined methodology sees CO concentration reach a maximum of 7.7% after 11 minutes. While the profiles for each of these fluctuate somewhat in the first 10 minutes they both diminish at approximately the same rate until the termination of the experiment.

As per the calculation methodology outlined in Chapter 3, and undertaken for each subsequent chapter when calculating the mass balance for each set of experiments, the total mass flow out of the system is calculated by integrating the concentration curves for each species, for a given flow rate (constant) of nitrogen carrier gas, enabling curves of cumulative conversion to be plotted as a function of time. **Figure 7-18** shows this result for Lochiel coal gasification under both modes of pyrolysis. The maximum carbon conversion due to gasification is approximately 85% after steam/nitrogen pyrolysis while the carbon conversion due to gasification is approximately 95% for gasification following pyrolysis carried out in pure nitrogen. The difference in cumulative conversion with time is prominent from approximately 50-60% carbon conversion. The time to 50% conversion due to gasification is approximately 50 minutes for both conditions.

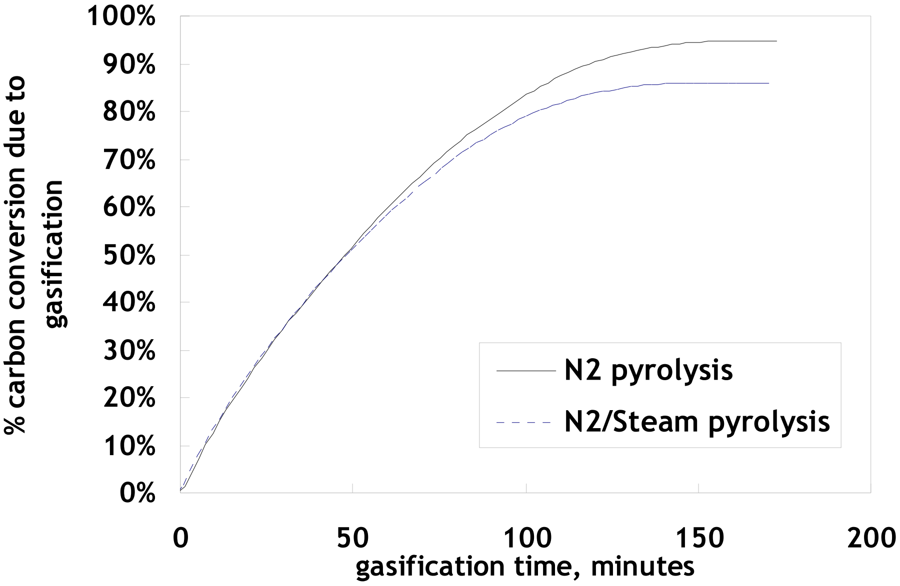


Figure 7-18 % carbon conversion due to gasification for air-dried Lochiel coal at 800°C in 25% v/v steam and nitrogen.

The concentration profile from air-dried Bowmans gasification undertaken at 800°C is shown in **Figure 7-19**. Results are presented for gasification following pyrolysis in nitrogen (solid lines) and gasification following pyrolysis in steam and nitrogen (dashed lines). **Figure 7-19** reveals, in a similar way to the Lochiel results, that gasification following pyrolysis in the steam/nitrogen atmosphere (25% v/v steam) results in a more rapid decrease in concentrations for all major species: hydrogen, carbon dioxide and carbon monoxide. It is clear from the Bowmans profile, when compared to the Lochiel profile, that the early stages of gasification (less than 10 minutes after coal addition) see greater evolution of hydrogen, carbon dioxide and carbon monoxide – this was reflected in the preceding discussion regarding the differences in total carbon conversion due to the addition of steam during pyrolysis.

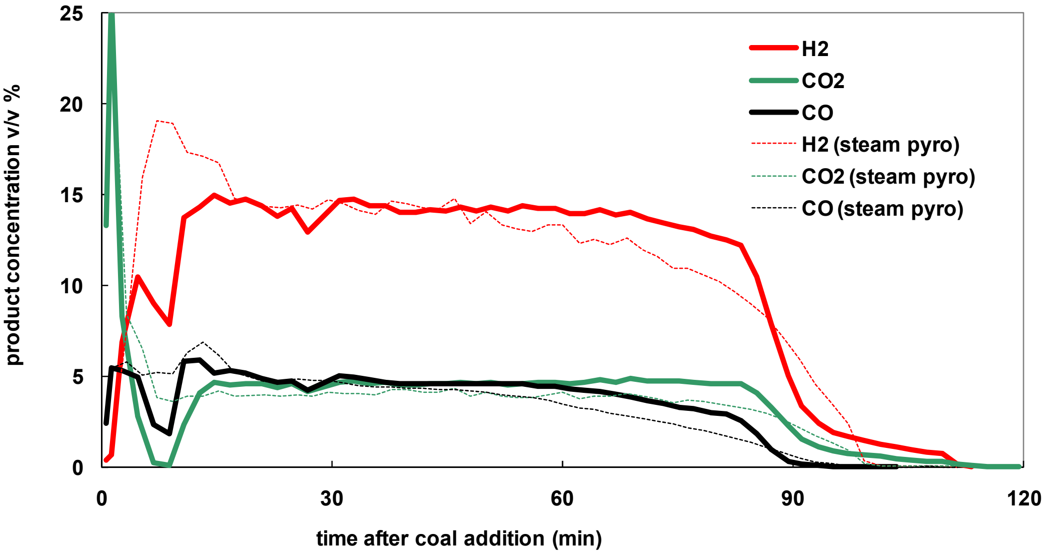


Figure 7-19 Concentration of major product gases and nitrogen carrier gas for fluidised-bed pyrolysis and gasification of air-dried Bowmans coal at 800°C. Solid lines indicate that pyrolysis was conducted in the absence of steam whereas dashed lines represent N_2/steam pyrolysis results.

Differing significantly from the Lochiel profile, however, is the shape of the curves. All major species show a period of near-constant concentration from 10-60 minutes after coal addition for both pyrolysis modes, and up to approximately 90 minutes for gasification following nitrogen pyrolysis. For reaction following nitrogen pyrolysis there is a sudden drop in concentration from about 85 minutes which stabilises after 90 minutes before a gradual decrease to 110 minutes. For gasification following pyrolysis in 25% v/v steam and nitrogen, this tail is not prevalent, with detection terminating at approximately 100 minutes. This termination time compares with about 170 minutes for Lochiel coal.

For the nitrogen pyrolysis mode, hydrogen concentration was detected at a maximum of 14.9% after 15 minutes, while for the steam-nitrogen pyrolysis mode, it was detected at 19% after 7.3 minutes. In the case of the separate pyrolysis mode, hydrogen concentration diminishes prior to the addition of steam, after which point it increases to achieve its maximum and then continues to diminish until the termination of the experiment. However, there is a pronounced decline in hydrogen concentration for the combined mode, after closely tracking the separate mode, from approximately 45 minutes after coal addition to the termination of the experiment at approximately 110 minutes.

For carbon dioxide concentration during nitrogen and nitrogen-steam pyrolysis, a maximum of approximately 26% was detected at the first sample interval at approximately 1.3 minutes after coal addition. For nitrogen pyrolysis, this diminishes to 0.1% by 9 minutes, while for the steam/nitrogen pyrolysis, a “steady state” concentration of approximately ±4% is achieved by 15 minutes and continues until approximately 90 minutes. Like hydrogen, the CO_2 concentration profile for the steam/nitrogen mode disengages from the nitrogen only mode profile from approximately 45 minutes after coal addition to the termination of the experiment.

For carbon monoxide, nitrogen pyrolysis sees a maximum concentration of 5.9% after 12.8 minutes, while steam/nitrogen pyrolysis sees CO concentration reach a maximum of 6.9% after 13.3 minutes. The profile for the separate mode diminishes to 1.8% at 8.8 minutes during pyrolysis. Once again, the CO profile for the steam/nitrogen mode diminishes at a faster rate when compared with nitrogen only.

Cumulative conversion versus time is shown in **Figure 7-20** for Bowmans coal. The maximum carbon conversion due to gasification is approximately 90% for gasification following steam/nitrogen pyrolysis while the carbon conversion due to gasification approaches 98% for gasification following pyrolysis carried out in nitrogen only. The difference in cumulative conversion with time, in a similar way to the difference between experiments undertaken with Lochiel coal, is apparent from approximately 50-60% carbon conversion, with a time to 50% conversion of approximately 40 minutes (*cf* 50 minutes for Lochiel).

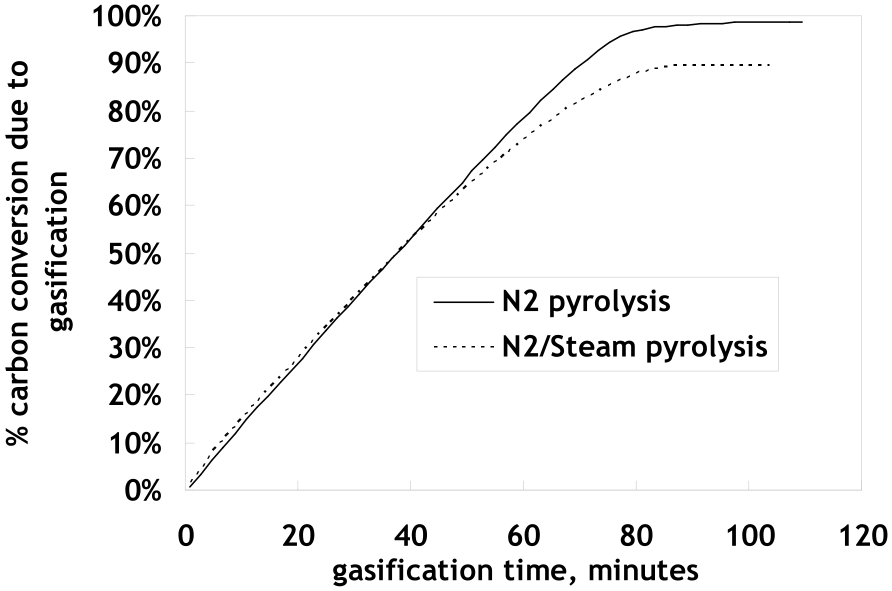


Figure 7-20 % carbon conversion due to gasification for air-dried Bowmans coal at 800°C in 25% v/v steam and nitrogen.

For Bowmans coal, the concentration versus time data in **Figure 7-20**, showing a linear relationship between conversion and time up to 80% conversion, indicates that there is a good fit between the experimental data and the shrinking core model under film diffusion control (which also equates to the zero order homogeneous model). For Lochiel, the 1st order homogeneous model (-ln(1-X)) has been used to obtain the reaction rate constant k (**Figure 7-21**) for comparison with results from Chapter 6. For both pyrolysis conditions, a reaction rate constant, k, of 0.034min^{-1} (slope = kP^{n}, where P = partial pressure of steam 0.25, n reaction order 0.6) is achieved. This is equivalent to those obtained using *acid-washed* Lochiel coal at 800° in the fixed-bed experiments described in Chapter 6 (0.035min^{-1}) and consequently, about an order of magnitude lower than that obtained for the air-dried coal at 800°C in the fixed bed (0.36min^{-1}). Clearly the fluidised bed pyrolysis conditions have significantly impacted the reactivity of the subsequent char.

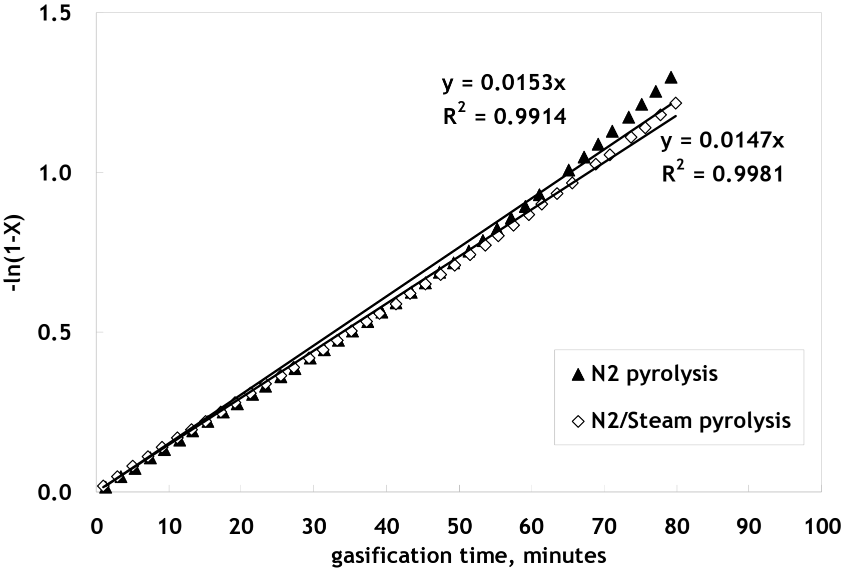


Figure 7-21 Comparison of homogeneous model predictions for carbon conversion with experimental data for steam fluidised-bed gasification of air-dried (AD) Lochiel coal (up to 80% conversion)

The temperature at which a coal undergoes pyrolysis (final temperature) and its subsequent holding time at that temperature are known to be major drivers of the subsequently formed char reactivity, and the influence of heat treatment has been reviewed extensively in the literature (Laurendeau, 1978; Miura *et al.* 1989). The three major changes occurring during heat treatment are reported as:

- Loss of oxygen and hydrogen atoms
- Conversion of mineral matter to metal oxides
- Loss of microporosity and carbon edges due to thermal annealing.

Miura *et al.* (1989) reviewed the effect of pyrolysis conditions on reactivity and generally, the reactivity was reported to *decrease* with the severity of char preparation conditions, that is, at higher final temperature and longer holding time. Notably, their review concluded that these effects were greater for low rank coals, expected due to the effects of thermal annealing and the loss of internal active sites. Earlier investigations by Blackwood *et al.* (1967) observed also this effect. Blackwood *et al.* (1967), while investigating the steam-hydrogen gasification reactivity of Victorian brown coals, proposed that final temperature had more of an effect on the gasification reactivity that the source of that coal.

However, in the review by Laurendeau (1978), it was reported that a particle's internal surface area was found to increase until the temperature of the particle reached 600-700°C, and then decrease rapidly due to internal realignment and ordering of the structure at temperatures in excess of 700°C. At higher heating rates, however, the more rapid volatile escape enhanced the development of greater porosity. Australian brown coals and lignites have long been known to have a well developed and open pore structure (Woskoboenko *et al.* 1991), demonstrated by their high moisture content. The distribution of internal volume or area over pore diameter determines the accessibility of the internal surface area to a gaseous reactant. However, despite the belief that increased heating rates encourage a more open pore structure, several studies have concluded that the porositiy of a coal sample, and hence its internal surface area, does not indicate the reactivity of char during gasification (Miura *et al.,* 1989; Adanez *et al.,* 1994).

Various studies have shown, however, that char reactivity increases with decreasing coal rank over a wide rage of conditions (Fung, 1982; Knight and Sergeant, 1982; Fung and Kim, 1983; Molina and Mondragon, 1998). There are several explanations on this inverse dependence of coal rank. Low rank coal has a high proportion of oxygen containing functional groups (Takarada *et al.,* 1985) and a higher content (and more even distribution of active minerals (ash) which act as catalysts to the gasification reaction (Ye*.,* 1994). The study of Takarada *et al.* (1985) identified exchangeable cations such as calcium and sodium as having a strong relationship to char reactivity, although gave no mathematical correlation.

XRD analysis of bed material removed from each of the experiments is shown in **Table 7-4**.

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).

Coal (pyrolysis)	**Co-dominant (sum>60%)**	**Sub-dominant (20-60%)**	**Minor (5-20%)**	**Trace (<5%)**
Lochiel (N_2 pyrolysis)	Amorphous Quartz (SiO_2) Oldhamite **(CaS)** Periclase (MgO)		Anhydrite **($CaSO_4$)** Nepheline **($NaAlSiO_4$)** Magnetite (Fe_3O_4)	Possible Monticellite ($CaMgSiO_4$) and/or Mayenite (Ca_{12} Al_{14} O_{33})
Lochiel (N2/Steam pyrolysis)	Amorphous Quartz (SiO_2) Periclase (MgO)	Gehlenite ($Ca_2Al_2SiO_7$)	Anhydrite **($CaSO_4$)** Magnetite (Fe_3O_4)	Oldhamite **(CaS)** Vaterite ($CaCO_3$) Nepheline **($NaAlSiO_4$)** Possible Monticellite ($CaMgSiO_4$) and/or Mayenite (Ca_{12} Al_{14} O_{33})
Bowmans (N_2 pyrolysis)	Periclase (MgO) Quartz (SiO_2)	Anhydrite **($CaSO_4$)** Oldhamite **(CaS)** Halite **($NaCl$)**	Magnetite (Fe_3O_4) Nepheline **($NaAlSiO_4$)** Possible Spinel (Mg Al_2 O_4)	Possible Mayenite ($Ca_{12}Al_{14}O_{33}$) Calcium magnesium sulphate **(Ca Mg_3 $(SO_4)_4$)**
Bowmans (N_2/Steam pyrolysis)	Periclase (MgO)	Quartz (SiO_2) Anhydrite **($CaSO_4$)** Oldhamite **(CaS)**	Magnetite (Fe_3O_4) Spinel (Mg Al_2 O_4)	Nepheline ($NaAlSiO_4$) Halite **($NaCl$)** Possible Monticellite ($CaMgSiO_4$) and/or Mayenite (Ca_{12} Al_{14} O_{33}) Sal Ammoniac (NH_4Cl)

For Lochiel coal gasification, comparing first the difference between the pyrolysis regimes, oldhamite (CaS) formation is encouraged by pyrolysis in nitrogen only regime, while anhydrite ($CaSO_4$) formation is encourage during pyrolysis in steam and nitrogen. The difference in the fate of sulphur as oldhamite is most prominent between the two modes: oldhamite is in the co-dominant phase of the residue when gasification follows pyrolysis in nitrogen, but only in trace quantities when following pyrolysis in steam and nitrogen. Calcium is present in trace amounts as veterite ($CaCO_3$) following gasification of char formed in steam/nitrogen only, while sodium is found as nepheline ($NaAlSiO_4$) in trace amounts for the same conditions, increasing to a minor phase after nitrogen pyrolysis.

For Bowmans, the major difference between the two pyrolysis modes is the fate of halite (NaCl). For pyrolysis in steam and nitrogen, halite is found in only trace quantities, while when pyrolysis is carried out in nitrogen, it is present in the sub-dominant phase. For both modes, anhydrite and oldhamite are found in the sub-dominant phase. Calcium magnesium sulphate ($CaMg_3(SO_4)_4$) is identified as a possible component present in the residue from gasification following pyrolysis in nitrogen only. Sodium is also found as nepheline in the minor phase for pyrolysis is nitrogen only, and as a trace constituent of the residue after gasification following steam/nitrogen pyrolysis.

Table 7-5 shows the total mass removed from the reactor as bed material and fines for each of the gasification experiments.

Table 7-5 Mass balance for each experimental method

Coal type (pyrolysis mode)	Coal in (g)	Bed removed (g)	Fines (g)	Conversion % (as per solid phase)
Lochiel (N2 pyrolysis)	300	15.9	11.6	90.80%
Lochiel (N2/Steam pyrolysis)	300	18.2	9.2	90.90%
Bowmans (N2 pyrolysis)	300	16.7	1.1	94.10%
Bowmans (N2/Steam pyrolysis)	300	11.1	9.8	93.00%

Based on these results, total mass conversion is approximately 91% for Lochiel gasification following both pyrolysis modes and 94% and 93% for Bowmans gasification following nitrogen and steam/nitrogen pyrolysis respectively. For gasification following Bowmans pyrolysis in nitrogen only, only a small quantity of fines was removed from the ash can.

Table 7-6 and **Table 7-7** show the percentage distribution of ash phase components removed from the reactor either from the rection zone or the ash can. These results indicate that over 50% of the original sodium in Lochiel coal remains in the bed post gasification for both pyrolysis modes. For Bowmans, this figure varies from approximately 35% for gasification following pyrolysis in nitrogen to 25% following pyrolysis in steam/nitrogen. While the figure for silicon showing greater than 100%, this is primarily due to a shortfall in the summation of oxides determined in the ash samples from which these data are derived, probably due to the presence of chlorides or carbonates in the ash which may be present in some samples. For calcium, Bowmans coal retains greater quantities following pyrolysis in nitrogen only.

Table 7-6 Total % of original ash components removed from the reaction zone.

Coal type (pyrolysis mode)	Si	Al	Fe	Ti	K	Mg	Na	Ca
Lochiel (N2 pyrolysis)	50.29%	43.35%	41.23%	55.50%	30.92%	37.50%	38.94%	40.40%
Lochiel (N2/Steam pyrolysis)	65.49%	52.11%	42.94%	62.82%	33.34%	47.42%	46.51%	41.66%
Bowmans (N2 pyrolysis)	106.81 %	74.31%	65.73%	92.02%	76.25%	55.46%	35.76%	92.88%
Bowmans (N2/Steam pyrolysis)	94.67%	42.64%	41.64%	54.78%	28.27%	28.99%	17.23%	70.11%

Table 7-7 Total % of original ash components removed as fines from the ash can.

Coal type (pyrolysis mode)	Si	Al	Fe	Ti	K	Mg	Na	Ca
Lochiel (N2 pyrolysis)	10.36%	23.25%	23.64%	25.19%	11.17%	26.70%	10.14%	24.49%
Lochiel (N2/Steam pyrolysis)	8.22%	18.44%	18.75%	19.98%	8.86%	21.17%	8.04%	19.42%
Bowmans (N2 pyrolysis)	2.10%	2.56%	2.37%	4.05%	2.17%	2.45%	0.90%	1.98%
Bowmans (N2/Steam pyrolysis)	18.68%	22.82%	21.09%	36.06%	19.32%	21.80%	8.01%	17.64%

Therefore while large quantities of sodium are retained in the bed, the XRD analysis shows that the sodium is retained in its non-catalytic form, that is, as halite ($NaCl$) and to a lesser extent, nepheline ($NaAlSiO_4$). Therefore, it appears that under the fluidised-bed conditions of this study, sodium (present as halite) is not readily converted to its corresponding organically bound form, and hence fails to produce significant catalytic activity. In Chapter 6 by comparison, where gasification rates at 800°C were calculated at an order of magnitude greater than under fluidised-bed conditions, no halite was found in the resultant residue, and only minor (for Bowmans) and/or trace amounts of nepheline.

Another feature of the fluidised-bed work that may assist in explaining the lack of reactivity under the conditions of this work is the distribution of carbon among the products of pyrolysis. As already highlighted in the previous section, the contribution of carbon dioxide to carbon conversion during pyrolysis is higher than for the fixed-bed work, almost 100% higher for Lochiel and some 50% for Bowmans. **Figure 7-22** shows the percentage carbon conversion as CO_2 to total carbon conversion (X_{CO2}/X_C) during fast and fluidised bed pyrolysis.

When examining the X_{CO2}/X_C, the value for Lochiel is approximately 25% for fast pyrolysis (in nitrogen) and 47% and 48% for fluidised-bed pyrolysis in nitrogen and steam/nitrogen respectively. BW has an X_{CO}/X_{CO2} of 40% for fast pyrolysis (in nitrogen), increasing to 57% and 55% for fluidised-bed pyrolysis in nitrogen and steam/nitrogen respectively. This data should be considered in light of **Figure 7-4** and **Figure 7-10** presented earlier in this chapter, which show that, in addition to the increase in relative carbon conversion as CO_2, the absolute carbon conversion as CO_2 increases significantly in moving from the fast to fluidised-bed environment. This increase in the absolute quantity of CO_2 evolved when conducting pyrolysis, along with a potential increase in tar phase conversion of carbon (containing abundant oxygen groups) may be an additional factor responsible for the very slow reaction rate during the subsequent steam gasification in the fluidised-bed when compared to the fixed-bed. With fewer sites for the fixing of sodium as an organically bound inorganic, and potentially with 45-75% of sodium leaving the reaction zone during the gasification experiments (see **Table 7-6** and **Table 7-7**, this due to the absence of a fines recycle loop) the steam gasification rate of carbon is significantly lower. Therefore, while the contention has always been that more 'violent' pyrolysis conditions create a char that is more readily gasified in steam, owing to a more open pore-network, this result does not appear to apply to these coals under the conditions of this study.

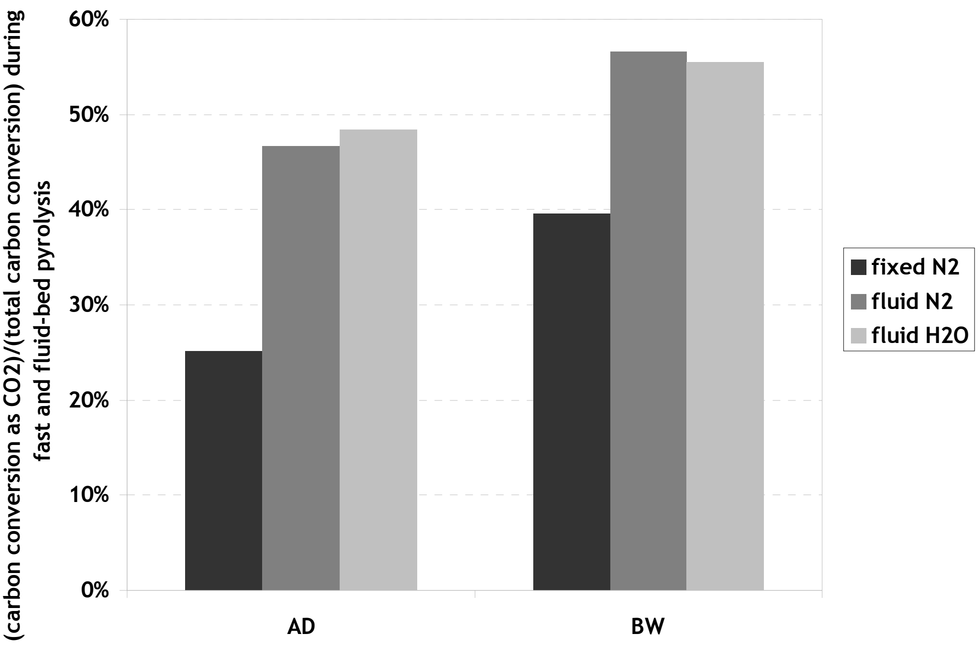


Figure 7-22 Comparison of the ratio of gas phase conversion of carbon as CO to the gas phase conversion of carbon as CO_2 during 800°C pyrolysis of air-dried Lochiel (AD) and Bowmans coal (BW) for fixed-bed, fast pyrolysis in nitrogen (fixed N_2) and fluidised-bed pyrolysis in nitrogen (fluid N_2) and 25%v/v steam/nitrogen mixture (fluid H_2O

While the concept of a more open pore structure being more readily 'attacked' by gasifying agent may be true for relatively unreactive coals of higher rank (and of which the literature contains an abundance of reactivity studies), this work may suggest that for low rank coals, whose structures are inherently more reactive given their already high oxygen content and developed pore network, higher heating rate pryolysis actually diminish the reaction rate in steam by readily releasing carboxyl groups that are necessary for the formation of organically bonded inorganics, which provide the catalytic effect required to gasify at a reasonable rate.

This proposition requires further study, which is outside of the scope of this thesis. The implications, however, are the same for sulphur gasification rate: as found in Chapter 6, the sulphur gasification rate is proportional to that of carbon for the air-dried samples. Therefore preserving the catalytic activity of the coal after pyrolysis is absolutely necessary to the reaction and release of sulphur species. An analysis of how this may be achieved is not presented here and sits outside the current scope of work for this thesis, although it will be essential for future study.

7.4 Summary & Conclusions

Pyrolysis and gasification tests were conducted in a 50mm internal diameter, atmospheric-pressure, fluidised-bed reactor in order to evaluate the work undertaken in the horizontal tube furnace regarding the behaviour of Lochiel and Bowmans coal.

During fluidised-bed pyrolysis of both Lochiel and Bowmans coal, a slightly greater total sulphur conversion to the gas phase is achieved than under fast pyrolysis conditions in a fixed-bed. The fluidised-bed enhances the relative concentration of COS and CH_3SH at the expense of H_2S, primarily as a result of a decrease in secondary cracking reactions of primary pyrolysis products. The carbon conversion, however, increases significantly in the fluisided-bed environment, more than doubling for both coals. The bulk of this increase comes in the form of increased conversion due to CO_2 and higher hydrocarbons. The presence of steam during the first 10 minutes of pyrolysis resulted in an increase in final carbon conversion due to gasification for both coals of approximately 5-10%.

The significant increase in carbon conversion during fluid-bed pyrolysis has the effect of increasing the final conversion of sulphur during subsequent steam gasification, with total sulphur conversion values of over 90% for both coals. While pyrolysis in either nitrogen or nitrogen/steam mix is not found to impact the observed sulphur conversion, XRD analysis of the residues removed from the reactor indicated that, for Lochiel coal, pyrolysis in nitrogen is found to increase the formation of oldhamite (CaS) (along with anhydrite in the minor phase). This is not observed for Bowmans gasification, where both anhydrite and oldhamite are found as the sub-dominant phase for both sets of pyrolysis conditions. This may indicate that sulphur in Bowmans coal is more closely associated with oxygen structures, a point supported by the presence of SO_2 in the gas phase for the Bowmans TPP experiments described in Chapter 4.

The rate of steam gasification, however, following pyrolysis under both regimes, is more than an order of magnitude slower when compared to the rates of reaction observed in the fixed bed gasification experiments of Chapter 6 (at the same temperature (800°C) and steam conditions (25% v/v). The achieved rate of steam gasification in the fluid-bed more closely reflects that of the acid-washed Lochiel sample in the fixed-bed at 800°C. Large amounts of sodium (as halite and nepheline) remained in the bed material following gasification in the fluid-bed, and significant quantities were elutriated (due to no fines recycle loop) suggesting that one reason for the lack of reactivity could be a lack of organically bound inorganic sodium.

In addition, analysis of the conversion of carbon as CO_2 during pyrolysis suggests that the fluidised bed environment, instead of creating a char that is more reactive to steam, may in fact diminish the catalytic gasification rate of these coals (and the temperature and steam conditions) due to large losses of the carboxyl functional group during pyrolysis in the fluid-bed. While high heating rates are believed to create open pore structures that may or may not increase a coals reactivity to steam, the loss of COO^- groups that results (as CO_2), instead of increasing the rate of reaction towards steam, may actually diminish it by providing fewer active sites for the exchange of inorganic sodium (or other) catalyst. This has significant implications for large scale gasification process with low rank coals where conventional wisdom suggests that increasing the heating rate during pyrolysis improves the coal's subsequent gasification reactivity.

8 CONCLUSIONS & RECOMMENDATIONS

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. 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. The outcomes of this work can be broadly grouped in the following key categories:

- Pyrolysis products
- Steam gasification behaviour
- Mineral matter considerations

This chapter provides a brief summary of each of these areas, discussing the implications of the results, and provides recommendations for further work to advance the current state of knowledge in this field, ultimately working towards the sustainable utilisation of these deposits.

8.1 Pyrolysis products

Temperature Programmed Pyrolysis (TPP) experiments (heating samples from ambient to 1200°C at 15 K.min^{-1}) using Lochiel and Bowmans coal were employed with continuous gas phase measurement of product gases (Chapter 4). Over 85% of the gas phase sulphur species were detected as hydrogen sulphide (H_2S) with methyl mercaptan (CH_3SH) and carbonyl sulphide (COS) comprising the balance. For the acid-washed Lochiel and air-dried Bowmans samples, sulphur dioxide (SO_2) 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 (Chapter 6). Final sulphur conversion did not increase with increasing final temperature with a complex re-attachment mechanism whereby evolved sulphur re-reacts 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 H_2S and no SO_2 in the product gas, the effect on carbon conversion and distribution of carbon between carbon monoxide (CO) and carbon dioxide (CO_2) was significant. The absence of SO_2 in the product gas for any of the fast heating rate experiments confirmed literature studies that suggest SO_2 is a product of secondary reactions of primary sulphur containing products.

In fluidised-bed pyrolysis experiments undertaken at 800°C (Chapter 7), the total sulphur and carbon conversion increased markedly relative to the fixed-bed heating rate processes, with a greater distribution of sulphur among CH_3SH and COS (at the expense of H_2S) and carbon among CO_2 and methane. When pyrolysis was undertaken in the presence of steam, while it was not possible to measure the sulphur containing gases in the product gas due to experimental limitations, the absolute conversion of carbon to the gas phase increased for both coals, particularly Bowmans, driven mainly by an increase in the relative conversion of CO_2. While the fluidised-bed environment resulted in a significant increase in carbon conversion during pyrolysis, it was found to have severe implications for the subsequent char reactivity during steam gasification.

The solid phase pyrolysis study by Telfer (1999) into the behaviour of Lochiel and Bowmans coal resulted in a view of these two coals that they were relatively similar. A key outcome of the pyrolysis work contained in this thesis is that, in examining the gas phase, the behaviour of sulphur contained in the two coals is quite different, suggesting that the two have very different structures and that the broad based assumption of the two coals having similar structure and pyrolysis/combustion/gasification behaviour is no longer appropriate.

8.2 Steam gasification

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, as mentioned in section 8.1. While the pyrolysis in the fluidised-bed was comparatively violent compared to the fixed-bed pyrolysis used to develop char for the experiments described in 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. This resulted in a rate of gasification under fluidised bed conditions, for the Lochiel coal, that better approximates that of the acid-washed samples in the fixed bed at equivalent steam and temperature conditions.

The relationship between sulphur and carbon conversion was investigated, and it was found that the assumption of equal conversion rates (in the litereature) was not valid under the conditions of the study. The sulphur conversion for Lochiel char at 800-850°C and Bowmans char for 750–850°C was found to be only 60% that of carbon for conversion up to 80%. For acid-washed coals, this rate was 50%, and only then from 20-80% carbon conversion. That sulphur and carbon do not convert at the same rate, suggesting that sulphur species become less reactive than carbon as the reaction proceeds, implies that some sort of re-attachment and re-ordering mechanism is occurring in the coal structure. The ultimate step in this mechanism is the formation of oldamite (CaS) and anhydrite ($CaSO_4$), both of which were detected in the ash residue removed following gasification and complete conversion of carbon.

The fluidised-bed system developed for this work, while having a dramatic effect on the carbon conversion during pyrolysis, seriously inhibited the char's subsequent reactivity. The implication of this work for industrial processes is significant: the creation of char must be carried out at relatively mild conditions (of final temperature and heating rate) for the South Australian coals employed in this study, in order to achieve a sufficient reactivity of that char during subsequent gasification.

8.3 Mineral matter considerations

For the low heating rate pyrolysis conditions of Chapter 4, calcium was found to play an important role in the retention of sulphur species as sulphides (CaS) for Lochiel, while for Bowmans, sodium played an important role in retaining sulphur as sulphates (Na_2SO_4). For char created in a fixed-bed under fast pyrolysis conditions of 800°C, there was increased anhydrite and oldhamite for Lochiel when compared with Bowmans coal, consistent with the fact that Lochiel coal contains three times the calcium.

The presence of halite in the Bowmans char, as a minor species, as opposed to a trace species for Lochiel, was believed to be impact the relative gasification rates for these chars, given that sodium is a known catalyst for steam gasification when bonded to carboxyl groups.

For Lochiel char, residue from the fixed-bed steam gasification experiments in Chapter 6 indicates that while the parent char contains sulphur species (minor phase, 5-20% wt) as anhydrite ($CaSO_4$) and oldhamite (CaS). For Bowmans, sulphur was found as thenardite (Na_2SO_4) and niningerite (MgS) while sodium was found as halite, the co-dominant phase in the char.

Under the fluidised-bed conditions of Chapter 7, oldhamite (CaS) formation increased during pyrolysis in nitrogen only, while anhydrite ($CaSO_4$) formation was greater during pyrolysis in steam and nitrogen for Lochiel. For Bowmans, the major difference between the two pyrolysis modes in the fluid-bed was the fate of halite (NaCl): for pyrolysis in steam and nitrogen, halite is found in only trace quantities, while when pyrolysis is carried out in nitrogen, it is present in the sub-dominant phase.

In Chapter 6, where gasification rates at 800°C were calculated at an order of magnitude greater than those achieved under fluidised-bed conditions, no halite was found in the resultant residue, and only minor (for Bowmans) and/or trace amounts of nepheline. This suggests that under the fluidised-bed conditions of this study, sodium (present as halite) is not readily converted to its corresponding organically bound form.

8.4 Implications and recommendations

This study has addressed the key issues with the evolution of sulphur over a range of pyrolysis and gasification systems, in order to provide insight into its potential behaviour during the utilisation of South Australia's low rank coals. As such, there are a number of divergent paths, on which successful commercialisation of these resources can move forward.

Regarding the coal structure, there would be a significant contribution to the understanding of how these coals behave during pyrolysis and gasification with an in depth study as to the nature of the coal sulphur structure, using an experimental programme of advanced TPP, TPR or TPO utilising GCMS to analyse tars and higher hydrocarbons. Given that the quantification and speciation of the tar component was only estimated in this work, this would prove very valuable from the perspective of one attempting to develop further a gasification model for their gasification.

One key aspect of this study was the dependence of the fate of sulphur, and the gasification rate of carbon (and consequently, sulphur) on the pyrolysis regime. Except for the TPP experiments, no direct quantification of the intra-particle heating rate has been attempted, and an experimental regime that examines all the phases post pyrolysis at well defined heating rates would assist greatly in extending the outcome of this thesis. It was clearly shown that, although the fixed-bed, fast pyrolysis creation of char was assumed to be representative of that found in a fluidised bed, and that this assumption is the basis for a large body of literature studying coal reactivity, this assumption does not hold for the steam gasification work of this thesis carried out in the fluid-bed.

The commercial implications of this assumption not being valid are significant: high heating rate pyrolysis may actually impinge on the reactivity of low rank coals and on that basis, more mild conditions (perhaps ex situ) for pyrolysis should be considered if high gasification rates and conversion are to be achieved in practice. Regarding the solid phase, novel in-bed sampling techniques are required for accurately determining the transformations taking place and the interaction of sulphur with the ash phase.

The extension of this work to incorporate other coals, particularly those located in South Australia, and ultimately, to trial these coals in pilot scale fluidised-bed apparatus, should be the aim of the immediate work resulting from this thesis, and an attempt should be made at that point to incorporate such a broad array of data on sulphur transformations into a suitable model of the gasification process.

9 REFERENCES

ABARE – Australian Bureau of Agricultural and Resource Economics, “Australian Mineral Statistics 2009, December quarter”, (2009)

ABBASIAN, J., R. REHMAT, et al., "Sulfation of Partially Sulfided Calcium-Based Sorbents", Ind. Eng. Chem. Res., 30, 1990-1994, (1991).

ACIL Tasman, “Fuel resource, new entry and generation costs in the NEM – Draft Report”, (2009)

AGARWAL, P. K., W. E. GENETTI, et al., "Devolatilisation of large coal particles in fluidized beds", Fuel, 63, 1748, (1984a).

AGARWAL, P. K., W. E. GENETTI, et al., "Model for devolatilization of coal particles in fluidized beds", Fuel, 63, 1157, (1984b).

ALLARDICE, D. J. and B. S. NEWELL, "Industrial Implications of the Properties of Brown Coals", The Science of Victorian Brown Coal, R. A. Durie; Butterworth-Heinemann Ltd, (1991).

ALVAREZ, T., A. B. FUERTES, et al., "Influence of coal oxidation upon char gasification reactivity", Fuel, 74, 729-735, (1995).

ATTAR, A., "Chemistry, thermodynamics and kinetics of reactions of sulphur in coal gas reactions: a review", Fuel, 57, 201-212, (1978).

ATTAR, A., "Sulfur groups in coal and their determinations", Analytical Methods for Coal and Coal Products, C. Karr; Academic Press, (1979).

ATTAR, A. and G. G. HENDRICKSON; "Functional groups and heteroatoms in coal", Coal Structure, Academic Press Inc, New York, (1982)

AZHAKESAN, M., K. D. BARTLE, et al., "Rapid pyrolysis as a method of characterizing coals for combustion", Fuel, 70, 322, (1990).

BASSILAKIS, R., Y. ZHAO, et al., "Sulfur and Nitrogen Evolution in the Argonne Coals: Experiment and Modeling", Energy & Fuels, 7, 710-720, (1993).

BERKOWITZ, N.; "An Introduction to Coal Technology",, Academic Press, New York, (1979)

BHATTACHARYA, S. P., "Gasification Fundamentals", A Continuing Education Course on The Science and Technology of Lignite Utilisation, Presented by the CRC for Clean Power From Lignite, Monash University, Melbourne, (2003).

BHATTACHARYA, S. P., I. BEAUPERT, et al., "Gasifier PDU: Activities in 2002-2003", CRC for Clean Power from Lignite Tenth Annual Conference, Swinburne University of Technology, (2003).

BHATTACHARYA, S. P., I. BEAUPEURT, et al., "Test Program Using the Gasifier PDU: Preliminary Results and their Implications", CRC for Clean Power from Lignite 9th Annual Conference, Monash Univerisity, (2002).

BLACKWOOD, J.D., CULLIS, B.D., and McCARTHY, D.J., “Reactivity in the system carbon-hydrogen-methane”, Australian Journal of Chemistry, 20(1967).

BLOCK, S. S., J. B. SHARP, et al., "Effectiveness of gases in desulphurization of coal", Fuel, 54, 113-119, (1975).

BRAUER, M. C. and Q. D. NGUYEN, "Measurement of the Rheological Properties of Coal Ash under Gasification Conditions", CRC for Clean Power from Lignite Tenth Annual Conference, Swinburne University of Technology, Melbourne, (2003).

BRIEDIS, A. J. and P. J. ASHMAN, "Gasification of Low-Rank Coal Under Fluidised Bed Conditions", CRC for Clean Power from Lignite 10th Annual Conference, Swinburne University of Technology, (2003).

BROOKER, D. and M. OH, "Iron sulfide deposition during coal gasification", Fuel Processing Technology, 44, 181-190, (1995).

CAI, H. Y., A. J. GUELL, et al., "Heteroatom distribution in pyrolysis products as a function of heating rate and pressure", Fuel, 72, 321, (1993).

CALKINS, W. H., "Investigation of organic sulfur-containing structures in coal by flash pyrolysis experiments", Energy & Fuels, 1, 59-64, (1987).

CALKINS, W. H., "The chemical forms of sulfur in coal: a review", Fuel, 73, 475-484, (1994).

CELIK, M. S. and I. YILDIRIM, "A new physical process for desulfurization of low-rank coals", Fuel, 79, 1665-1669, (2000).

CHAFFEE, A. L., "Water, Water Everywhere: a Drop to Drink? (An Overview of MTE Supporting Research)", CRC for Clean Power from Lignite Tenth Annual Conference, Swinburne University of Technology, (2003).

CHEN, H., B. LI, et al., "Effects of mineral matter on products and sulfur distributions in hydropyrolysis", Fuel, 78, 713-719, (1999).

CHEN, H., B. LI, et al., "Decomposition of pyrite and the interaction of pyrite with coal organic matrix in pyrolysis and hydropyrolysis", Fuel, 79, 1627-1631, (2000).

CLAYTON, S., A. HOADLEY, et al., "Development of a Laboratory Scale Continuous MTE Process", CRC for Clean Power from Lignite Tenth Annual Conference, Swinburne University of Technology, (2003).

CRC - Cooperative Research Centre for Clean Power from Lignite, "Victorian Government Challenge for Energy", submission, February (2005)

CZAPLICKI, A. and W. SMOLKA, "Sulfur distribution within coal pyrolysis products", Fuel Processing Technology, 55, 1-11, (1998).

DEVANATHAN, N. and S. C. SAXENA, "A model for the devolatilization of large coal particles", Chemical Engineering Science, 41, 2442-2446, (1986).

ESIPC - Electricity Supply Industry Planning Council, "Annual Planning Report", June (2007).

FANG, Y., J. HUANG, et al., "Experiment and mathematical modeling of a bench-scale circulating fluidized-bed gasifier", Fuel Processing Technology, 69, 29-44, (2001).

FUNG, D.P.C., “Laboratory gasification of five Canadian coals”, Fuel 62, 139-144, (1982).

FUNG, D.P.C. and KIM, S.D., “Laboratory gasification study of Canadian coals 2. Chemical reactivity and coal rank”, Fuel 62, 1337-1340, (1983).

FURIMSKY, E., A. D. PALMER, et al., "Distribution of volatile sulphur containing products during fixed bed pyrolysis and gasification of coals", The Canadian Journal of Chemical Engineering, 69, 869-875, (1991).

GARCIA-CALZADA, M., G. MARBAN, et al., "Decomposition of CaS particles at ambient conditions", Chemical Engineering Science, 55, 1661-1674, (2000).

GARCIA-LABIANO, F., J. ADANEZ, et al., "Sulfur release during the devolatilization of large coal particles", Fuel, 75, 585-590, (1996).

GARCIA-LABIANO, F., E. HAMPARTSOUMIAN, et al., "Determination of sulfur release and its kinetics in rapid pyrolysis of coal", Fuel, 74, 1072-1079, (1995).

GEORGE, A. M. and G. H. MACKAY, "Petrology", The Science of Victorian Brown Coal, R. A. Durie; Butterworth-Heinemann Ltd, (1991).

GEORGE, G. N., M. L. GORBATY, et al., "Direct determination and quantification of sulphur forms in coals from the Argonne Premium sample program", Energy & Fuels, 5, 93-97, (1991).

GLOE, C. S. and G. R. HOLDGATE, "Geology and Resources", The Science of Victorian Brown Coal, R. A. Durie; Butterworth-Heinemann Ltd, (1991).

GLUSKOTER, H. J., N. F. SHIMP, et al., "Chapter 7", Chemistry of Coal Utilization, H. H. Lowry and M. A. Elliot; Wiley, (1981).

GOYAL, A., ZABRANSKY, R.F., and REHMAT, A., “Gasification Kinetics of Western Kentucky Bituminous Coal Char”, Ind. Eng. Chem. Res., 28, 1767-1778, (1989).

GRYGLEWICZ, G., "Effectiveness of high temperature pyrolysis in sulfur removal from coal", Fuel Processing Technology, 46, 217-226, (1996).

GRYGLEWICZ, G. and S. JASIENKO, "Sulfur groups in the cokes obtained from coals of different ranks", Fuel Processing Technology, 19, 51-59, (1988).

GRYGLEWICZ, G. and S. JASIENKO, "The behaviour of sulphur forms during pyrolysis of low-rank coal", Fuel, 71, 1225-1229, (1992).

HANSON, S., J. W. PATRICK, et al., "The effect of coal particle size on pyrolysis and steam gasification", Fuel, 81, 531-537, (2002).

HEIDENREICH, C., "Mathematical modelling of large coal particle devolatilisation", PhD Thesis, The University of Adelaide Department of Chemical Engineering, (1999).

HOPPESTEYN, P. D. J., W. DE JONG, et al., "Coal Gasification and Combustion of LCV Gas", Bioresource Technology, 65, 105-115, (1998).

HUFFMAN, G. P., S. MITRA, et al., "Quantitative analysis of all major forms of sulphur in coal by x-ray absorption fine structure spectroscopy", Energy & Fuels, 5, 574-581, (1991).

HUYNH, D., S. HUYNH, et al., "Development Program of MTE Lignite Dewatering Process", CRC for Clean Power from Lignite Tenth Annual Conference, Swinburne University of Technology, (2003).

HUYNH, S., M. MCINTOSH, et al., "Process Design Considerations for MTE Plant", CRC for Clean Power from Lignite Tenth Annual Conference, Swinburne University of Technology, (2003).

IBARRA, J. V., A. J. BONET, et al., "Release of volatile sulfur compounds during low temperature pyrolysis of coal", Fuel, 73, 933, (1994a).

IBARRA, J. V., J. M. PALACIOS, et al., "Influence of Weathering on the sulphur removal from coal by pyrolysis", Fuel Processing Technology, 21, 63-73, (1989).

IBARRA, J. V., J. M. PALACIOS, et al., "Evidence of reciprocal organic matter-pyrite interactions affecting sulphur removal during coal pyrolysis", Fuel, 73, 1046-1051, (1994b).

JUNG, K. and B. R. STANMORE, "Fluidized bed combustion of wet brown coal", Fuel, 59, 74, (1980).

KARACA, S., "Desulfurization of a Turkish lignite at various gas atmospheres by pyrolysis. Effect of mineral matter", Fuel, 82, 1509-1516, (2003).

KELEMEN, S. R., G. N. GEORGE, et al., "Direct determination and quantification of sulphur forms in heavy petroleum and coals
1 The X-ray photoelectron spectroscopy (XPS) approach", Fuel, 69, 939-944, (1990).

KELEMEN, S. R., M. L. GORBATY, et al., "Thermal reactivity of sulphur forms in coal", Fuel, 70, 396-402, (1991).

KELEMEN, S. R., S. N. VAUGHN, et al., "Transformation kinetics of organic sulphur forms in Argonne Premium coals during pyrolysis", Fuel, 72, 645-653, (1993).

KHAN, M. R., "Prediction of sulphur distribution in products during low temperature coal pyrolysis and gasification", Fuel, 68, 1439-1449, (1989).

KOLODNEY, M., J. YERUSHALMI, et al., "The behaviour of mineral matter in a fluidized bed gasifying coal - The Ignifluid process", Trans. and Journal of the Br. Ceramic Society, 75, 85-91, (1976).

KOSMINSKI, A., "Reactions between Sodium and Silicon Minerals during Gasification of Low-rank Coal", PhD Thesis, The University of Adelaide Department of Chemical Engineering, (2001).

KNIGHT, A.T. and SERGEANT, G.D., “Reactivity of Australian coal-derived chars to carbon dioxide”, Fuel 61, 145-149, (1982).

KUCUKBAYRAK, S. and E. KADIOGLU, "Desulphurisation of some Turkish lignites by pyrolysis", Fuel, 67, 867, (1988).

KWON, T.W., KIM, S.D. and FUNG, P.C., “Reaction Kinetics of char-CO_2 gasification”, Fuel, 67, 530, (1988).

KWON, T.W., KIM, J.R., et al., “Catalytic steam gasification of lignite char”, Fuel, 68, 416, (1989).

LACOUNT, R. B., R. R. ANDERSON, et al., "Sulphur in coal by programmed-temperature oxidation", Fuel, 66, 909, (1987).

LACOUNT, R. B., D. G. KERN, et al., "Advances in coal characterization by programmed-temperature oxidation", Fuel, 72, 1203-1208, (1993).

LAFFERTY, C. J., S. C. MITCHELL, et al., "Investigation of organic sulphur forms in coals by high pressure temperature-programmed reduction", Fuel, 72, 367, (1993).

LILIEDAHL, T., K. SJOSTROM, et al., "A thermodynamic study of dolomite as hydrogen sulphide adsorbent when prolysing or partially gasifying coal", Fuel, 71, 797, (1992).

LOLJA, S. A., "Desulfurization of coal by air + steam at 400°C in a fixed bed", Fuel, 74, 1834-1838, (1995).

MA, R. P., R. M. FELDER, et al., "Evolution of hydrogen sulfide in a fluidized bed coal gasification reactor", Industrial and Engineering Chemistry Research, 28, 27-33, (1989).

MAA, P. S., C. R. LEWIS, et al., "Sulphur transformation and removal for Western Kentucky coals", Fuel, 54, 62-69, (1975).

MANN, M.D., KNUTSON, R.Z., et al., “Modeling reaction kinetics of steam gasification for a transport gasifier”, Fuel, 83, 1643-1650, (2004)

MANZOORI, A. R., "Role of the Inorganic Matter in Agglomeration and Defluidisation during the Circulating Fluid Bed Combustion of Low-rank coals", PhD Thesis, The University of Adelaide Department of Chemical Engineering, (1990).

MARINOV, V., S. P. MARINOV, et al., "Ash agglomeration during fluidized bed gasification of high sulphur content lignites", Fuel Processing Technology, 31, 181-191, (1992).

MASON, D. M., "The behaviour of iron-sulfur species in fluidized-bed gasification of coal", Fuel Processing Technology, 30, 215-226, (1992).

MASSEY, M. J., D. V. NAKLES, et al., "Effluents from Synthane Gasification of Lignite", MCCULLOUGH, D. "Agglomeration and Defluisdisation Behavioru of High-Sodium, High-Sulphur South Australian Lignite under Fluidised Bed Gasification Conditions", PhD Thesis, The University of Adelaide Department of Chemical Engineering, (2007).

MCCULLOUGH, D., P. J. MULLINGER, et al., "Impact of Temperature and Air/fuel Ratio on Agglomeration Behaviour of Lochiel Coal under Gasification Conditions", CRC for Clean Power From Lignite 10th Annual Conference, Swinburne University of Technology, Melbourne, (2003).

MCKENZIE, L. and C.-Z. LI, "Formation of NOx and NOx Precursors during the Gasification of Victorian Lignite", CRC for Clean Power From Lignite 10th Annual Conference, Swinburne University of Technology, Melbourne, (2003).

MCMURRAY, J.; "Organic Chemistry",, Books/Cole Publishing Company, Pacific Grove CA, (1996)

MEDVEDEV, K.P. and PETROPOLSKAYA, V.M., “Volatility of Different Forms of Sulphate Sulphur in the Carbonisation of Coals”, UKhIN, 10-13, (1966)

MIDDLETON, S. P., J. W. PATRICK, et al., "The release of coal nitrogen and sulfur on pyrolysis and partial gasification in a fluidized bed", Fuel, 76, 1195-1200, (1997).

MITCHELL, S. C., C. E. SNAPE, et al., "Determination of organic sulphur forms in some coals and kerogens by high pressure temperature-programmed-reduction", Fuel Processing Technology, 37, 53-65, (1994).

MIURA, K., K. MAE, et al., "Analysis of Formation Rates of Sulfur-Containing Gases during the Pyrolysis of Various Coals", Energy & Fuels, 15, 629-636, (2001).

MOLINA, A. and F. MONDRAGON, "Reactivity of coal gasification with steam and CO2", Fuel, 77, 1831-1839, (1998).

MONDRAGON, F., A. JARAMILLO, et al., "The effects of morphological changes and mineral matter on H2S evolution during coal pyrolysis", Fuel, 78, 1841-1846, (1999).

MONDRAGON, F., W. RUIZ, et al., "Effect of early stages of coal oxidation on its reaction with elemental sulphur", Fuel, 81, 381-388, (2002).

MORRIS, J. P. and D. L. KEAIRNS, "Coal devolatilization studies in support of the Westinghouse fluidized-bed coal gasification process", Fuel, 58, 465-471, (1979).

MULCAHY, M. F. R., W. J. MORLEY, et al., "Combustion, Gasification and Oxidation", The Science of Victorian Brown Coal, R. A. Durie; Butterworth-Heinemann Ltd, (1991).

OCAMPO, A., E. ARENAS, et al., "An experimental study on gasification of Colombian coal in fluidised bed", Fuel, 82, 161-164, (2003).

OLIVELLA, M. A., J. M. PALACIOS, et al., "A study of sulfur functionalities in fossil fuels using destructive-(ASTM and Py-GC-MS) and non-destructive-(SEM-EDX, XANES and XPS) techniques", Fuel, 81, 405-411, (2002).

PATRICK, J. W., "Sulphur release from pyrites in relation to coal pyrolysis", Fuel, 72, 281, (1993).

PEELER, J. P. K. and H. J. POYNTON, "Devolatilization of large coal particles under fluidized bed conditions", Fuel, 71, 425, (1992).

PIRSA – Primary Industry and Resources South Australia; "South Australian Coal Resources",www.pir.sa.gov.au (http://outernode.pir.sa.gov.au/__data/assets/image/0017/11285/coal_state.gif accessed 2 April 2009), (2009)

QUYN, D.M., “Transformations of Alkali and Alkaline Earth Metallic Species during Gasification of Victorian Brown Coal”, PhD Thesis, Monash University Department of Chemical Engineering, (2002).

RAYMOND, R. J. and R. GOOLEY, "A Review of Organic Sulphur Analysis in Coal and a New Procedure", Scanning Electron Microscopy, 1, 93, (1978).

ROBINSON, L., "Coal minerals affect sulfur in processing", Hydrocarbon Processing, 57, 213, (1978).

ROSS, D. P., "Devolatilisation and volatile matter combustion during fluidised-bed gasification of low-rank coal", PhD Thesis, The University of Adelaide Department of Chemical Engineering, (2000).

S.A.D.M.E., "South Australian Department of Mines and Energy", Coal Deposits in South Australia, Information Sheet 9, (1991)

SCIAZKO, M. and K. KUBICA, "The effect of dolomite addition on sulphur, chlorine and hydrocarbons distribution in a fluid-bed mild gasification of coal", Fuel Processing Technology, 77-78, 95-102, (2002).

SHARMA, A., H. KADOOKA, et al., "Effect of microstructural changes on gasification reactivity of coal chars during low temperature gasification", Energy & Fuels, 16, 54-61, (2002).

SINHA, R. K. and P. L. J. WALKER, "Desulphurization of coals and chars by treatment in various atmospheres between 400 and 600°C", Fuel, 51, 329-331, (1972).

SMOOT, L. D. and P. J. SMITH; "Coal Combustion and Gasification", The Plenum chemical engineering series, Plenum Press, New York, (1985)

SNOW, R. D., "Conversion of Coal Sulfur to Volatile Sulfur Compounds during Carbonization in Streams of Gases", Ind. Eng. Chem., 24, 903-909, (1932).

SOLOMON, P. R., M. A. SERIO, et al., "Coal Pyrolysis: Experiments, Kinetic Rates and Mechanisms", Prog. Energy Combust. Sci., 18, 133-230, (1992).

SONG, B. H. and S. D. KIM, "Catalytic activity of alkali and iron salt mixtures for steam-char gasification", Fuel, 72, 797-803, (1993).

STUBINGTON, J. F. and SUMARYONO, "Release of volatiles from large coal particles in a hot fluidized bed", Fuel, 63, 1013, (1984).

SUE-A-QUAN, T. A., G. CHENG, et al., "Coal gasification in a pressurized spouted bed", Fuel, 74, 159-164, (1995).

SUGAWARA, K., K. ABE, et al., "Dynamic behaviour of sulfur forms in rapid pyrolysis of coals with alkali treatment", Fuel, 74, 1823-1829, (1995).

SUGAWARA, K., Y. ENDA, et al., "Effect of Hydrogen Sulfide on Organic Sulfur Behaviour in Coal and Char during Heat Treatments", Energy & Fuels, 17, 204-209, (2003).

SUGAWARA, K., T. GUN-JI, et al., "Effects of Particle Density and Sulfur Forms on Pyrolysis Desulfurisation in Rapid Heating of Coals", Energy & Fuels, 11, 1272-1277, (1997).

SUGAWARA, K., Y. TOZUKA, et al., "Dynamic behaviour of sulfur forms in rapid pyrolysis of density-separated coals", Fuel, 73, 1224-1228, (1994a).

SUGAWARA, K., Y. TOZUKA, et al., "Effect of heating rate and temperature on pyrolysis desulfurization of a bituminous coal", Fuel Processing Technology, 37, 73-85, (1994b).

SUGAWARA, T., K. SUGAWARA, et al., "Dynamic behaviour of sulphur forms in rapid hydropyrolysis of coal", Fuel, 70, 1091, (1991).

SUGAWARA, T., K. SUGAWARA, et al., "Dynamic behaviour of sulphur forms in hydropyrolysis of coals", Fuel, 67, 1263-1268, (1988).

SUGAWARA, T., K. SUGAWARA, et al., "Kinetics of change in sulphur forms in hydropyrolysis of coals", Fuel, (1989).

SUGAWARA, T., K. SUGAWARA, et al., "Characteristics of rapid hydropyrolysis of coals in a free fall pyrolyser", Fuel, 69, 1177-1185, (1990).

TAKARADA, T., TAMAI, Y., and TOMITA, A., “Reactivities of 34 coals under steam gasification”, Fuel, 64, 1438-1442, (1985).

TELFER, M., "Sulphur transformations during pyrolysis of low-rank coals and characterisation of Ca-based sorbents", PhD Thesis, The University of Adelaide Department of Chemical Engineering, (1999).

TING, F. T. C., "Coal Macerals", Coal Structure; Academic Press, (1982).

TONMUKAYAKUL, N. and Q. D. NGUYEN, "Rheological Study of Alkali Sulphate Mixtures (Ca-Mg-Na)-SO4 at High Temperatures", CRC for Clean Power From Lignite 9th Annual Conference, Monash University, Melbourne, (2002).

TRIMMNER, J. M. and N. VAN DER BURGH, "Use of scanning electron microscopy and energy-dispersive X-ray microanalysis", Fuel, 63, 1645, (1984).

TSAI, S. C., "Chemical Desulfurization of West Kentucky Coal Using Air and Steam", Ind. Eng. Chem. Process Des. Dev., 25, 126-132, (1986).

TSENG, B. H., M. BUCKENTIN, et al., "Organic Sulphur in Coal Macerals", Fuel, 65, 385-390, (1986).

WALL, T. F., A. LOWE, et al., "Mineral mater in coal and the thermal performance of large boilers", Prog. Energy Combust. Sci., 5, 1-29, (1979).

WATKINSON, A. P., J. P. LUCAS, et al., "A prediction of performance of commercial coal gasifiers", Fuel, 70, 519, (1991).

WILLIAMS, A., M. POURKASHANIAN, et al.; "Combustion and Gasification of Coal",, Taylor & Francis, New York, (2000)

WILLIAMS, R., "So what's different about South Australia?", Industry Induction Course for CRC for Clean Power from Lignite, Morwell, Victoria, (2001).

WOSKOBENKO, F., STACY, W.O., and RAISBECK, D. Physical Structure and Properties of Brown Coal. The Science of Victorian Brown Coal: Structure, Properties and Consequences of Utilisation. RA Durie. Oxford, Butterworth-Heinemann, 151-246 (1991).

XU, W.-C. and M. KUMAGAI, "Nitrogen evolution during rapid hydropyrolysis of coal", Fuel, 81, 2325-2334, (2002).

XU, W.-C. and M. KUMAGAI, "Sulfur transformation during rapid hydropyrolysis of coal under high pressure by using a continuous free fall pyrolyser", Fuel, 82, 245-254, (2003).

YAN, H. M., C. HEIDENREICH, et al., "Modelling of bubbling fluidised bed coal gasifiers", Fuel, 78, 1027-1047, (1999).

YE, D.P. "Gasification of South Australian Lignite", PhD Thesis, The University of Adelaide Department of Chemical Engineering, (1994).

YERBURY, A.J. and ASHMAN, P.J., "Gasification Reactivity of Australian Low-Rank coal under Fluidised-bed Conditions. 11th Annual Conference, CRC for Clean Power from Lignite, Monash University, (2004)

YERGEY, A. L., F. W. LAMPE, et al., "Nonisothermal kinetics studies of the hydrodesulfurization of coal", Ind. Eng. Chem., Process Des. Develop., 13, 233-240, (1974).

YERUSHALMI, J., M. KOLODNEY, et al., "Agglomeration of ash in fluidized beds gasifying coal: The Godel phenomenon", Science, 187, 646-648, (1975).

YRJAS, K. P., M. HUPA, et al., "Pressurized stabilization of desulfurization residues from gasification processes", Energy & Fuels, 10, 1189-1195, (1996a).

YRJAS, K. P., C. A. P. ZEVENHOVEN, et al., "Hydrogen Sulfide Capture by Limestone and Dolomite at Elevated Pressure. 1. Sorbent Performance", Industrial and Engineering Chemistry Research, 35, 176-183, (1996b).

ZIELKE, C.W., CURRAN, G.P., et al., "Desulphurization of Low Temperature Char by Partial Gasification", Industrial and Engineering Chemistry, 46, 53-56, (1954)

ZHIGUANG, S., B. D. BATTS, et al., "Hydrous pyrolysis reactions of sulphur in three Australian brown coals", Organic Geochemistry, 29, 1469-1485, (1998).

APPENDIX A – UNCERTAINTY ANALYSIS

The following Appendix deals with the analysis of uncertainty associated with the data presented in this thesis. The discussion focuses on two key areas of uncertainty: that associated with the repeatability of the experiments, and that uncertainty associated with the individual results themselves. Therefore the errors associated with this calculation of evolving rate are dependent on the errors associated with:

- Determination of gas species concentrations
- Calculation methodology
- Initial errors associated with coal analysis

A1 Gas analysis

Table AI shows the gas species used to calibrate the micro-GC, including the manufacturer's stated uncertainty range for each species. For each gas species this is between 1% and 2%. The table also indicates the standard deviation obtained during a typical calibration whereby at least 5 samples of the gas species were sampled by the micro-GC, with the mean response area used to calculate the calibration parameters. In each case, the standard deviation from the mean is shown. The uncertainty is then calculated as three times the standard deviation from the mean (Himmelblau, 1978), and in each case, this is between 1.5% and 3%.

Table AI Quoted manufacturer uncertainties for gas species used in the analysis of concentration for this work

Species	concentration (% v/v)	Manufacturer uncertainty (+/-% v/v)	Response area standard deviation % abs
CH4	3.4	0.04	0.5
CO2	10.3	0.2	0.8
	23.9	0.2	1.0
C2H4	0.93	0.02	1.0
C2H6	1.14	0.02	1
H2	19.2	0.2	0.8
H2S	1	0.02	1
O2	21	(NA, air)	1
COS	1.5	0.03	0.8
N2	41.68	Balance	0.6
	100	Balance	0.5
	89.7	Balance	0.7
	79	Balance	0.9
	85	Balance	0.7
C3H6	0.99	0.02	1.05
C3H8	0.99	0.02	1
SO2	0.0481	0.001	0.9
CH3SH	0.0477	0.001	1
C2H5SH	0.0469	0.001	1
CS2	0.0494	0.001	1.1

Since the estimated concentration is a product of the response area (%v/v per unit area) and the calibration gas, the uncertainty associated with the concentration data obtained by the micro-GC is, in the worst case scenario, calculated as the square root of the product of these uncertainties squared according to the quadrature method (Himmelblau, 1968):

$$z = z(x,y) \qquad \text{Eq A-1}$$

$$\sigma_x = \sqrt{\left(\frac{\delta_z}{\delta_x}\sigma_x\right)^2 + \left(\frac{\delta_x}{\delta_y}\sigma_y\right)^2} \qquad \text{Eq A-2}$$

Where z is an arbitrary function with variables x and y. $\sigma_x, \sigma_y, \sigma_z$ are the errors associated with x, y, and z.

For the gas phase data from the micro GC, the uncertainty is therefore:

$$\sigma_{gas} = \sqrt{(2\%)^2 + (3\%)^2}$$ Eq A-3

This means that for the concentration curves presented in this work, the associated uncertainty is a maximum of 3.6%, and varies according to gas phase species.

A2 Calculation of conversion

When calculating the conversion of a particular species, the gas phase concentration is used in conjunction with the measured nitrogen flow rate. Nitrogen is measured using electronic Mass Flow Controllers (MFCs) across the range of experiments undertaken for this work. These devices have tolerances guaranteed by the manufacturers, where they are regularly calibrated by qualified personnel. All MFCs used in this work were appropriately calibrated, and the worst case assumed uncertainty with the flow measurements is +/-1%. The calculation methodology, outlined above, gives the following steps for deriving molar flow rate from normalised concentration curves:

$$molar\ flow\ rate = \frac{C_{species}}{C_{N_2}} \times \frac{molN_2}{min}$$ Eq A-4

$$= \frac{\frac{n_{species}}{V}}{\frac{n_{N_2}}{V}} \times \frac{molN_2}{min}$$ Eq A-5

$$= n_{species} \times \frac{1}{min}$$ Eq A-6

This is then integrated to give the total moles of species over the course of the experiment (for TPP and steam gasification experiments in both fixed and fluid mode). The uncertainty associated with the above calculation is, once again, calculated by the quadrature method:

$$\sigma_{mol.min^{-1}} = \sqrt{\sigma\, C_{species}{}^{2} + \sigma\, C_{nitrogen}{}^{2} + \sigma\, flowrate_{nitrogen}{}^{2}}$$

Eq A-7

$$\sigma_{mol.min^{-1}} = \sqrt{3.6\%^{2} + 2\%^{2} + 1\%^{2}}$$

Eq A-8

This gives a maximum uncertainty figure of 4.2% for the molar flow rate of species. For TPP, fixed and fluid-bed steam gasification experiments, the curve of molar flow rate is then integrated to provide an estimate of the total conversion of species (which has an associated uncertainty with the integration method, and the uncertainty associated with the initial quantification of carbon, sulphur and other species found in the coal) while for the fixed bed, fast pyrolysis experiments, no integration is necessary, since the concentration data is taken at one point in time.

With respect to the initial condition of the coal, the Australian standard (AS 1038.11) stipulates repeatability figures that indicate, for total sulphur determination (used in this work to calculate the sulphur conversion) a value of 0.1%. This means that, for the determination of conversion, the overall uncertainty will not increase significantly from the 4.2% uncertainty associated with the determination of molar flow rate.

A3 Trapezoidal integration method

The Trapezoidal integration method, where the integrand is concave up, leads to an underestimation of the total area. This implies that for the TPP work, where the evolving rate curves show a significant evolution of product over the 200-600°C range, there is an underestimation in total conversion. The conversion at this point, for the major sulphur species, constitutes over 90% of the total sulphur conversion. This means that where there is the potential to overestimate the conversion, as the integrand is concave down, accounts for only 10% of the total potential conversion of sulphur to the gas phase. A discussion of the validity of using the integration method for the TPP, fixed and fluid bed steam gasification experiments is included below.

A4 Temperature Programmed Pyrolysis (TPP)

Several experimental methods were used to calculate the repeatability of the TPP experiments associated with this work. The first method involved the use of mass spectrometry for selected runs to determine whether the shape of the concentration curves obtained via micro-GC analysis captured the actual evolution of species (hence to confirm that the integration method to determine the mass balance was valid). Figure A.1 shows the H_2S concentration curve obtained for the AW TPP experiment and the curve for m/z = 34 (inferred to be H_2S, curve smoothed to remove noise). These curves show excellent agreement on the key shape features, including inflexion points.

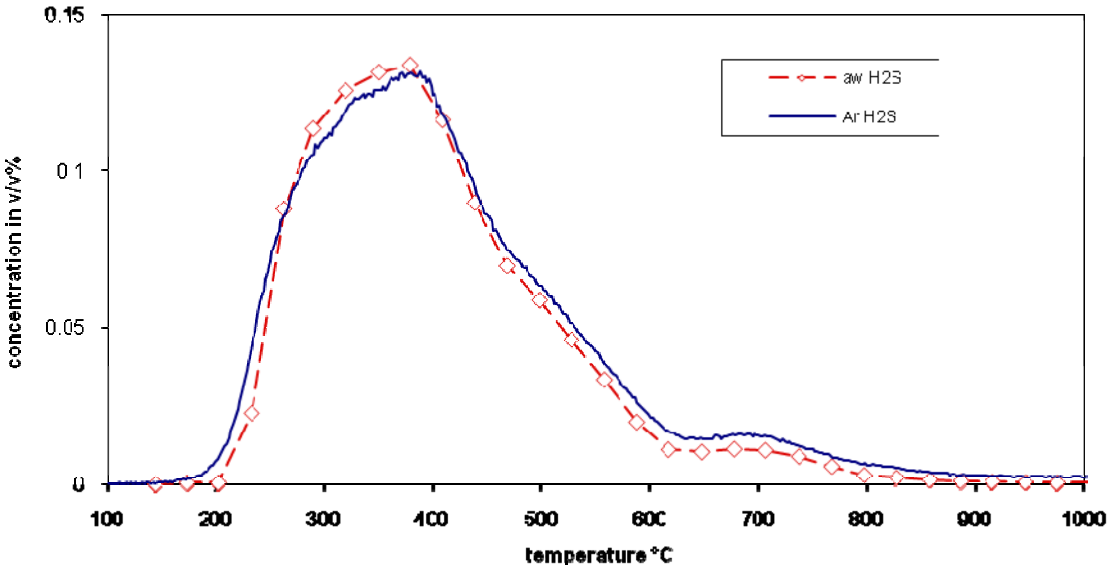


Figure A.1 H_2S concentration data for acid-washed Lochiel TPP, compared with m/z = 34 data set obtained during mass spectrometry for the same TPP experiment.

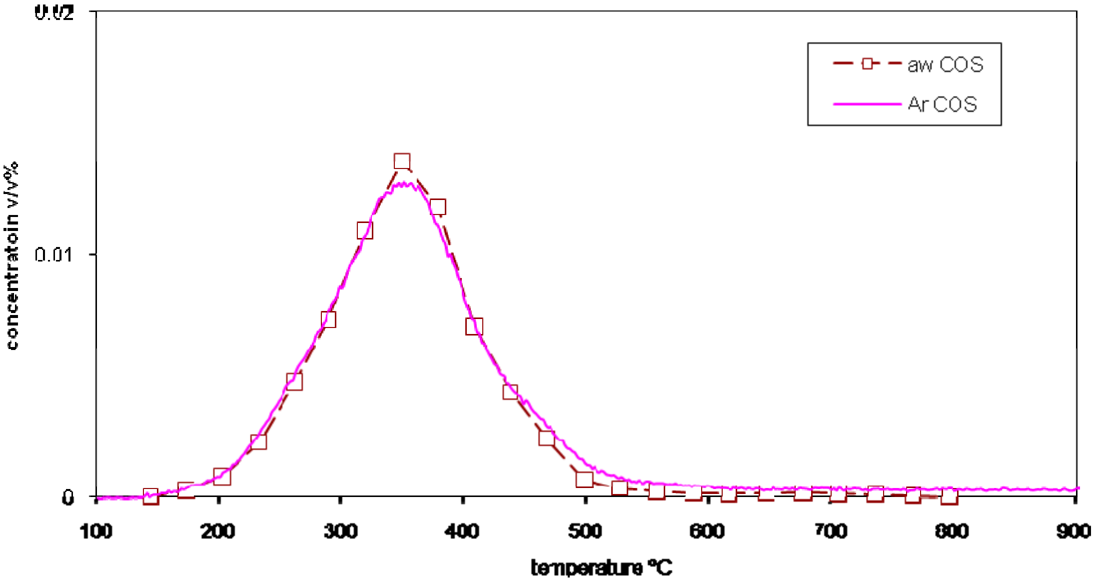


Figure A.2 COS concentration data for acid-washed Lochiel TPP, compared with m/z = 60 data set obtained during mass spectrometry for the same TPP experiment.

With respect to the repeatability of these experiments, Figure A.3 shows the repeat runs obtained for AW coal, using mass spectroscopy on SIM mode, for m/z = 34 (H_2S inferred). This shows the raw data for each run (un-smoothed) and indicates good agreement between experiments. To estimate the repeatability of this approach, the average area under the curve was derived for each profile and the standard deviation calculated. The uncertainty is then calculated as three times the standard deviation from the mean (Himmelblau, 1978). Each TPP experiment was repeated 2 to 3 times and the average uncertainty estimated by this method was in the range 5-10% for each coal and treatment type. Repeat runs were generally carried out over consecutive days, in order to allow passive cooling of the apparatus to room temperature, and in each case the final run was used to derive the data presented in Chapter 4.

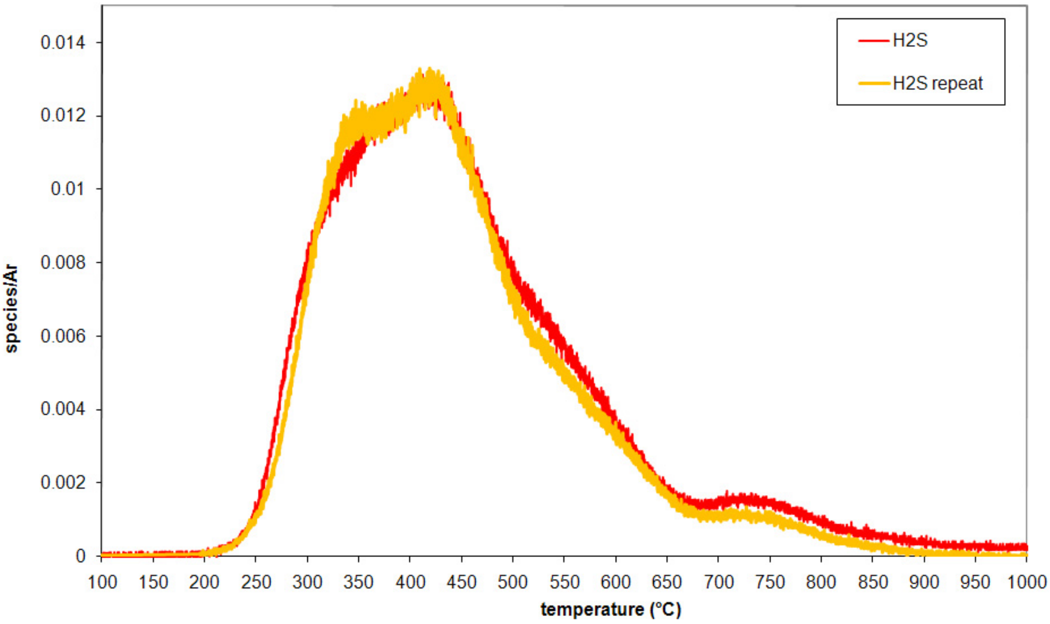


Figure A.3 Repeat runs for m/z = 34 (inferred H_2S) data set obtained during mass spectrometry for TPP of acid-washed Lochiel coal.

A5 Fast pyrolysis

The following section details the uncertainty associated with the data presented for the fixed-bed pyrolysis experiments in Chapter 5. As described in Chapter 3, Experimental Methodology, these experiments were conducted over a range of final operating temperatures between 700-1000°C, utilising Teflon bags to capture the entire product mix for 5 minutes of pyrolysis. Figure A.4 below shows the normalised H_2S/Ar signal (H_2S, m/z = 34) obtained via mass spectrometry, as a function of time, for a range of final temperatures, showing the justification for the 5 minute pyrolysis timeframe. System lag time is shown at just over 2 minutes from addition of coal to detection of first product gas.

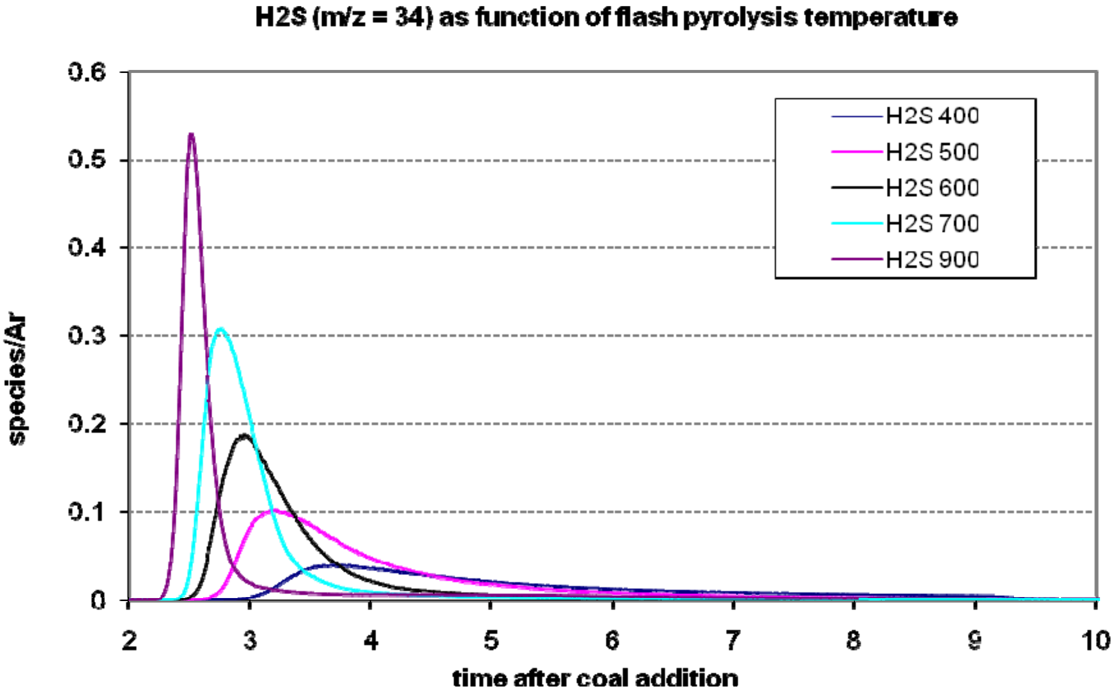


Figure A.4 m/z = 34 datasets for fast pyrolysis runs for final temperatures between 400-900°C showing H_2S evolution curves with respect to time after coal addition.

Figure A.5 shows the results for the MS spectra obtained for AD pyrolysis over a series of three runs at 900°C final temperature. The SIM mode shown was run to evaluate the specific ions present and the SCAN mode selected for m/z 34 (H_2S inferred), 32 (O_2 inferred) and 60 (COS inferred). To estimate the repeatability of this approach, the average area under the curve was derived for each profile and the standard deviation calculated (in this case at 5.4% for the H_2S profile). The uncertainty is then calculated as three times the standard deviation from the mean (Himmelblau, 1978) giving a figure of +/-16.4%.

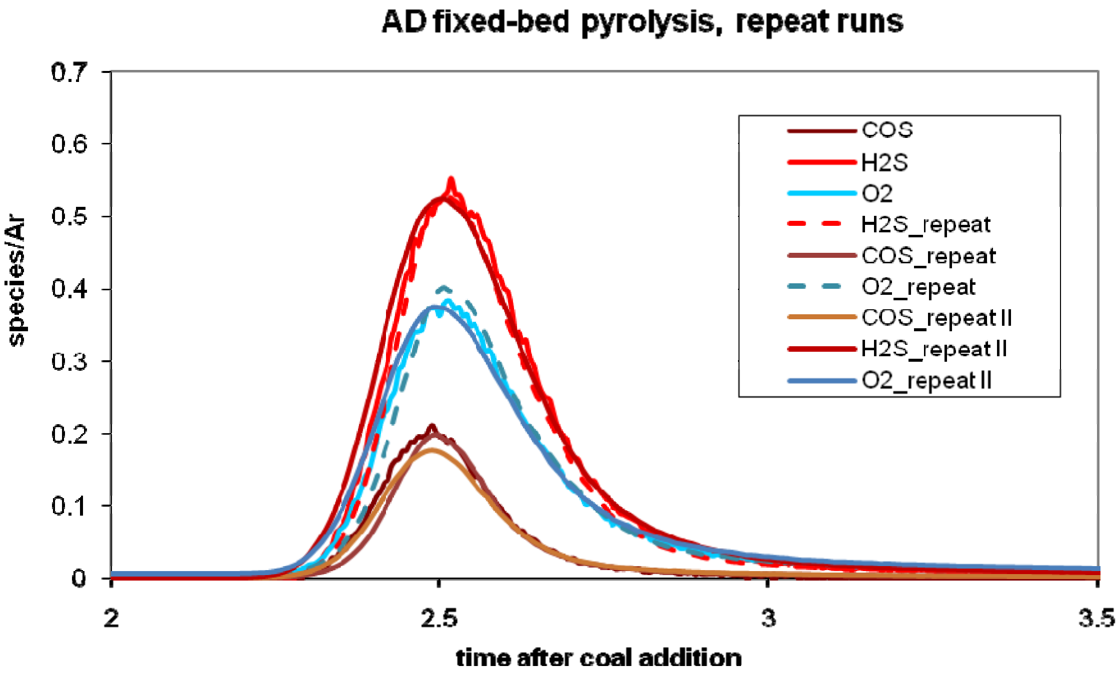


Figure A.5 AD fast pyrolysis results at 900°C for repeat runs, for m/z = 34 (H_2S inferred), m/z = 32 (O_2 inferrred) and m/z = 60 (COS inferred)

Using the MS to provide comfort around repeatability, each of the subsequent runs presented in this work was then repeated 2-3 times using the Teflon bags to recover the total gas over a 5 minute period. Using the micro-GC to evaluate the concentrations of product gas, and then the methodology described above to generate a total moles of each species produced, enabled the determination of conversion for sulphur and carbon. Runs were carried out over the course of the same day or at least in a consecutive two day period, and in each case the final run was used to derive the data presented in Chapter 5, with the calculated repeatability uncertainty figures for each species and all runs estimated in the range 2-7% for carbon species and 5-15% for sulphur species. The calculated uncertainty figures for the carbon conversion and sulphur conversion obtained were described previously, with a maximum estimated uncertainty of 4.2%.

Figure A.6 shows the range of solid phase conversion obtained by measuring the mass of solid phase recovered after the fast heating rate pyrolysis experiments and expressing as a percentage of the total mass of coal pyrolysed. Estimates of uncertainty were obtained for this data, again using three standard deviations from the mean (Himmelblau, 1968). Results are shown in Table A.II, indicating that the uncertainty for char and ash recovery falls between 6 and 13% for each of the fixed-bed pyrolysis experiments. For each of the subsequent runs and each of the coal types and treatments, the repeatability uncertainty was estimated at between 5-15%.

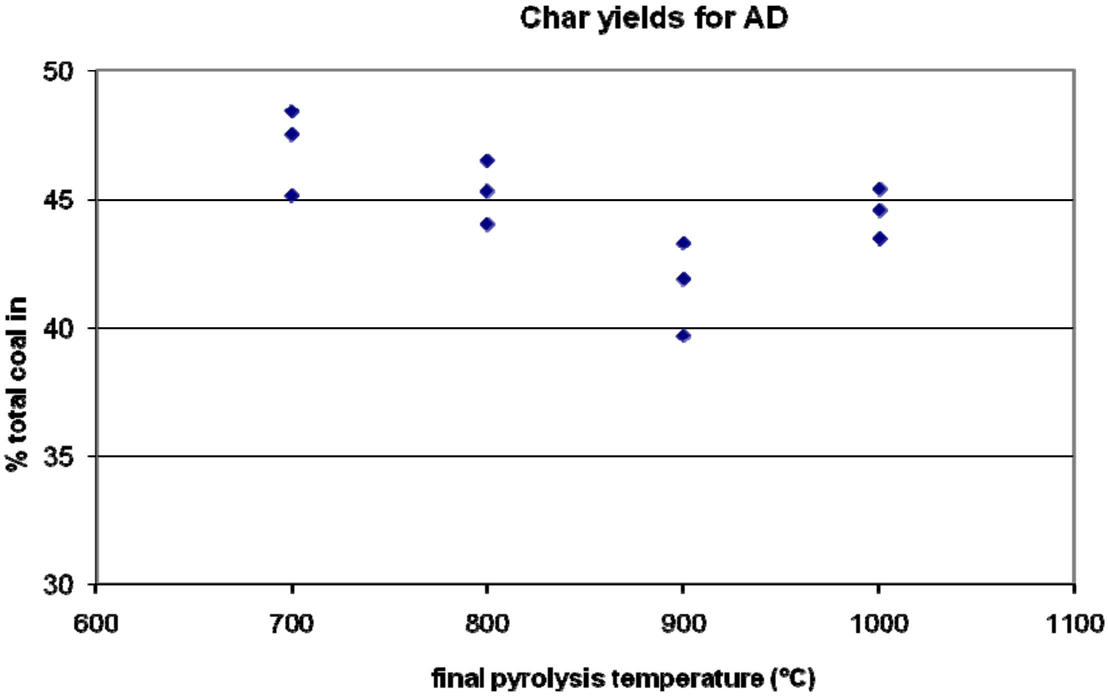


Figure A.6 Solid phase conversion of coal (char yields) expressed as a percentage of the total coal reacted for AD during fixed-bed pyrolysis experiments between final temperatures of 700-1000°C

Table A.II

Pyrolysis temperature	**700°C**	**800°C**	**900°C**	**1000°C**
Average % recovered	47.03	45.28	42.61	44.49
Standard deviation	1.69	1.22	1.81	0.95
3 x st dev	5.06	3.65	5.42	2.86
Uncertainty %	**11%**	**8%**	**13%**	**6%**

A6 Steam gasification experiments

The steam gasification experiments undertaken in both the fixed and fluidised bed environments are subject to the same levels of uncertainty described above, in terms of the gas species concentration, mass flow rates of reactants, and the subsequent calculation of mass balances and conversion data.

The two additional sources of uncertainty lie in the measurement of the flow rate of steam to the apparatus (using peristaltic pumps) and the measurement of temperature in the fluidised bed. As described in the experimental section these were regularly calibrated.

The uncertainty associated with these two measurements, however, has no impact on the calculation of the conversion data presented in this thesis, only on the calculation of kinetic parameters and the conclusions with respect to the rates of gasification. Since the kinetic parameters themselves are derived from the Arrhenius plots, the regression values (R^2) themselves account for the uncertainty associated with these parameters.

A7 Summary and Conclusions

The analysis presented in this chapter estimates the uncertainty associated with the calculation of conversion values for each of the experimental regimes described in this thesis between 5% and 15%. The analysis shows that experiments undertaken show good repeatability, depending on the particular apparatus and experimental regime, and this was confirmed by comparison of gas concentration profiles with mass spectrometry data sets obtained for specific species.