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**PARTITIONING OF SULPHUR AND NITROGEN IN
PYROLYSIS AND GASIFICATION OF COAL IN A FLUIDISED
BED**


by

Stephen Philip Middleton

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of
degree of Ph.D. of Loughborough University

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ABSTRACT

The aim of this study was to gain a better understanding of the processes governing the distribution of the heteroatoms, sulphur and nitrogen, between the various products formed during fluidised bed pyrolysis/gasification under conditions particularly relevant to industrial hybrid combined cycle power generation.

A novel bench-scale fluidised bed reactor capable of heating coal up to 1050°C in an inert or oxidising atmosphere was designed and commissioned to produce pyrolysis and gasification chars. Using this apparatus to study a range of UK coals, experimental data on the distribution of sulphur and nitrogen between char, tar and gases during fluidised bed pyrolysis and between char and gases on partial gasification were collected. On pyrolysis both the nitrogen and sulphur were found to shift preferentially into the volatile matter. The pyrolysis chars possessed N/C' and S/C' weight percent ratios, normalised to the wt.% C of the parent coal, of less than 1. The N/C' and S/C' weight percent ratios of the pyrolysis chars were both found to increase with increased coal rank. On gasification the loss of nitrogen closely matched the carbon loss with progressive burn out of the char, the chars of the higher ranked coals possessing N/C' ratios closer to 1 than the lower ranked coals. The sulphur loss during gasification appeared independent of coal rank. A single relationship was found to explain the coal-sulphur behaviour with progressive char burnout for all seven coals studied. There was also found to be no significant change in the S/C' and N/C' ratios of the chars when varying the reaction temperature between 850°C and 1050°C under pyrolysis or gasification conditions.

These experimental findings are discussed in relation to the published literature and their significance is examined with regard to combined cycle power generation by means of the air blown gasification cycle (ABGC) currently under development in the UK.

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LIST OF SYMBOLS

A	Weight percent ash content (dry basis)	
C	Weight percent carbon content (dry ash free basis)	
d	Mean particle diameter, m	(Section 4.2.3.2)
D_c	Gas cyclone diameter, m	
d_p	Mean particle diameter, m	
E	Activation energy, J.mol^{-1}	
exp	2.718	
G	Weight percent of coal gasified (dry ash free basis)	
g	Gravitational acceleration, 9.81 m.s^{-2}	
k	Rate constant	
L	Total carbon mass loss of char, wt%	
N/C	Nitrogen to carbon mass ratio of char	
N/C'	Nitrogen to carbon mass ratio of char normalised to that of parent coal	
P	Pressure, kPa	
Q	Volumetric flow rate, $\text{m}^3.\text{s}^{-1}$	
Q_{mf}	Volumetric flow rate at minimum fluidisation, $\text{m}^3.\text{s}^{-1}$	
Q_t	Volumetric flow rate at terminal velocity of char, $\text{m}^3.\text{s}^{-1}$	
Q_{op}	Operating bubbling fluidisation volumetric flow rate, $\text{m}^3.\text{s}^{-1}$	
R	Molar gas constant, $8.314 \text{ J.mol}^{-1}.\text{K}$	
Re	Reynolds number	
S/C	Sulphur to carbon mass ratio of char	
S/C'	Sulphur to carbon mass ratio of char normalised to that of parent coal	
T	Temperature, K	
U_{mf}	Minimum fluidisation velocity, m.s^{-1}	
U_t	Terminal velocity of a particle, m.s^{-1}	

Greek symbols

Δ	Difference
ϵ_{mf}	Porosity of a bed of particles at point of minimum fluidisation
ϕ_s	Sphericity of particle
μ	10^{-6}
μ	Viscosity of a fluid, Pa.s
ρ_s	Density of fluidised solid, kg.m^{-3}
ρ_g	Density of fluidising gas, kg.m^{-3}

Special

C_x (x = number, 0, 10, 15 or 20) denotes a fluidised bed char produced in x vol.% O_2/N_2 gas mixture.

Any symbol with subscript coal or char refers to the properties pertaining to the parent coal or the char.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND AND INTRODUCTION

Coal is utilised world-wide for power generation and is still the largest single fuel used for this purpose. However, serious concerns over the effects on our environment such as global warming, ozone depletion and acid rain have caused conventional coal combustion for power generation to become less attractive. Coupled with emissions of the greenhouse gas CO_2 , coal contains elements such as sulphur and nitrogen which on combustion are known can contribute to the above effects via emissions of SO_2 and NO_x . Increased environmental awareness of the international community has brought about agreements such as the EC directive on emissions from large combustion plant, making it necessary for EC member states to reduce their emissions of NO_x and SO_2 from new and existing combustion plants $>50\text{MW}$ thermal input.

Alternative sources of fuel exist such as natural gas and oil which generally contain less nitrogen and sulphur and are more convenient to handle. An increased use of these fuels in the short term may help the situation. However, coal remains one of the most important strategic resources, being the most abundant and evenly spread fossil fuel around the world.

New technologies are being retrofitted to existing large coal combustion plant such as low NO_x burners and flue gas desulphurisation. Perhaps even more promising are coal utilisation processes which are inherently cleaner. Fluidised bed combustion falls into this category. Fluidised beds possess excellent heat and mass transfer characteristics enabling a wider range of coal types to be burnt efficiently at relative low temperatures. The low temperatures mean the NO_x emissions from them are lower than conventional pulverised fuel burners and sorbent material such as limestone can be used in the bed itself, removing up to 95% of SO_2 produced in-situ.

Utilising the advantages of fluidised beds is the aim of a process under development in the UK. Under the general heading of hybrid combined cycle power generation, the

air blown gasification cycle (ABGC) partially gasifies coal to produce a low calorific fuel gas for combustion in a gas turbine which generates electricity. The waste heat from the turbine is utilised in a separate steam cycle. The partially gasified char is removed and burnt in a circulating fluidised bed boiler, the heat from which also contributes to the steam cycle. This type of process has potential efficiencies of up to 45% and with potentially lower SO_2 and NO_x emissions.

A knowledge of how sulphur and nitrogen contained in the coal behaves, under these conditions, is essential if these types of processes are to be optimised to minimise gaseous pollutant emissions of NO_x and SO_2 . The objective of this study was to contribute to this knowledge by designing and constructing an experimental reactor capable of producing chars and tars under conditions most relevant to the ABGC process. These chars and tars could then be analysed for sulphur, nitrogen and carbon contents. By studying the partitioning of sulphur and nitrogen between the char, tar and gases on pyrolysis and gasification the effects of experimental conditions and parent coal properties could be quantified.

A number of experimental techniques to produce pyrolysis and gasification chars were examined. All were assessed on a number of criteria including ability to produce enough quantity of char for analysis, size, ease of use, applicability and cost. The choice of system was a bench-scale fluidised bed reactor capable of heating coal up to 1050°C , producing chars of known residence time in an inert or oxidising atmosphere and of sufficient quantity for chemical analysis.

This thesis reports the design and development of the novel fluidised bed reactor and the data obtained from the experimental studies on a range of UK coals. The findings are discussed in relation to the published literature and their significance is examined with regard to fluidised bed combustion and the gasifier and combustion stages of the ABGC.

1.2 LAYOUT OF THESIS

In the first part of the thesis, Chapter 2, the current technical literature is reviewed focusing on the areas most relevant to the matter of this research topic. The literature review focuses on five main areas, coal and the environment, the nature of coal in terms of physical and chemical properties, coal combustion and the industrial use of coal as fuel for power generation in pulverised fuel boilers and in fluidised beds.

Chapter 3 summarises the background to the project and details its main aims and objectives at the time of its conception. In this chapter the proposed experimental programme is also discussed along with a series of questions that the research aimed to answer.

Chapter 4, Experimental Studies, covers the work carried out in the first part of the project to design and construct the laboratory scale fluidised bed reactor. The commissioning of the system is also reported. The last section of this chapter details in full the developed experimental char production and analysis method.

In the last two chapters, Chapter 5 presents the experimental results and discusses the main points and Chapter 6 contains the main conclusions drawn from the study along with recommendations for future work.

The Appendices, detailing the calculations made to determine (A) the operating conditions for the fluidised bed system and (B) the pyrolysis mass balance, the analytical data for the coals used (as supplied by the CRE Coal Bank) and preliminary data for limestone in-bed experiments are included at the back of the thesis along with the References.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

2.1.1 SUMMARY OF CONTENTS

The current relevant literature pertaining to the subject of the thesis is reviewed in this Chapter. The objective of this is to explore the available technical information in sufficient detail to generate a comprehensive background to the subject matter, critically discuss general trends from current research and describe the application of the relevant industrial processes.

The chapter is split into five main sections covering, i) a brief explanation of the effect of coal utilisation on the environment, ii) the nature of coal - classification, chemical structure, forms of sulphur and nitrogen, iii) the science of coal combustion - pyrolysis, char morphology, char burnout and gaseous pollutant formation, iv) pulverised fuel combustion (PF) - burner configurations, control of gaseous pollutant emissions and v) fluidised bed combustion (FBC) - fluidisation, applications, gaseous emissions from FBC and performance comparison with conventional PF combustion.

2.1.2 COAL AND THE ENVIRONMENT

Coal has been utilised by man as a fuel for hundreds of years and is still the major single source of fuel for power generation world-wide. However, the combustion of coal in conventional plant can lead to the formation of excessive gaseous pollutant emissions. Legislation concerning the reduction of most of these pollutants in the atmosphere has made it necessary to clean up power station emissions and/or utilise cleaner combustion technologies.

The future success of coal as a fuel for modern power generation depends on its competitiveness as a resource and the ability to develop processes which utilise it more efficiently and cleanly.

2.1.2.1 Coal resources

Coal has been an important resource in industry since it was first used in iron smelting in place of charcoal in the early 18th century. Until the middle of this century coal was by far the most important fuel used in power generation, locomotion, domestic gas supply, heating and coal-tar chemicals. The discovery of large crude oil deposits and the birth of the petrochemical industry saw a decline in some of the above applications since oil and natural gas were easier to handle and more efficient in certain applications. Despite this, world-wide coal production has continued to increase with a continued increase in international energy consumption.

However, coal has a significant advantage over all other fossil fuels in that its resources far outweighs all of them. Estimates of world fuel resources put coal at 6 times more than oil and oil shales combined¹, leaving a conservative 300 years supply of coal left. If not in the short term, in the long term there is little doubt that coal will have to be exploited further with the decline of other fossil fuels.

Coal has another advantage over other fossil fuels and that is that it is more evenly spread around the world than any other fossil fuel making it strategically a very useful commodity. Figure 2.1 shows the coal-bearing regions of the world.

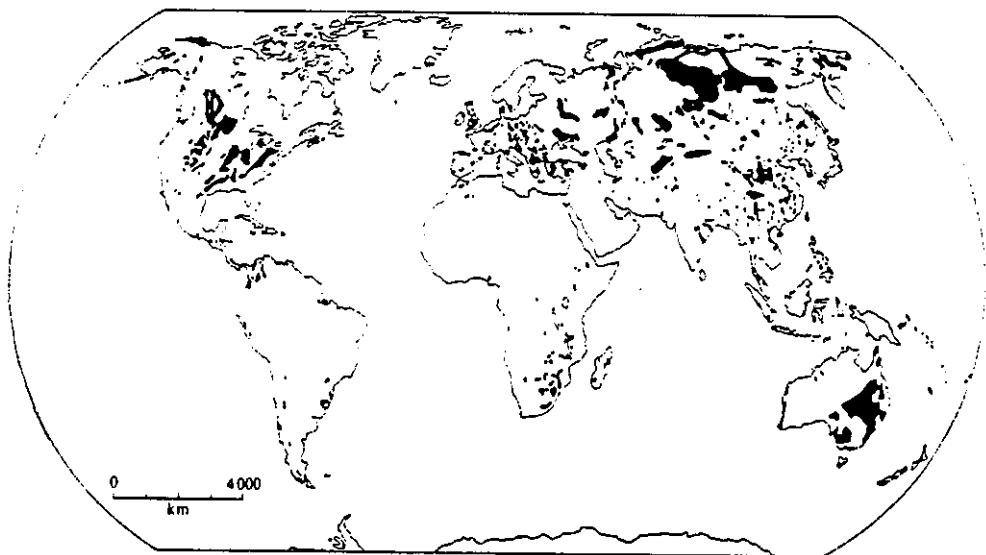


Figure 2.1. The coal-bearing regions of the world¹.

2.1.2.2 Environmental effects of coal combustion

Coal is a fossil fuel containing mainly carbon and hydrogen, with smaller quantities of oxygen, sulphur and nitrogen and trace quantities of virtually all other elements. When coal is burnt the main products of combustion are CO_2 and H_2O . Sulphur and nitrogen contained in the coal oxidise to sulphur dioxide, SO_2 and nitrogen oxides, NO_x and at high enough temperatures nitrogen in the air can be oxidised to NO_x . Sections 2.3.2.2 and 2.3.2.3 discuss SO_2 and NO_x formation from coal combustion in more detail. In large enough quantities these gaseous emissions have an effect on the chemistry of the environment.

CO_2

As mentioned above, the main product of coal combustion is CO_2 . At local concentrations of below 1% it is harmless on inhalation. Of more concern is its behaviour in the atmosphere and its implication in the 'greenhouse effect' and hence contribution to global warming. CO_2 absorbs infrared radiation resulting in higher net temperatures in the lower part of the atmosphere. Whereas the annual man made, or anthropogenic, emissions of CO_2 due to fossil fuel combustion are small compared to total atmospheric CO_2 content (5.3×10^9 tonnes in 1980 compared to around total 720×10^9 tonnes in the atmosphere²), it is feared that the cumulative effects could be enough to raise global temperatures significantly in decades to come. For this reason countries are looking to reduce their emissions of CO_2 and the UK has received a recently stated policy of achieving a 20% reduction by 2010. Alternative fuels, alternative power generation and greater fuel efficiency are all options available for the reduction of CO_2 emissions.

SO_2 and NO_x

Both of these species contribute to the problems associated with acid deposition and acid rain; acidification of ground waters, building erosion and deforestation. The effects of acid rain were first brought to light in the 1960's when Sweden began to suggest that the acidification of some of their lakes could be linked with the transport of SO_2 in the air³.

It is now accepted that NO_x and hydrocarbons also contribute to the problem of deforestation as precursors of ozone².

NO_x also is a precursor of photochemical smog. NO_2 in the lower atmosphere is broken down by ultra violet light forming oxygen radicals which go on to produce ozone, the main agent in the formation of photochemical smog.

There is no doubt that coal combustion is the major source of man made SO_2 emissions, however, for NO_x emissions the contribution from transport, and especially from road transport using the internal combustion engine, is considerable. Table 2.1 shows the estimated emissions of SO_2 , NO_x , CO and other pollutants by source in the UK.

Table 2.1 Estimated UK emissions of primary pollutants by source type for 1989²

<i>Thousand tonnes</i>				
Source	Black smoke	SO_2	NO_x	CO
Domestic	191	135	68	339
Commercial/industrial	92	683	337	342
Power stations	25	2644	785	47
Refineries	2	109	36	1
Road vehicles Petrol	15	22	702	5649
Diesel	182	30	596	102
Railways	-	3	32	12
Other	5	65	144	31
Total emission	512	3699	2700	6522

Others

Nitrous oxide, N_2O , is also generated in some combustion processes and is also termed a greenhouse gas. It is associated more with fluidised bed combustion of coal, see section 2.5, than more traditional forms of coal combustion. On a molecule to molecule basis it has more of a 'greenhouse' effect than CO_2 , but it is not yet legislated against.

2.1.2.3 European emissions legislation

Until 30 years ago the control of emissions from combustion systems had been of only national concern, with the bulk of the policies being related to the local health based issues. In the UK the London smog of 1952, which brought about the clean air act of 1956, made people more aware of the importance of emission control. This only really brought about an increase in industrial chimney height and the adoption of smokeless zones for control of domestic fossil fuel emissions⁴.

By the late 1970's worries over deforestation in Scandinavian countries and parts of Germany led to certain European countries signing agreements on the reduction of SO₂ and NO_x from power generation. In 1982, at the Human Environment conference in Stockholm, Germany announced its own strict limits on emissions and pressed the EC Commission to formulate a directive on the prevention of air pollution in Europe.

In 1988 a directive proposed by the Commission of European Communities was agreed on⁵, reducing emissions of NO_x and SO₂ from existing and new large combustion plant >50 MWth. Each member state was set target reduction levels to meet by 1993, 1998 and 2003 based on 1980 emission levels. The directive sets out overall annual targets for each member state for existing plant and all new plant has to meet actual emission limit levels. In the UK the directive is enforced by Her Majesty's Inspectorate of Pollution, HMIP, as part of the Environmental Protection Act 1990. Tables 2.2 and 2.3 show the emission ceiling targets for existing plant for each member state. Figure 2.2 shows the SO₂ limit values for new plants, with the NO_x limit values for new plants detailed in table 2.4. All figures are based on those listed in European directive 88/609/EEC⁵, the figures in mg/Nm³ assuming 6 vol.% oxygen in the flue gas at atmospheric pressure.

Compared to other member states the UK has relatively lower targets to meet. This does not mean it will be easy, at the date of signing the UK still heavily relied on indigenous coal supplies for the majority of its power generation. This has meant an increase in the UK of smaller natural gas turbines for new power generating plant. For existing plant the power generating companies have used retrofit technology on some of their larger power plants to bring them within the total annual limits for NO_x and SO₂ emissions.

Table 2.2. Emission targets for SO₂ from existing plant, Directive 88/609/EEC⁵

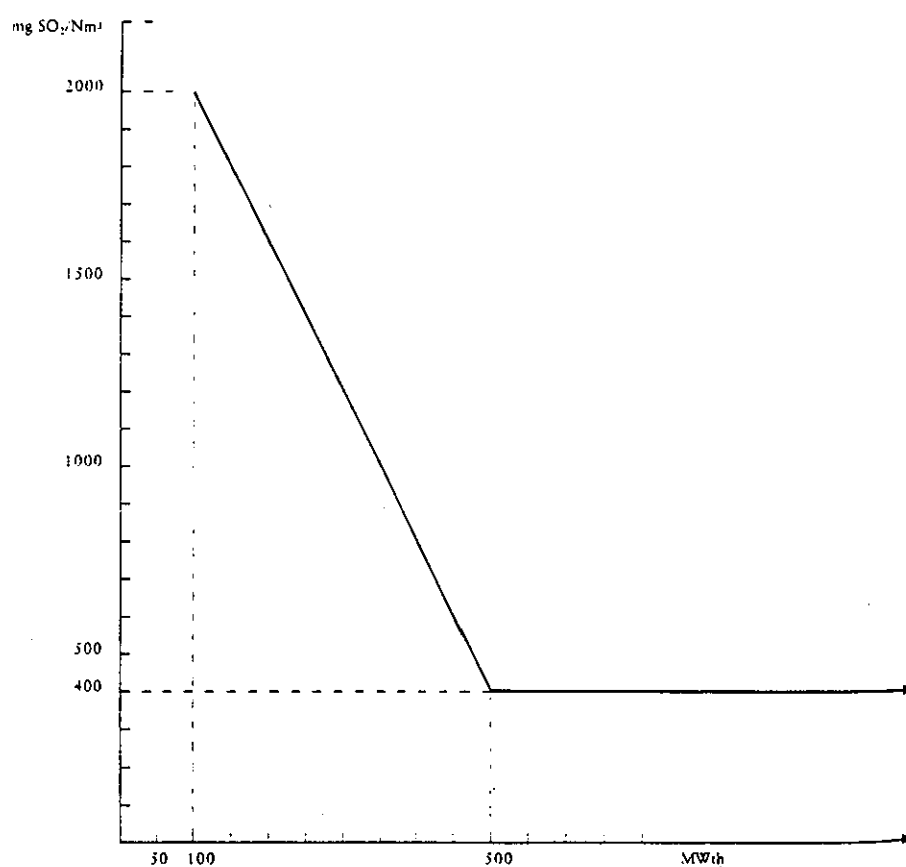
Member states	1980 SO ₂ levels (ktonnes)	Emission ceiling (ktonnes/ year)			% reduction over 1980 levels		
		Phase 1 1993	Phase 2 1998	Phase 3 2003	Phase 1 1993	Phase 2 1998	Phase 3 2003
Belgium	530	318	212	159	- 40	- 60	- 70
Denmark	323	213	141	106	- 34	- 56	- 67
Germany	2 225	1 335	890	668	- 40	- 60	- 70
Greece	303	320	320	320	+ 6	+ 6	+ 6
Spain	2 290	2 290	1 730	1 440	0	- 24	- 37
France	1 910	1 146	764	573	- 40	- 60	- 70
Ireland	99	124	124	124	+ 25	+ 25	+ 25
Italy	2 450	1 800	1 500	900	- 27	- 39	- 63
Luxembourg	3	1.8	1.5	1.5	- 40	- 50	- 60
Netherlands	299	180	120	90	- 40	- 60	- 70
Portugal	115	232	270	206	+102	+135	+ 79
United Kingdom	3 883	3 106	2 330	1 553	- 20	- 40	- 60

Table 2.3. Emission targets for NO_x from existing plant, Directive 88/609/EEC⁵

Member states	1980 NO _x levels (as NO ₂) (ktonnes)	Emission ceiling (ktonnes/year)		% reduction over 1980 levels	
		Phase 1 1993	Phase 2 1998	Phase 1 1993	Phase 2 1998
Belgium	110	88	66	- 20	- 40
Denmark	124	121	81	- 3	- 35
Germany	870	696	522	- 20	- 40
Greece	36	70	70	+ 94	+ 94
Spain	366	368	277	+ 1	- 24
France	400	320	240	- 20	- 40
Ireland	28	50	50	+ 79	+ 79
Italy	580	570	428	- 2	- 26
Luxembourg	3	2.4	1.8	- 20	- 40
Netherlands	122	98	73	- 20	- 40
Portugal	23	59	64	+ 157	+ 178
United Kingdom	1 016	864	711	- 15	- 30

Table 2.4. Emission limit values for NO_x for new plant, Directive 88/609/EEC⁵

TYPE OF FUEL	LIMIT VALUES (mg/Nm^3)
Solid fuel in general	650
Solid fuels with less than 10% volatile compounds	1 300
Liquid	450
Gaseous	350

**Figure 2.2. Emission limit values for SO_2 for new plant, Directive 88/609/EEC⁵**

2.2. NATURE OF COAL

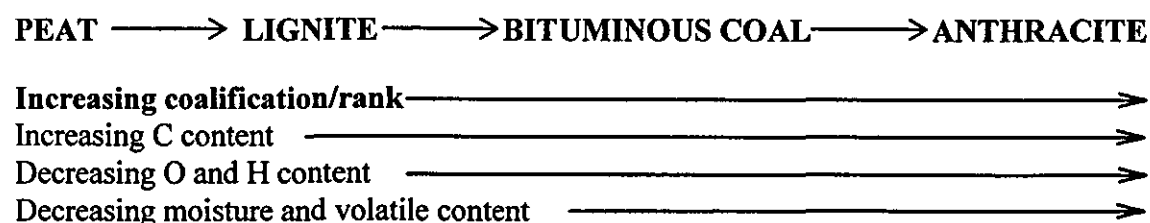
2.2.1. COAL STRUCTURE⁶

Essentially, coal is a fossilised organic substance formed by the action of heat and pressure over time on peat formed from the remains of plant material. This organic 'rock' is made up from many different compounds containing elements of C, O, H, S and N, and some mineral matter. Coal structure is not a homogeneous mixture of various compounds, but is heterogeneous in nature, inherited from the diversity of plant life and hence source material found in the original peat bed.

2.2.1.1 The formation and composition of coal

The formation of coal begins through microbiological processes acting upon fallen plant material to form peat. As the peat bed thickens, and sediment is deposited on top of this, the overburden increases resulting in the peat being exposed to increasing pressures and temperatures in a changing geochemical environment. Progressively through this process moisture and volatiles are driven off from the developing coal forming first lignite/ brown coal, bituminous coal and finally anthracite. The development of coal during this geochemical stage is termed *coalification*. Coalification begins after peat has been formed, the developing coal structure then undergoes varying physical and chemical changes which generally see an increase in aromatisation of compounds to eventually produce anthracite. This process leads ultimately to pure graphite.

From peat through to anthracite the total carbon content increases. A measure of this increase in carbon content, or degree of metamorphosis, is said to be a measure of rank. Other generalised trends with rank are shown below.



2.2.1.2. Macerals

Decomposed plant material in the form of peat is the precursor of coal and so coal possesses some of the fossilised properties of that plant material. Therefore, the differences in the original plant make-up of various coals and the extent to which this plant material initially decomposes gives rise to coals being composed of different petrographic constituents. These different constituents are termed *macerals*. Macerals are grouped into three main categories according to their plant origin and behave differently when viewed under the microscope with reflected light. They are as follows:

- Vitrinite*: The main constituent of coal having a fibrous cellular structure originating from the woody tissue of plants. When viewed under reflected light appears light grey to white and has a high reflectance. The reflectance of vitrinite, as with all macerals, can increase with rank.
- Exinite (or Liptinite)*: This group of macerals originate from plant material other than woody tissue such as spores, plant waxes and resins. Liptinite has a lower reflectance than vitrinite.
- Inertinite*: Relatively structureless macerals originating from extremely decomposed or charred plant material. Inertinite has the highest reflectance of the three maceral groups. Figure 2.3 shows more features of the major classes of macerals⁷.

SOURCE MATERIAL	FATE IN PEAT SWAMP	METAMORPHIC EFFECTS	MACERAL SUBCLASS	MACERAL CLASS	MICROSCOPIC IDENT. CRITERIA (POLISHED)	COMPOSITION IN TYPICAL BIT. COAL		
Protein	Decomposes (contributes N)					%C	%H	%O
'Wood' (lignin, cellulose)	Humified	[Deoxygenated Dehydrogenated Aromatized]	Vitrinite	Vitrinite	Domonates, grey-white	83.8	5.3	7.6
	Charred	?	Fusinite	Inertinite	Angular, cellular, bright	95	2.0	3.0
	Decomposed	?	Micronite		Fine grained, bright			
Exines	Incorporated	[Bitumenized' Dehydrogenated Aromatized]	Exinite	Liptinite	Thin strips, dark*	84.8	6.9	4.0
Resins	Incorporated	?	Resinite		Spherical, dark*			

* In low-vol bituminous and anthracites, liptinite indistinguishable from vitrinite.

Figure 2.3 Main features of the major classes of macerals⁷

2.2.1.3 Chemical Structure

Any plant which decomposes to form coal contains various polymeric constituents. The polymer compounds found in plant material can be generalised as falling into four main groups; Cellulose - found in the cell walls of the plant, lignin - essentially the cement which binds the cellulose fibres together, waxes/resins - least susceptible to chemical attack and proteins - polymers derived from a series of amino acids and responsible for the nitrogen content of coal.

Cellulose is susceptible to biochemical attack and degrades relatively easily. Lignins, however, are resistant to degradation and it is thought that during coalification monocyclic aromatic units could be condensed with aliphatic lignin structures to produce larger polycyclic units such as naphthalene and anthracene⁸.

Because of its heterogeneous nature, characterising the detailed structure of coal proves difficult. Some modelling of the chemical structure of coal concentrates on hypothetical average molecules, such as that one shown in figure 2.4.⁹, which shows a large macromolecule made up from smaller aromatic units linked by aliphatic bridges.

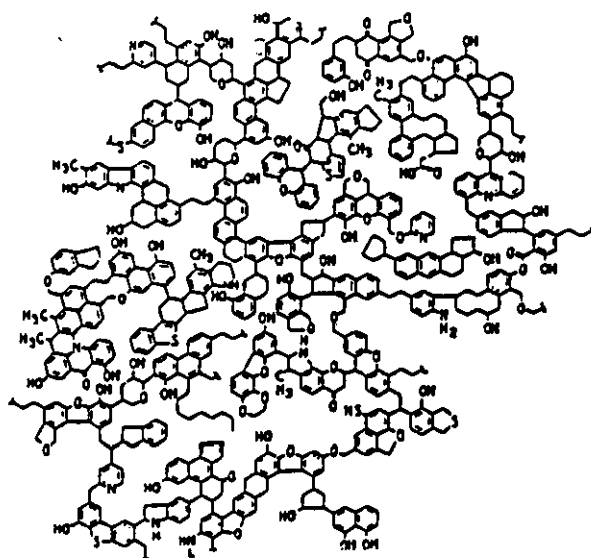


Figure 2.4. A model of the structure of a bituminous coal⁹

Alternatively, the structure can be modelled in a more general way, for example considering coal as existing of a two component system comprising of a crosslinked network of aromatics with aliphatic bridges filled with smaller molecules with varying structures. What is generally agreed though, is that with coalification, the proportion of C in aromatic compounds increases with the O/C and H/C ratio decreasing. The size of the aromatic units also increase with rank, rising rapidly from low-bituminous up to anthracite.

Methods of investigating the chemical structure of coal vary from chemical degradation and deriving the original coal structure from the fragments identified, to the non-destructive methods of X-ray absorption spectroscopy. Recent developments in coal structure research and methods in coal structure research are reviewed in more detail by Matthias⁸.

2.2.2. COAL CLASSIFICATION

A number of coal classification systems have evolved based on both scientific and commercial principles. Some systems such as the Seyler chart developed in the UK in the early part of this century contains valuable scientific classification of coal parameters based on its elementary composition. However, the relationship between the properties of a coal and its elementary composition is complicated resulting in the Seyler chart not being adopted by many industrial laboratories. Therefore systems have developed in individual countries giving more direct information about a coal as a fuel or behaviour on coking or gasification. The parameters measured are usually based on volatile matter, calorific value, coking and caking properties.

Nearly all commercial systems are primarily based on the volatile matter of the coal, those coals with the lowest, <10%, volatile matter being termed usually as anthracites, those with volatile contents between 20% and 30% referred to in some way as coking coals, and for coals with greater than 30% volatile matter, the systems differ in their classification approach. In the UK, adopted by British Coal, the Gray-King assay was

chosen as a measure of the coking properties of the coal. In the Gray-King assay the coal is heated in a tube at 5°C/min and the coke formed is examined visually, and given a code (see van Krevelen et al⁶). The drawback of the Gray-King assay is that it can often involve a lengthy procedure. In other countries such as France, the swelling index of the coal was used: the coal is heated rapidly in a crucible and the coke shape compared against standard shapes, this gives an indication of how the coal behaves under rapid heating combustion conditions but no information about its coking properties. In the USA the calorific value based on an ash and moisture free basis was chosen, the drawback here was that a lot of the coals were given similar classification but had significantly differing quality. As a result, the moisture content of the coal at 30°C and a humidity of 97% was also taken into consideration.

A more widespread classification system in use is the International Classification of Hard Coals agreed to in 1956, see Table 2.5. The system was formulated to standardise the classification of coal and drew from the different methods used internationally. It uses a 3 digit code. The first digit indicates the *class*. This is the rank of the coal based on its volatile matter content and above 33% (daf) the calorific value at 30°C and 96% humidity. The second digit indicates a *group* representing the caking properties of the coal measured on a solid carbonised sample, two alternative parameters are given. The final digit denotes the *sub-group* which indicates the coals coking properties. Here two alternative parameters are given, both measure the size change of a crushed sample of coal heated at a standard heating rate under standard conditions.

Table 2.5. INTERNATIONAL CLASSIFICATION OF HARD COALS

GROUPS (DETERMINED BY COKING PROPERTIES)			CODE NUMBERS										SUB-GROUPS (DETERMINED BY COKING PROPERTIES)		
Group Number	Alternative Group parameters		The first figure of the code number indicates the class of the coal, determined by volatile matter content up to 33% and by calorific parameter above 33% VM. The second figure indicates the group of coal, determined by caking properties. The third figure indicates the sub-group, determined by coking properties										sub-group number	Alternative sub-group parameters	
	Free swelling index	Roga index												Dilatometer test (% dilat.)	Gray-King assay
3	>4	>45					435	535	635				5	>140	G8
						334	434	534	634				4	50-140	G5-G8
						333	433	533	633	733			3	0-50	G1-G4
						332 _a	332 _b	432	532	632	732	832	2	<0	E-G
2	2.5-4	20-45				323	423	523	623	723	823		3	0-50	G1-G4
						322	422	522	622	722	822		2	<0	E-G
						321	421	521	621	721	821		1	contraction only	B-D
1	1-2	5-20			212	312	412	512	612	712	812		2	<0	E-G
					211	311	411	511	611	711	811		1	contraction only	B-D
0	0-0.5	0-5		100	200	300	400	500	600	700	800	900	0	non-softening	A
Class number			0	1	2	3	4	5	6	7	8	9	The following classes have an approximate volatile matter content of: 6: 33-41% 7: 33-44% 8: 35-50% 9: 42-50% Coal samples ≤ 10% ash		
Class parameters	volatile matter (daf)		0-3	>3-10	>10-14	>14-20	>20-28	>28-33	>33	>33	>33	>33			
	Heat of combustion, kJ/kg (af) (equil with air at 30°C, 96% hum.)		—	—	—	—	—	—	>32450	>30150-32450	>24550-30150	≤25540			

2.2.3. SULPHUR AND NITROGEN IN COAL

The heteroatoms of both sulphur and nitrogen are found in coal. Knowledge of how sulphur and nitrogen is bound into the coal structure is important in helping understand the formation of their oxides during coal combustion or gasification processes.

2.2.3.1 Inorganic sulphur

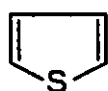
Coal contains both organic and inorganic forms of sulphur. The proportion of the two can vary depending on the type of coal. Metal sulphides account for most of the inorganic sulphur found in coal. The majority of inorganic sulphur is present as iron sulphide in the form of FeS_2 , sulphides of zinc, lead and iron/copper (chalcopyrite) being present in very small quantities. FeS_2 forms two crystalline structures; pyrite (cubic) and marcasite (orthorhombic), both are usually termed together as pyrite as this is usually the most predominant form¹⁰. The pyrite in coal usually exists as framboids (1-40 μm in diameter) or aggregates up to millimetres in diameter. It is thought that pyrite may be formed in the coal by the reaction of H_2S with ferric, or ferrous ions present in the ground waters during the coals geological history^{11,12}.

Inorganic sulphur can also be present in much smaller amounts as sulphates of barium, calcium and iron, but sulphate sulphur usually accounts for less than 0.1% of the total sulphur in coal. Elemental sulphur usually accounts for less than 0.2%.

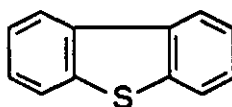
2.2.3.2 Organic sulphur

Organic sulphur in coal can be present in aliphatic, aromatic and heterocyclic (usually thiophenic) structures¹¹, see below.

1. Aliphatic compounds, sulphides and disulphides (CH_3SH , R-S-R and R-S-S-R).
2. Aromatic sulphides and disulphides (Ar-S-Ar and Ar-S-S-Ar).
3. Thiophenic compounds.



Thiophene



Dibenzothiophene

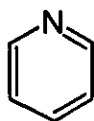
The majority of organic sulphur in high ranked coal is thiophenic¹³. Higher concentrations of aliphatic sulphur compounds tend to be found in lower rank coals. Trends show the general aromatic sulphur content (thiophene and aromatic sulphides) increasing, and the aliphatic sulphur content decreasing with increasing coal rank¹⁴. One explanation proposed for this involves the thermal stability of these different forms of sulphur. Aliphatic compounds are thermally less stable than aromatic and thiophenic compounds and during the coalification process these compounds may change through aliphatic sulphides (R-S-R) to thiophenes via a series of condensation reactions. Alternatively they may be destroyed leaving behind the thiophenes and aromatic compounds^{11,15}. Generally, lower rank coals have lower (total) sulphur contents.

It is likely that the organic sulphur in low sulphur coals is derived from the sulphur contained in the original plant material with higher sulphur coals deriving their sulphur from the bacterial reduction of the sulphates that are found in salt water that can make its way into the peaty material during diagenesis¹⁶. H_2S is thought to react with the peat, incorporating sulphur into the organic matter.

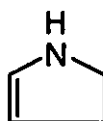
2.2.3.3. Nitrogen

Nitrogen in coal differs to sulphur in that all the nitrogen in coal is present in organic compounds associated with the carbonaceous structure of the coal as it in fact originates from the proteins found in the original source plant material.

Nitrogen in coal is present chemically bound in the organic matrix as pyridinic and pyrrolic compounds with some evidence of small quantities of quaternary nitrogen and amine groups. Examples of pyridinic and pyrrolic structures are shown below.



Pyridine (six membered ring)



Pyrrole (five membered ring)

The total nitrogen of coal has been shown to vary with rank. Bouda et al¹⁷ found in a study of Indonesian coals that the total nitrogen increases with rank up to 80wt.% C (daf) and then drops off markedly.

A similar study on UK coals¹⁸ shows a similar trend for total nitrogen to increase with rank, reaching a maximum at around 85% C (dmmf), then decreasing with a further increase in rank. It was also noticed that the C/N ratio of the coal decreased, between 80 and 85%, indicating an accumulation of nitrogen in relation to the carbon. Loss of carbon atoms during diagenesis, in the form of hydrocarbons, is offered as an explanation to this reduction of the C/N ratio particularly as, during coalification, decarboxylation is said to be complete when the carbon content exceeds about 80wt.% C (daf).

Burchill's¹⁸ study of UK coals, using X-ray photoelectron spectroscopy (XPS) shows pyrrolic nitrogen to be the predominant form of nitrogen in coal. Pyridinic nitrogen increased with coal rank between 80-90 wt% carbon content whilst the pyrrolic nitrogen began to decrease above 84 wt% carbon content. This trend is shown in Figure 2.5.

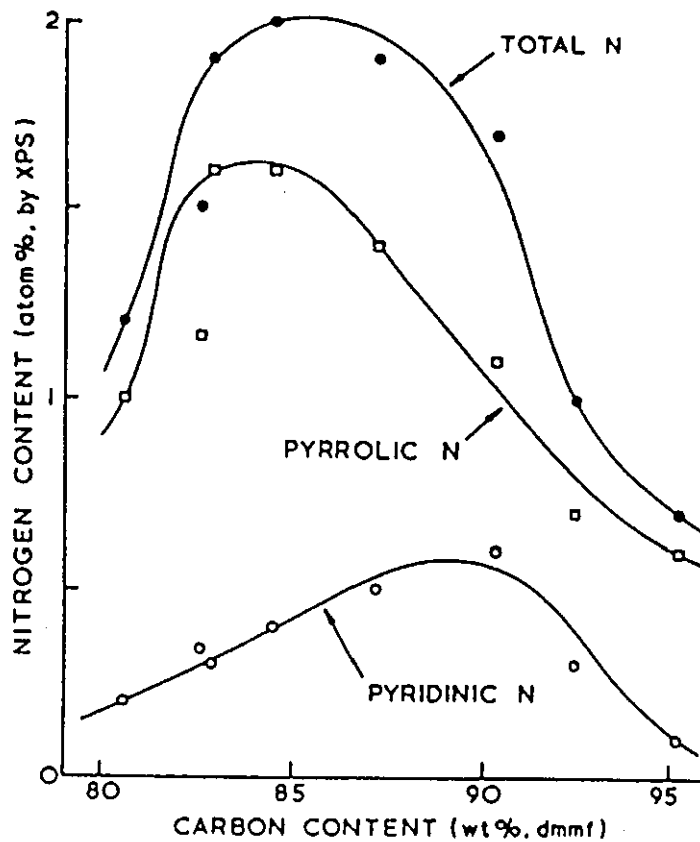


Figure 2.5 Variation of nitrogen functionality with coal rank.¹⁸

It is generally agreed that pyrrolic nitrogen is the predominant form of nitrogen in coal, with pyridinic N increasing with rank¹⁹. Discrepancies, however, in the analytical techniques of XPS and X-ray absorption near-edge structure spectroscopy (XANES) have lead to doubts in the actual quantity of quaternary nitrogen and the existence of amine groups in coal.^{19, 20}

2.2.4 MINERAL MATTER

Coals contain a component of mineral matter and can be regarded as being unbound to the organic part of the coal. The mineral matter itself can be made up from differing quantities of inorganic compounds, the bulk of which are usually alumino-silicates such as kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ making up 50% by mass of the mineral matter content. The rest is usually made up of carbonates of Fe, Ca and Mg, gypsum CaSO_4 , pyrite FeS_2 and silica SiO_2 . There are also present small quantities of trace elements such as Ni, Cu, Cr, Pb and Zn which have implication on gaseous emissions and the disposing of ash with possible leaching of these metals into ground waters.

When a coal is heated or burnt the mineral matter loses around 10% of its mass with the release of CO_2 and H_2O during calcination. The material left after complete combustion of a coal is termed the ash. The behaviour of the ash during combustion at elevated temperature is important to combustion applications. Ashes with a low fluid temperatures are suited to applications which remove the ash in liquid state and high fluid temperature ashes are suited to solid state removal. Also important to consider is the transition of the ash from solid to liquid state, determining at what temperatures the ash is likely to soften and agglomerate or stick to the walls of a furnace or to boiler tubes.

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2.3 COAL COMBUSTION SCIENCE

2.3.1. COAL ON HEATING

The behaviour of coal during heating and thermal decomposition can have significant effects on the subsequent combustion process, such as:

- the ignition and stability of flames
- reactivity of chars produced
- conversion of sulphur and nitrogen species to SO_2 and NO_x

2.3.1.1. Devolatilisation

When a coal particle is heated it begins to decompose and volatile material is driven off. This decomposition is termed devolatilisation or pyrolysis and is the first stage of all combustion and gasification processes. Up to temperatures of 300°C some water is driven-off from the coal along with the desorption of some gases contained in the pores of the particle structure. Above 400°C , depending on the rate of heating, coal softens to a plastic state during which gaseous hydrocarbons, liquid tar and other gases evolve from the coal. During this plastic phase a coal particle can swell drastically and change shape; angular coal particles can become almost spherical after devolatilisation. The swelling properties of a coal particle mainly depend on the coal type, heating rate and size of coal particle. At temperatures above 550°C the developing char begins to harden as its structure stabilises and shrinks back slightly. Figure 2.6 shows the typical devolatilisation behaviour of coal identifying the regions of volatile release and particle size change²¹.

The amount of volatile matter given off by a particular type of coal during devolatilisation depends mainly on the pyrolysis temperature; increasing with increasing temperature. The type of species evolved during devolatilisation varies with coal type. Heating rate and pyrolysis temperature can also have an effect on the amount and type of volatile matter. Primary and secondary reactions can occur within the char particle causing the cracking of high boiling point tars; leading to the formation of lower molecular weight

tars and light hydrocarbon gases. Oxygen is evolved from coal as H_2O , CO and CO_2 , occurring up to temperatures of around 1050°C ²².

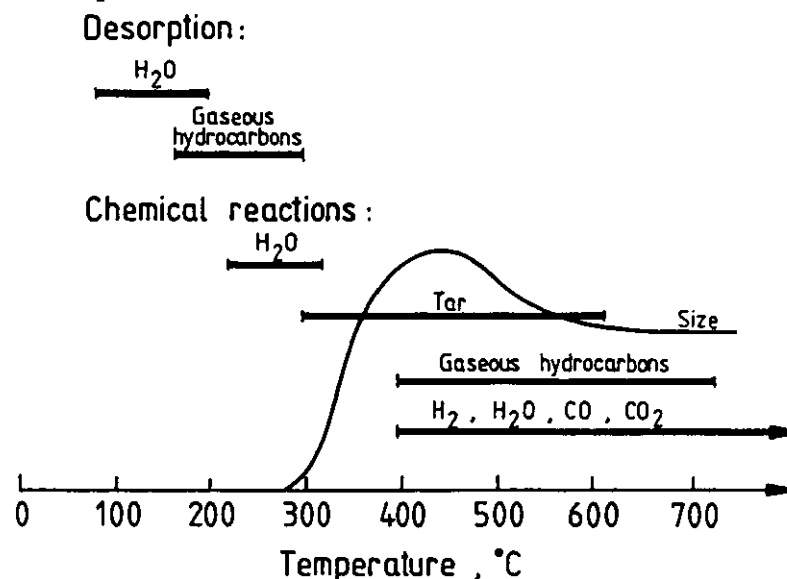


Figure 2.6. Regions of volatiles release during particle heating.²¹

At temperatures between 300 and 600°C high molecular weight tars and permanent hydrocarbon gases dominate the yield of volatiles. The release of hydrocarbon gases lasts to higher temperatures. Table 2.6 shows typical gaseous species evolved during devolatilisation and how temperature and coal type effect the proportion of individual species evolved, Wyodak is a sub-bituminous coal the other two coal types were not specified in the paper²². Increasing the heating rate has been shown to increase the yield of liquid products produced on pyrolysis^{23,24}. This may be due, in part, to the pyrolysis products being evolved quicker and condensing before secondary reactions take place.

Table 2.6. Comparison of the wt. fractions of major gas species after pyrolysis at 1000°C and 1400°C ²².

Species	Coal mass-fraction represented by gas collected at designated temperatures					
	Arkwright coal		Wyodak coal		Illinois No. 6 coal	
	$T = 1000^\circ\text{C}$	1400°C	1000°C	1400°C	1000°C	1400°C
CO	0.030	0.057	0.107	0.202	0.060	0.123
CH_4	0.035	0.057	0.027	0.036	0.024	0.020
CO_2	0.003	0.008	0.094	0.067	0.026	0.024
C_2H_6	0.011	0.002	0.009	0.001	0.005	0.001
C_2H_4	0.015	0.028	0.007	0.023	0.005	0.013
C_2H_2	0.000	0.008	0.000	0.004	0.000	0.002
Sum of gas detected	0.094	0.225	0.244	0.333	0.120	0.183
Wt.-fraction lost	0.428	0.459	0.540	0.608	0.461	0.579
Sum/wt.-fraction lost	0.220	0.490	0.452	0.548	0.260	0.316

The heating value and make-up of the volatile mixture produced on initial devolatilisation will have an effect on the ignition and heat-up of the other coal particles during the early part of the combustion process, especially in pulverised coal flames.

2.3.1.2. Pyrolysis chars

Even before a coal particle is heated it has a porous structure and may possess a large internal surface area consisting of many inter connected pores of various sizes. The size distribution of these pores fall into the following categories: Micropores $<2\text{nm}$, mesopores $2 - 50\text{nm}$ and macropores $>50\text{nm}$. During pyrolysis the physical properties of coal particles change; shape, size and internal surface area are all affected.

When heated rapidly, most coal particles swell. The extent to which they swell depends on the type of coal, particle diameter and particle heating rate. The free swelling index gives some indication of how a coal behaves on heating but does not take into account different heating rates. At the high rates of heating found in pulverised fuel and fluidised bed combustion, the movement of the volatiles through the plastic phase of the coal during devolatilisation has a significant effect on the physical structure of the final char. Some coal particles become almost liquid-like with bubbles of volatiles erupting from the particle surface²². As a result the particles swell and change shape, becoming more spherical in appearance. Particles formed like this exhibit large porosities. Other particles may behave differently; the coal becomes less plastic and the volatiles erupt from fissures or cracks formed during heating. As a result this type of particle swells less and retains a similar shape to the parent coal particle. In certain cases the pores on the outside of a coal particle may start to close during devolatilisation causing large pressures to build up leading to particles rupturing.

The maceral composition of the coal particle also plays a role in its behaviour during rapid heating. Rapid pyrolysis experiments on density separated coals²⁵ has found the lighter fraction, containing the most exinite, to produce chars with the highest internal surface area. The heavier fraction, containing mainly inertinite, produced chars with the lowest internal surface areas. The yield of volatiles from these density fractions was also seen to follow the same trend; volatile yield decreasing with increased density. Figure

examples of the typical morphology of chars produced from the different density fractions of coal during rapid pyrolysis.

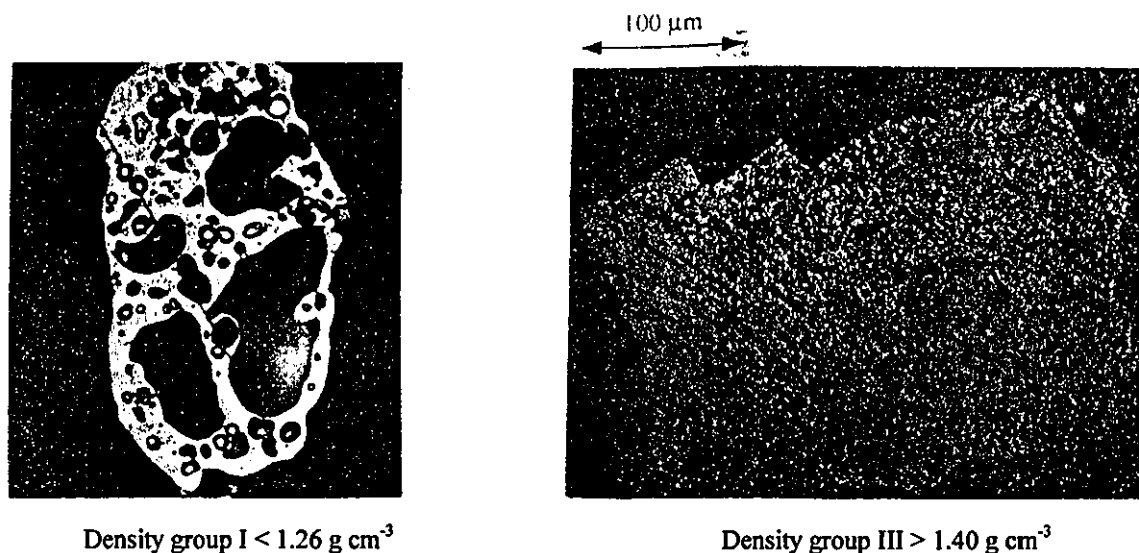


Figure 2.7. Reflected light micrographs of pyrolysis chars typical of the different density fractions.²⁵

Other work²⁶ shows the structural differences observed amongst pyrolysis char particles produced at 1230°C using the ICCP classification of chars²⁷. Particle shapes can vary from spherical with one distinct pore (cenosphere), honeycomb in appearance with many pores (network) or relatively unchanged in appearance (solid).

2.3.1.3. Coal sulphur during pyrolysis

As discussed in section 2.2.3, sulphur in coal occurs in organic and inorganic forms. Pyrite (FeS_2) accounts for the majority of inorganic sulphur, whilst the organic sulphur is made up of varying quantities of aromatic sulphides, aliphatic and heterocyclic compounds depending, to a degree, on coal rank^{13,14}.

During devolatilisation a considerable amount of the coal sulphur is released into the volatiles and unlike nitrogen, the majority of this release is into the gaseous phase^{28,29}. Pyrolysis typically sees a depletion of the sulphur concentration in the char with respect to the parent coal. The main components of sulphur release during devolatilisation are H_2S , CS_2 , COS and thiophenic-based compounds.

The type of sulphur present in the coal can affect the quantity of sulphur released into the volatiles. Lower rank coals may contain larger quantities of aliphatic sulphur that readily evolves at low pyrolysis temperatures, whereas higher ranked coals may contain a higher proportion of thermally more stable thiophenic compounds. The yield of sulphur into the gaseous pyrolysis products tends to be the highest for low rank coals, with some anthracites showing no significant release of sulphur into the gas below temperatures of 700°C³⁰.

The decomposition of the pyritic sulphur contained in the coal also contributes to the volatile sulphur release. Work by Grygiewicz et al³¹, concluded that above 330°C pyrite in coal begins to decompose. At 700°C all pyrite had decomposed to leave behind ferrous sulphide (FeS) in the char. It is argued that some of this sulphur released forms bonds with the char matrix, and that the conversion of some of the sulphidic sulphur to thiophenic sulphur occurs during pyrolysis. Above 1000°C the ferrous sulphide begins to decompose. At this temperature thiophenic sulphur compounds can still persist in the char.

The maceral composition of the coal can effect the sulphur release during devolatilisation. At high rates of heating (4000 - 6000 K/s), results²⁵ from pyrolysis experiments on a density separated low sulphur coal showed a tendency for the lighter density fraction (more concentrated with exinite) to release the most sulphur into the volatiles during pyrolysis. What was of particular interest was that this fraction released half of its organic sulphur into the tar, 40wt.% remaining in the pyrolysis char.

2.3.1.4. Coal nitrogen during pyrolysis

How nitrogen is bound into the coal structure (see section 2.2.3) determines, to a certain degree, how it behaves during devolatilisation. Nitrogen is known to exist in coal bound in the organic matrix present mainly as pyridinic (six membered ring) and pyrrolic (five membered ring) compounds¹⁸. The proportion of these nitrogen functionalities in coal is thought to change during pyrolysis. Wójtowicz et al²⁰ have shown that as the severity of devolatilisation increases, the transformation of pyrrolic nitrogen to pyridinic nitrogen

progresses in the remaining pyrolysis char. Under high temperature and prolonged heating conditions (900°C for 1 hour), all remaining pyrrolic-N was converted to the more thermodynamically stable pyridinic form in the char. It is to be noted that in this study the presence of quaternary nitrogen was attributed to oxidised pyridinic forms of N. There is also evidence³² that some lower rank coals contain a significant amount of aliphatic (amine group) nitrogen and that this form of nitrogen is readily lost on devolatilisation of the coal; up to 70% of the total nitrogen being expelled with volatiles.

Of particular interest to the study of coal combustion processes, is how the nitrogen present in the coal becomes distributed between the pyrolysis char, tar and gases. Significant release of coal nitrogen does not begin until temperatures of around 350°C are reached. At pyrolysis temperatures below 1000°C, experimental results²² show that the wt.% of the total nitrogen released into the volatiles is essentially the same as the wt.% coal lost to volatiles. At pyrolysis temperatures above 1000°C the proportion of the nitrogen released into the volatiles increases above that of coal volatiles generated, leading ultimately to negligible quantities of nitrogen remaining in the pyrolysis char produced at 1800°C. This implies that at higher temperatures the aromatic rings that hold the nitrogen split, releasing the nitrogen from the coal matrix into the volatiles. This is consistent with the findings of Chen et al³³ in a study of 6 coals. It was found that at devolatilisation temperatures above 900°C nitrogen carries on being released into the volatiles when the formation of the char has effectively finished.

Experiments by Solomon et al³⁴ on a suite of coals ranging in rank from lignite to high volatile bituminous coal studied the distribution of nitrogen between the pyrolysis products char, tar and gas with changing devolatilisation temperature. The results in figure 2.8. show how, as a function of devolatilisation temperature, the proportion of nitrogen remaining in the char follows closely the weight percentage of char remaining. The solid black line represents the model proposed by the authors showing the proportion of N dropping below the wt.% of char at around 1100°C.

The model that Solomon et al³⁴ proposed is a first order kinetic model which defines two distinct forms of nitrogen release during devolatilisation (assuming devolatilisation temperatures below 1000°C). Initially the nitrogen is released in the heavy tar molecules without any substantial change in the molecular form from the parent coal. Then at higher temperatures nitrogen is released from the char as the N-containing rings decompose. These two processes have quite different rates with the latter being two orders of magnitude less than the first.

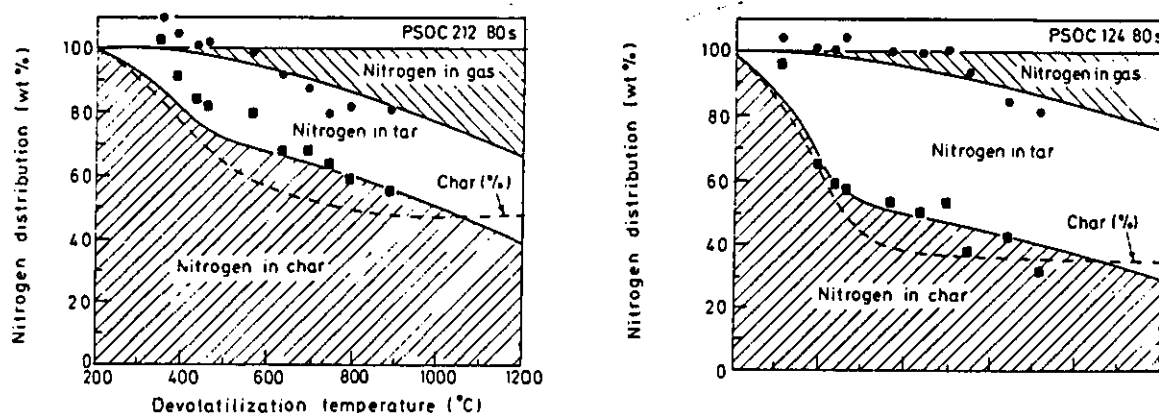


Figure 2.8. Nitrogen distribution in pyrolysis products, experimental results for two bituminous coals³⁴ (Solid line denotes model; dashed line is wt.% char formed).

Wanzl et al²⁸ showed, in pyrolysis experiments on two German high volatile coals, that at 800°C the pyrolysis reaction was over within 4 seconds (heating rate 6000 K/s) and that the pyrolysis tars contained almost identical concentrations of nitrogen as the parent coal.

Some studies^{22,34} have found there to be a slight concentration of nitrogen in the char during the initial stages of devolatilisation. This can be explained by the evolution of nitrogen free compounds such as CO, CO₂, H₂O and CH₄.

2.3.2. COMBUSTION OF COAL PARTICLES

During the initial stage of combustion a coal particle heats up rapidly and releases considerable amounts of volatile matter (see section 2.3.1.1). This initial volatile matter can burn some distance from the particle in a detached pre-mixed flame. The rate of volatile release then drops forming an attached diffusion flame with fuel rich regions surrounding the particle. The porous carbonaceous residue remaining after devolatilisation is then consumed by the available oxygen heterogeneously in a spherical diffusion flame. Figure 2.9 shows a schematic of a single coal particle burning in air through these three stages (based on a description by Wendt²²).

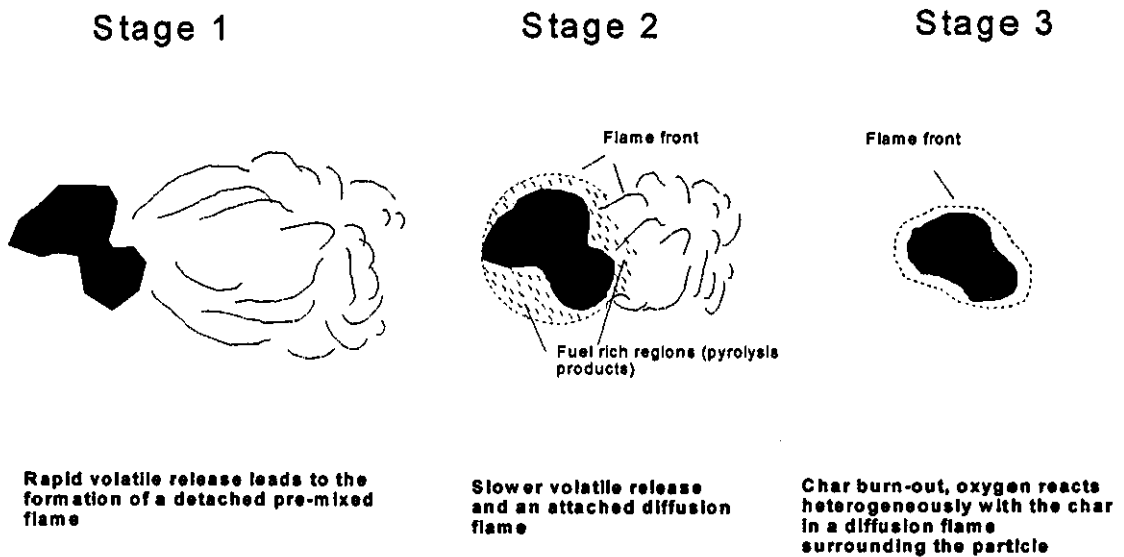


Figure 2.9. A schematic of a single coal particle burning

In practical combustion processes these three stages of coal combustion do not occur perfectly sequentially. In reality coal particles are not spherical and all three stages may be occurring simultaneously on one particle as it receives different local heating conditions.

In combustion processes that require stable flames, as in pulverised fuel combustion, the initial volatile release of a type of coal becomes important. It is this which determines flame speed and therefore affects the positioning of the flame with respect to the burner

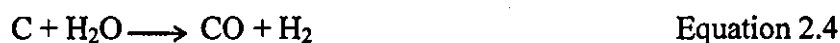
nozzle. The way in which the volatile matter is formed and its effect on the char structure is also important in the later char burn out phase.

2.3.2.1. Char burn out

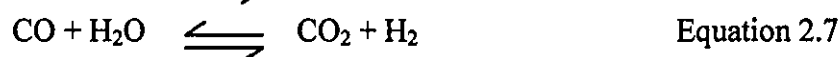
Once all the volatile matter has been driven off from a coal particle, heterogeneous combustion of the char particle begins. The oxidant diffuses from the bulk gas through the stagnant layer of gas surrounding the particle and reacts with the char. The reaction products then diffuse away back into the bulk gas. Two overall reactions of carbon with oxygen take place at the particle surface at temperatures $<700^{\circ}\text{C}^{21}$.



As the combustion temperature increases there is a build up of reaction products around the particle surface. Other heterogeneous reactions now take place and if the presence of water vapour is also considered, the following reactions occur:



And homogeneously in the gas phase:



Not all the reaction takes place on the outer surface of the char particle. Coal chars can be highly porous and much of the available surface area is contained internally in narrow pores. Therefore, three steps exist that can control the rate of combustion of a coal char particle: i) chemical reaction, ii) pore diffusion and iii) gas-film diffusion

These rate controlling steps produce different regimes or *zones* of combustion³⁵. At low particle temperatures the chemical reaction is so slow that the oxygen from the bulk gas diffuses easily to and into the particle; *zone I*. The uniform oxygen concentration means the reaction takes place throughout the volume of the char particle. The combustion reaction in zone I is therefore controlled by the chemical reaction kinetics.

At higher temperatures in *zone II*, the rate constant of the chemical reaction increases significantly according to the Arrhenius term $\exp(-E/RT)$. The oxygen still diffuses effectively to the particle and penetrates the pores, but because of the increased rate of the heterogeneous reaction, its concentration in those pores is greatly reduced. So here a combination of pore diffusion and chemical reaction kinetics controls the overall combustion reaction.

Finally, at even higher temperatures *zone III* kinetics are observed. Here the chemical reaction is so fast that the oxygen is quickly consumed at the particle surface. The overall reaction is therefore controlled by the diffusion of the oxygen (or oxidant) from the bulk gas to the particle surface. Figure 2.10 shows the general relationship between the particle temperature and the combustion reaction rate constant.

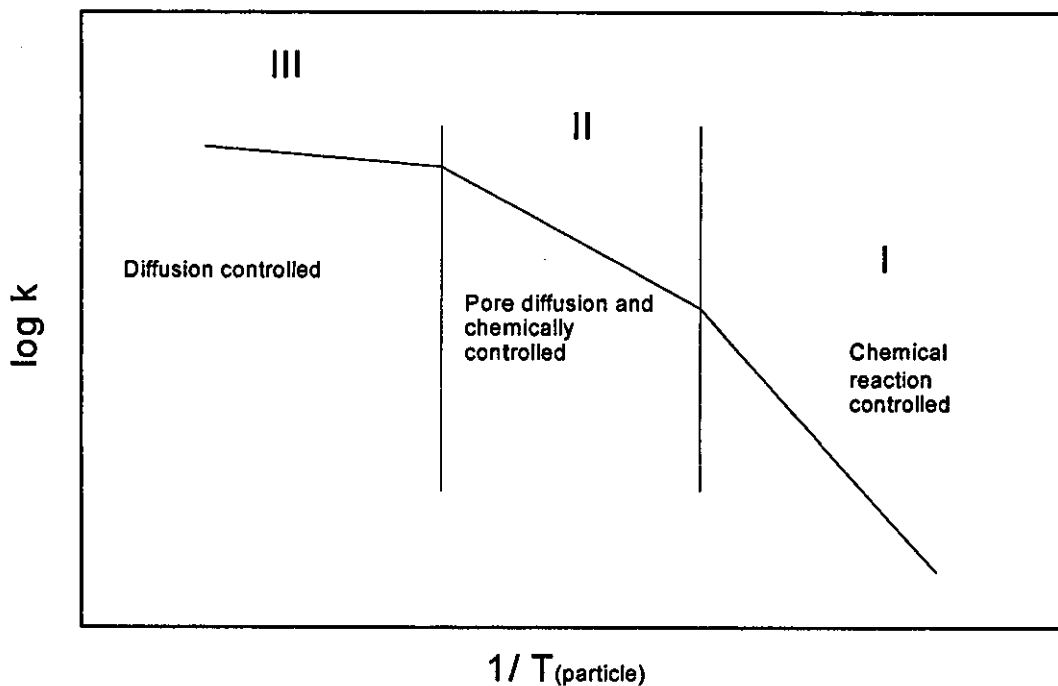


Figure 2.10. Combustion rate constant as a function of particle temperature

The temperature at which a combustion reaction shifts zones depends on the porous structure of the char and on the particle size. Wendt²² reviews some of the results reporting the differences in combustion rates found between brown coal and bituminous coal chars. He concludes that there is evidence to support a strong link between the devolatilisation processes forming pores and the subsequent burn-out rate of the char.

Particle diameter also has an effect. The smaller the particle diameter the larger the mass transfer coefficient. For this reason small particles in industrial combustion processes tend to burn following zone II kinetics. The larger the particle diameter the lower the temperature at which the combustion converts to fully diffusion controlled, zone III²¹.

2.3.2.2. Formation of sulphur dioxide (SO₂)

Previous sections have discussed how sulphur is bound into the coal structure (2.2.3.1 and 2.2.3.2) and how this sulphur behaves during devolatilisation (2.3.1.3). The main components of sulphur release during heating of a coal particle are H₂S, CS₂ and COS^{28,29}. During combustion of a coal particle these sulphur species are readily oxidised further to SO₂.

The environmental impact of SO₂ emissions from coal combustion processes is well documented²⁻⁴; SO₂ is the major cause of acid rain. Techniques exist that can remove SO₂ from the exhaust gases of various industrial combustion/ gasification processes. These will be discussed in detail in the sections covering pulverised fuel combustion and fluidised bed combustion.

2.3.2.3. Formation of the oxides of nitrogen (NO_x)

Oxides of nitrogen are produced during the combustion of coal. Nitric oxide (NO) is the major oxide of nitrogen in flue gases with nitrogen dioxide (NO₂) and nitrous oxide (N₂O) forming much smaller quantities. NO and NO₂ contribute to the problems of acid rain and photochemical smog, N₂O is a greenhouse gas. The term NO_x is commonly used to describe the sum of the two nitrogen oxides, NO and NO₂.

There are two sources of NO in the combustion of coal; oxidation of atmospheric nitrogen and oxidation of the nitrogen bound in the coal (fuel nitrogen). During coal combustion the major portion comes from the latter source. Coal typically contains between 1 and 2.5% nitrogen by mass (daf).

In coal combustion processes which produce high flame temperatures in excess of 1200°C, such as pulverised coal burners, some NO_x is produced from the oxidation of molecular nitrogen present in the combustion air. The majority of NO produced in this way follows the Zeldovich mechanism³⁶, the two principle reactions being.



In fuel rich mixtures however, the following reaction becomes important, (extended Zeldovich)



Equation 2.8 is the rate determining step in the formation of NO. The overall rate of 'thermal NO' production is highly dependent on combustion temperature, and to a lesser degree on O concentration and residence time. As a consequence, thermal NO reduction techniques rely on controlling the flame temperature, air/ fuel ratio and residence times at peak combustion temperatures³⁷.

Some NO can be produced rapidly in the flame front by the 'prompt' mechanism, here fragments of hydrocarbons directly attack the nitrogen molecules. 'prompt NO' is associated with fuel rich regions, the main contributors being CH and CH₂³⁸ (see equations 2.11 and 2.12), but is only a weak function of temperature.



As Figure 2.11 shows, the products from these reactions go on further to form NO

The most important source of NO_x in coal combustion processes is from the nitrogen bound in the coal itself, or fuel-N. The oxidation of nitrogen containing compounds is rapid, occurring in the time span comparable to that of the combustion reactions³⁶.

The mechanisms that govern the conversion of fuel-N to NO_x are numerous. Figure 2.11 taken from Bowman et al³⁹ shows the mechanisms involved in the conversion of fuel-N to NO, also showing the formation of 'prompt NO'.

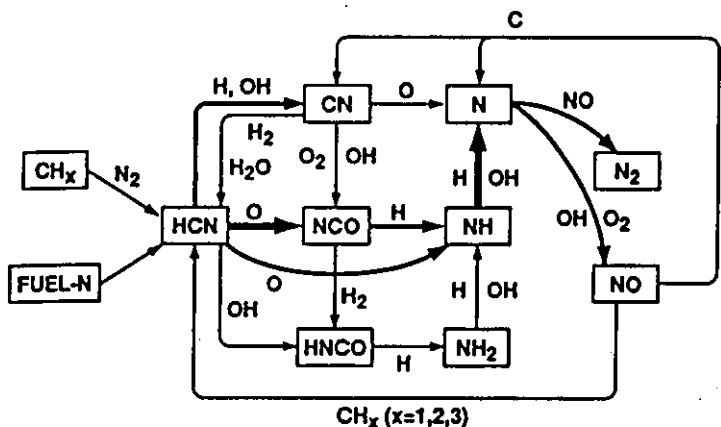


Figure 2.11. The various reaction mechanisms involved in the formation of NO from fuel-N and the 'prompt' route³⁹.

This can be simplified further to models such as the one shown in figure 2.12³⁸. Here, it is assumed that all the fuel-N is initially converted to HCN and then eventually either oxidised to give NO or reduced to give NH_3 or N_2 . In fuel lean conditions the formation of NO is favoured, in fuel rich conditions more NH_3 and N_2 is produced. Also there is increased chance that the re-burn reaction will occur, depleting NO.



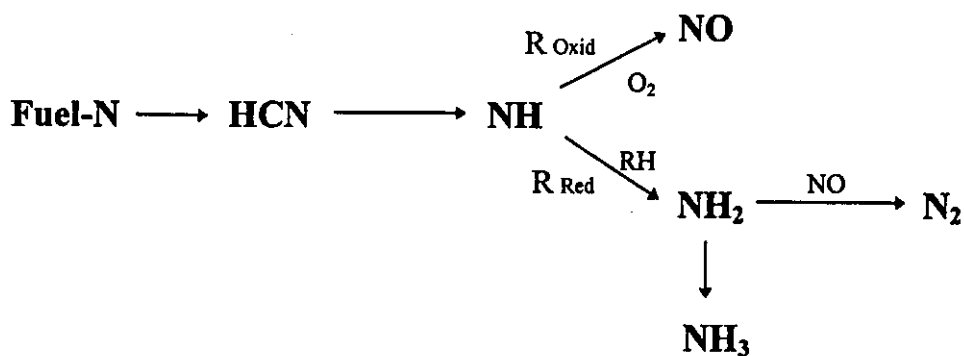


Figure 2.12 Simplified model of fuel-N conversion during coal combustion

NO can also be reduced back to molecular nitrogen, catalysed by the coal char particle itself. Work by Shimizu et al⁴⁰ on the combustion of coal chars observed that those chars possessing the highest internal surface area, hence having a higher combustion rate, produced the lowest conversion of char-N to NO_x due to a reduction of NO. Other work⁴¹ has reported the same effect.

When coal particles are burnt they initially release a certain amount of volatiles containing some fuel-N and if produced in a fuel lean environment will readily form NO. Burning the coal initially in a fuel rich environment can therefore reduce the quantity of NO_x formed by utilising the mechanisms described above. Secondary air can then be supplied to complete the combustion process i.e. the burn-out of the coal char. This is the principle behind air staging low NO_x burner design adopted in most modern industrial combustion applications to reduce NO_x emissions (discussed in Sections 2.4 and 2.5 on pulverised fuel combustion and fluidised bed combustion respectively).

2.4. PULVERISED FUEL COMBUSTION

The majority of coal fired power stations in the UK, and indeed the world, use pulverised coal ($<100\mu\text{m}$) as their fuel for steam generation. The small particle sizes ensure rapid combustion and hence fast heat release rates are obtained suitable for large scale power generation. However, one drawback of using pulverised fuel combustion is its impact on the environment in the form of gaseous pollutants, namely oxides of nitrogen and sulphur. Careful burner design and retrofit technologies now exist which can significantly reduce these emissions.

2.4.1. PULVERISED FUEL BURNERS

In typical pulverised fuel burners the pulverised coal particles (mean size of $60\mu\text{m}$ and not usually greater than $100\mu\text{m}$) are transported to the burner nozzle by a primary air supply. This primary air usually consists of around 20% of the total air needed in the combustion process. To give flame stability and to keep the combustion chamber as small and as compact as possible the quantity of primary air used is usually chosen to give maximum flame speed and still maintain effective transport of the suspended solids (for particles of this size the transport velocity of the air stream needs to be around 20m/s). Secondary air is usually fed around the flame to complete the combustion process

The combustion itself takes place in a chamber lined with steel tubes containing water. To utilise the chamber volume effectively burners are used in multiples. Figure 2.13 shows a schematic of a pulverised fuel boiler. The drawbacks of pulverised fuel combustion are that for the fast heat release required, the fuel and air mixtures have to be fed into the combustion chamber quickly, therefore a large combustion chamber is needed for complete combustion of the coal in the flame. Fly ash choking of exhaust flues can be a another drawback.

The way a p.f. burner mixes the primary and secondary air in the flame is important and affects combustion efficiency, char burn out and pollutant formation. The different firing configurations and type of burner are discussed below.

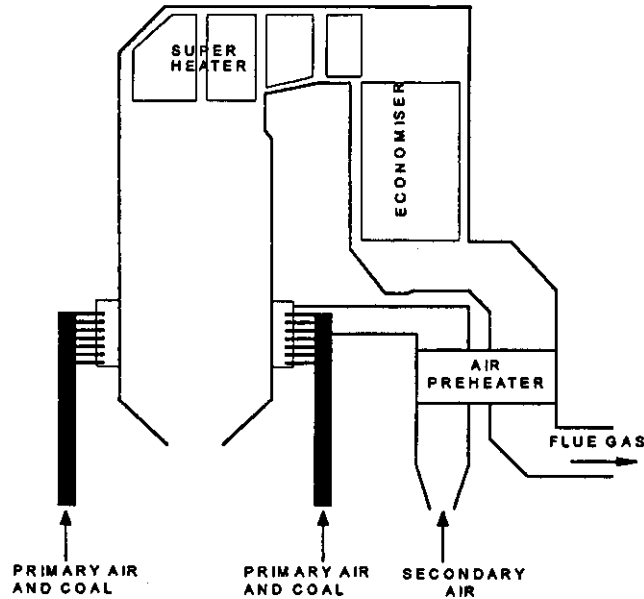


Figure 2.13. A schematic of a pulverised fuel boiler

2.4.1.1. Wall fired

Figure 2.14 shows a schematic of a wall fired flame. The burner fires into a chamber lined with water cooled tubes. The burner imparts swirl to the primary air/fuel mixture promoting hot air recirculation to help stabilise the flame. Secondary air is introduced, with swirl, around the outside of the primary air/fuel to complete char burn out.

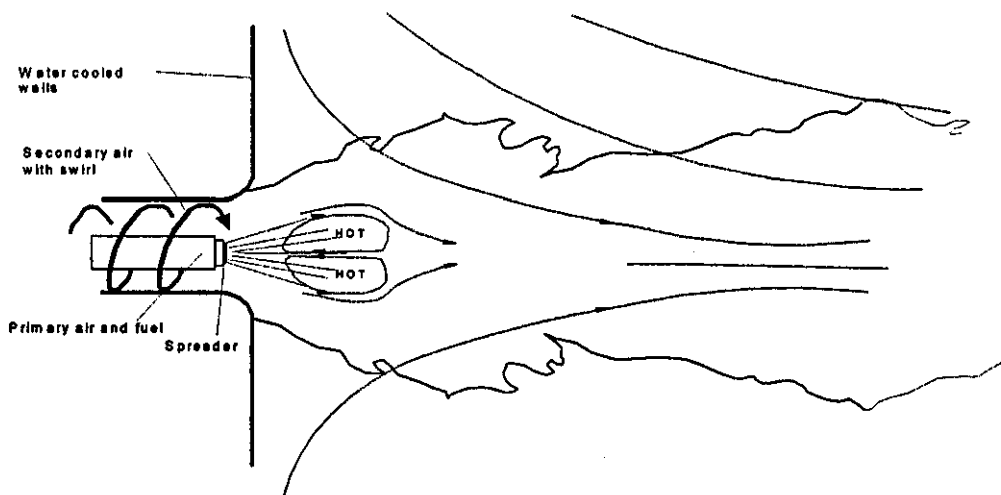


Figure 2.14. A wall fired flame

The coal particles enter the chamber and receive radiated heat from the walls, the flame and from the convection of hot recirculating gases. The coal then rapidly devolatilises, the volatiles ignite and react with the oxygen in the primary air stream. The remaining volatiles and char are burnt later in the flame utilising the secondary air. It is important at the initial devolatilisation stage to avoid excessive contact of early generated nitrogen species with oxygen as this results in high NO_x emissions. Too little air in the primary supply, though, could delay particle ignition and lead to the flame becoming detached and to the possibility of it blowing out.²²

Wall fired burners can be mounted on one side of a chamber giving an easy configuration of air/fuel supply. The disadvantage of this is poor flame stability and uneven heating of the chamber walls. Usually to avoid this, burners can be mounted on opposite walls. This has the advantage of increasing the temperature of the recirculating gases and leads to greater flame stability. More even heating of the chamber walls can also be achieved using opposite side wall burners.

2.4.1.2. Tangentially fired

Here the burners are placed in each corner of a combustion chamber with a square cross section. Each burner fires tangentially as shown in Figure 2.15. Primary air and coal are introduced at the centre of each burner with the secondary being introduced on the outside. Fired in this way, a fuel rich zone is produced in the centre of the chamber. Here most of the initial volatiles are produced before being oxidised by the secondary air. This results in reduced NO_x emissions due to the NO formed in the fuel rich region being reduced to N_2 .

With this type of firing there is considerable flame-to-flame contact. This, along with good hot gas recirculation, helps to give excellent flame stability. No swirl is imparted to the fuel/air mixture in tangentially fired units and the added flame stability allows axial burners to be used. Very even heating of the walls is also achieved.

One disadvantage of a tangentially fired unit is a higher degree of slagging in the combustion chamber.

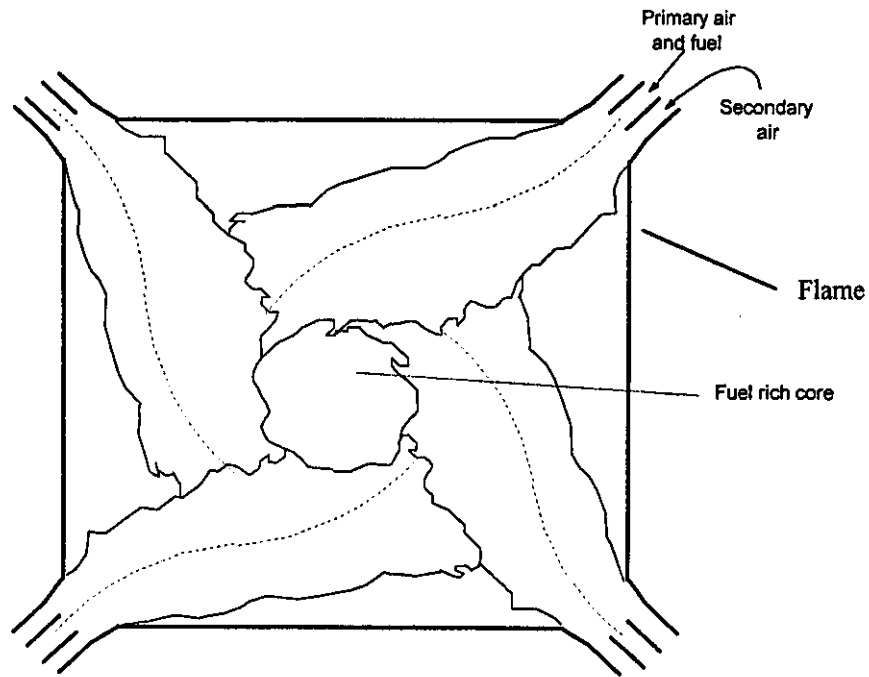


Figure 2.15. Tangential firing (corner firing)

2.4.1.3. Cyclone firing

Cyclone fired units use a larger coal particle size of around 0.5mm. The coal and primary air are injected into a prechamber tangentially at high velocity ($100 - 150\text{ms}^{-1}$). The secondary air is introduced to swirl in the same direction. The burn is very intense producing high flame temperatures and a high rate of heat release. This causes the ash particles to melt forming a slag layer on the walls of the prechamber. The high centrifugal forces cause the coal particles to be thrown onto the prechamber wall, sticking there, and extending their residence time. Some tertiary air is added along the axis of the burner to burn fines in the central vortex of the cyclone. The hot combustion gases pass through into the main chamber where most of the heat transfer takes place.

Generally low ash-fusion point coals are used in cyclone burners. The prechamber is usually tilted slightly to allow the slag to be tapped off, 90% of the ash can be removed in this way²¹. One drawback of cyclone burners as a consequence of their intense combustion process, is high NO_x emissions.

2.4.2. REDUCING EMISSIONS DURING PULVERISED FUEL COMBUSTION

During the intense pulverised fuel combustion process, oxides of nitrogen and sulphur readily form. Controlling the emissions of these pollutants is possible within the pulverised fuel combustion process or as retrofit technology. These have significant implications on either the overall efficiency of the combustion process or the capital/running costs of the plant. However, with strict control on gaseous emissions from large combustion plant throughout Europe becoming stricter, these technologies are having to be utilised more and more.

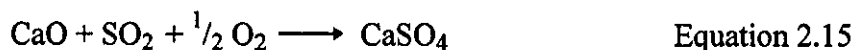
2.4.2.1. Direct SO₂ removal

During pulverised fuel combustion most of the sulphur present in the coal is oxidised to SO₂. One of the methods open to reduce the emissions of SO₂ is to directly remove it from the combustion process by injecting the flame with an absorbent such as limestone. The sorbent can be added with an air supply around the flame which is subsequently mixed into the flame.

Initially the limestone calcines to give calcium oxide, following the overall equation:



The calcium oxide reacts with the sulphur dioxide in the combustion chamber following the overall reaction:



This process is cheap in comparison to the large capital expenditure of flue gas desulphurisation but is difficult to optimise. Direct removal of SO₂ in a pulverised fuel flame is only effectively possible in the temperature region 750°C to 1100°C. Below 750°C calcination of the limestone does not take place and above 1100°C the CaSO₄ formed begins to decompose. Overall flame temperatures in pulverised fuel combustion

are usually in the region of 1600°C . Careful flame aerodynamics through burner design can be used to recirculate gases in the combustion chamber to bring flame temperatures down, in certain regions, to those more suitable for sulphur removal.

It is unlikely that under conditions applicable to the UK that the maximum removal of sulphur, with this process, would be above 40% with a stoichiometric ratio of limestone to sulphur⁴². This type of process is more suited to smaller industrial boilers where lower quantities of fly ash and waste limestone are produced.

2.4.2.2. Flue gas desulphurisation (FGD)

Flue gas desulphurisation has become the most widespread method of sulphur removal from p.f. processes. FGD uses a sorbent to neutralise the SO_2 in the flue gases which exit the p.f. boiler. Early attempts at FGD proved effective in the 1930's at Battersea where water from the river Thames was used to scrub the flue gases generated by the power station. Higher chimneys, however, proved just as effective at reducing local ground level concentrations of SO_2 . Such a process would not be suitable for modern day applications, and indeed most modern commercial methods of FGD can remove more than 90% of SO_2 from flue gases⁴².

Many different FGD processes exist, most of them using limestone as the feed sorbent. The two most commonly used processes are discussed below.

Limestone sludge process

This is most commonly used in the USA. A lime or limestone slurry is used to remove the sulphur from the flue gases. The resulting waste product is a sludge containing a mixture of calcium sulphate, calcium sulphite and unspent sorbent. Disposing of the sludge is difficult, it is difficult to dewater and is usually disposed of in ponds or disused mines. Fly ash can be used as a fixing agent to make the sludge more stable.

Limestone gypsum process

The previously described process has the disadvantage of disposal problems. The limestone gypsum process gets round this problem by producing a product of saleable grade from the FGD process. Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is used in the cement industry as a setting retardant and in the building industry for plaster board. Essentially the process further oxidises the calcium sulphite, as produced in the limestone sludge processes, and with further dewatering and quality control processes, produces marketable grade gypsum. The technology is well established and in fact the limestone gypsum process dominates the FGD market in Europe and Asia⁴³. In the USA most large coal fired plants are remote from gypsum use and therefore the limestone gypsum process is a less economically attractive option⁴².

Large scale limestone-gypsum FGD plants are used by the UK's two main power generating companies. Powergen has just recently commissioned a limestone gypsum FGD plant at their 2000 MW p.f. power plant at Ratcliffe-on-Soar, UK, and is similar to the FGD process used by National Power at Drax. Figure 2.16 shows a schematic of the process.

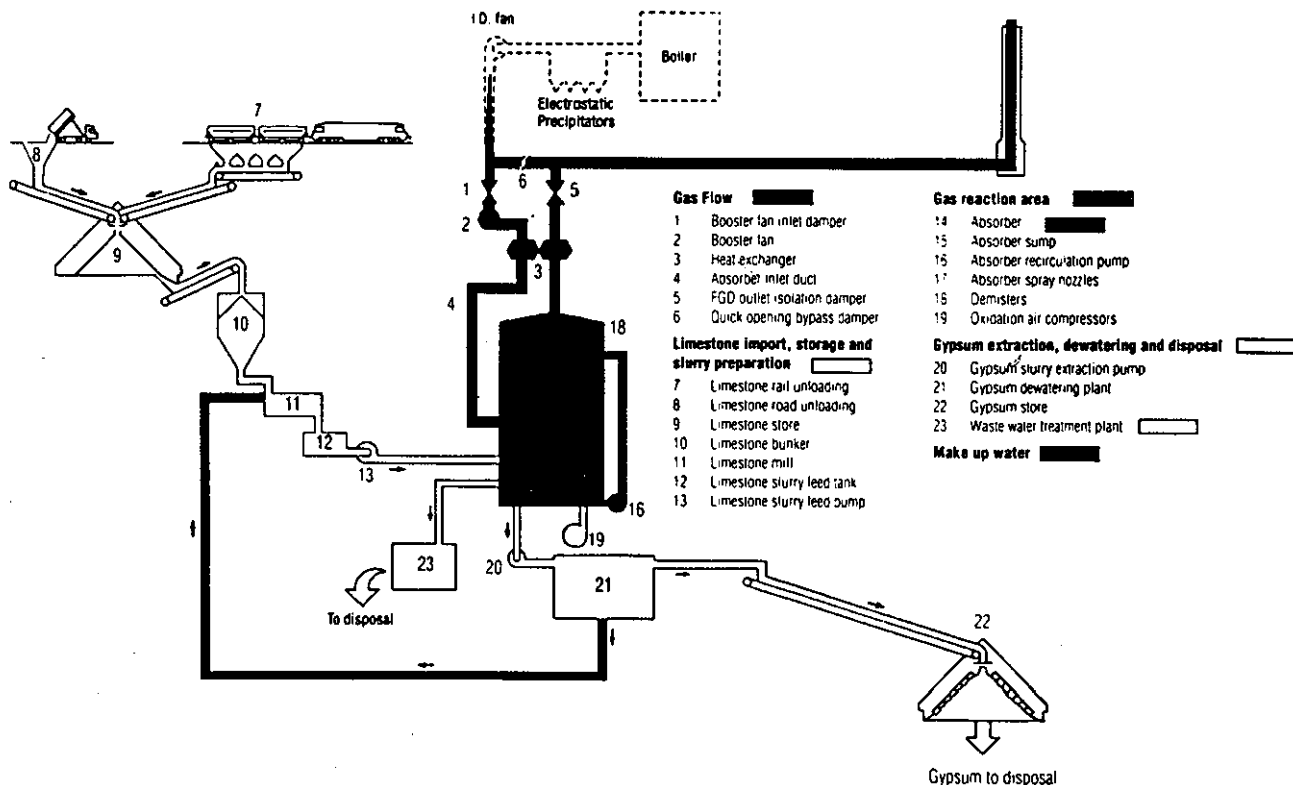
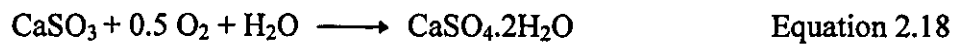
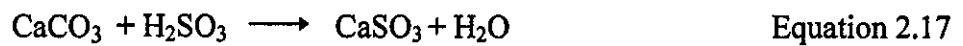


Figure 2.16. The limestone gypsum FGD process at Ratcliffe-on-Soar⁴⁴.

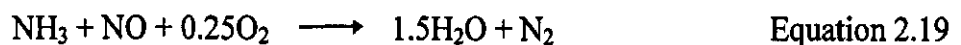
The flue gases from the boiler pass through booster fans into the heat exchangers which cool the inlet gas passing into the absorber and reheat the treated gas to 80°C to give it buoyancy and help it exit from the stack. Once in the absorber, the flue gases are sprayed with a limestone slurry. The limestone reacts with the SO₂ in the gases first producing calcium sulphite. This is then oxidised to calcium sulphate (gypsum) at the bottom of the absorber vessel by reacting it with injected compressed air. The overall reactions are as follows:



To ensure saleable gypsum is produced high purity limestone is used for the process. The slurry containing the gypsum is continuously removed from the bottom of the absorber vessel and separated from any limestone by hydrocyclone before being batch centrifuged. The grade of gypsum produced is typically 95 wt.% CaSO₄·2H₂O. When fully operational, on average, 480,000 tonnes of saleable grade gypsum will be produced each year by the Ratcliffe FGD plant⁴⁴.

2.4.2.3. Selective Non-Catalytic Reduction (SNCR) of NO_x

A direct way of reducing NO_x from p.f. combustion processes is to spray a solution of ammonia into the hot combustion gases at temperatures of 920 - 1000°C. As a result the NO_x is reduced to N₂ following the equation:



Any excess ammonia is oxidised to N₂.

This is termed Selective Non-Catalytic Reduction (SNCR). Greater efficiencies can be achieved if a metal catalyst is used.

2.4.2.4. Selective Catalytic Reduction (SCR) of NO_x

Up to 90% removal of NO_x can be achieved if a catalyst such as titanium oxide is used in the above process³⁵, this is termed Selective Catalytic Reduction (SCR). A lower operating temperature of about 350 - 400°C is required for optimum use of the catalyst in the SCR processes.

2.4.2.5. Low NO_x burners

By careful aerodynamic design of the pulverised fuel burner a reduction in NO_x emissions can be achieved. The mixing of the pulverised fuel with air in the initial part of the flame has a significant influence on the formation of NO_x . Lower NO_x emissions can be achieved if the devolatilisation of the coal takes place in a fuel rich environment. Nitrogen species evolved during this process can then be reduced to N_2 . Wall fired low NO_x burners achieve this by allowing gradual mixing of the primary air/fuel mixture and the secondary air. Usually the secondary air is split into secondary and tertiary supplies. The near burner environment stays fuel rich. The secondary air has a high degree of swirl to keep the flame stable and the tertiary air is introduced around the outside to complete the char burnout part of the combustion process. Figure 2.17 shows the principle behind a low NO_x burner. This type of burner can reduce NO_x levels by up to 50% over conventional pulverised fuel burners²¹.

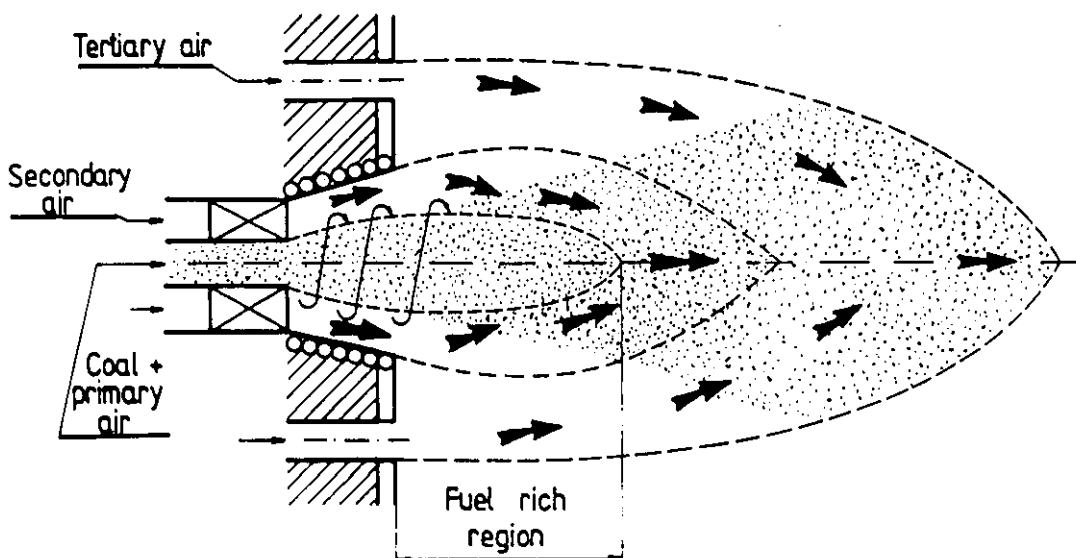


Figure 2.17. The basics of a low NO_x burner²¹

A reduction of NO_x emissions from tangentially fired units is more difficult as they inherently produce lower emissions than conventional wall fired units, as explained above. Lower NO_x emissions from tangentially fired units can be achieved by introducing a curtain of air around the inside of the combustion chamber wall which results in a more gradual mixing of the fuel and air mixture. This also helps reducing the slagging of the combustion chamber walls.

Air-staging and fuel-staging are also techniques which exist to reduce NO_x emissions on their own or coupled with other techniques such as low NO_x burners. Furnace air-staging involves introducing secondary air above the burners to complete combustion. Around 70-90% of the total air is introduced with the fuel to the burners producing a fuel rich region reducing the formation of NO_x from fuel-nitrogen. The secondary overfire air produces a lower temperature secondary combustion zone which reduces the formation of thermal- NO_x . Fuel-staging or reburn involves three distinct furnace zones, the first zone operates in a slightly fuel-lean environment, above this in the second zone fuel (natural gas, oil or coal) is introduced which reduces some of the NO_x formed to N_2 (see Equation 2.13, Section 2.3.2.3), the third zone introduces overfire air in a fuel-lean environment to complete the combustion process. Up to 70% NO_x reduction can be achieved using reburn.

2.5 FLUIDISED BED COMBUSTION (FBC)

2.5.1 FLUIDISED BEDS

Fluidised bed reactors have a wide range of uses throughout industry including calcining, catalytic cracking of hydrocarbons and, of particular interest to this study, combustion. The main attraction of utilising fluidised bed technology for the combustion of coal is the intensive heat and mass transfer characteristics. As a result the following are achievable: very efficient fuel utilisation, high heat transfer at relatively low temperatures and reduced emissions of NO_x compared to conventional fired boilers.

2.5.1.1 Fluidisation

Initially when gas is passed upward through a static bed of particles the gas diffuses through the bed and the pressure drop across it is proportional to the flow rate. As the flow rate is increased there becomes a point where the frictional force exerted by the upward flowing gas equals the weight of the particles. At this point the bed dilates slightly as the particles rearrange themselves, offering less resistance to the flow of gas. This is known as the point of minimum fluidisation and at flow rates above this the bed is said to be fluidised. Increases in flow rate above the minimum fluidisation velocity are not accompanied by an increase in pressure drop. Figure 2.18 shows the relationship between pressure drop and gas velocity through a bed of fine particles.

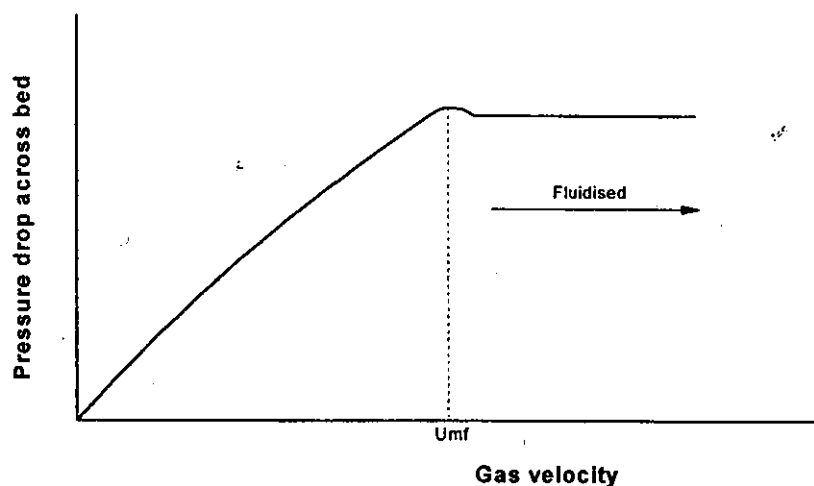


Figure 2.18 ΔP across a bed of particles with increasing gas velocity, where U_{mf} is the minimum fluidisation velocity.

The velocity of gas that is required for minimum fluidisation can be calculated from Equation 2.20⁴⁵ for small Reynolds number, $Re < 20$. As the gas velocity is increased the bed dilates further until a velocity is reached which is equal to the terminal velocity, or transport velocity, of the particles. At this point particles are removed from the bed and are transported out with the fluidising gas. The terminal velocity of a particle can be calculated from Equation 2.21⁴⁵, assuming a spherical particle and a Reynolds number between 0.4 and 500.

$$U_{mf} = \frac{(\Phi_s d_p)^2}{150} \cdot \frac{\rho_s - \rho_g}{\mu} \cdot g \left(\frac{\epsilon_{mf}^3}{1 - \epsilon_{mf}} \right) \quad Re < 20 \quad \text{Equation 2.20}$$

$$U_{t(spherical)} = \left(\frac{4 (\rho_s - \rho_g)^2}{225 \rho_g \mu} \cdot g^2 \right)^{1/3} \cdot d_p \quad 0.4 < Re < 500 \quad \text{Equation 2.21}$$

Gas-solid systems do not fluidise smoothly, the dimensions of the reactor, the gas distributor and properties of the gas/ solids all affect the behaviour of the particles within the bed. At moderate flow rates above the minimum fluidisation velocity, fluidising gas coalesces into bubbles which travel up through the bed of particles at velocities greater than the mean velocity eventually bursting at the surface. This bubbling of the bed promotes vertical mixing of the solid particles creating a fairly fast circulating motion.

Irregularities can occur in fluidised beds. If the reactor diameter is too small and the gas flow rate sufficiently high the bubbles can coalesce with each other and span the diameter of the reactor rising up slowly and reduce the good solids mixing; this is termed 'slugging'. With very fine particles channelling can occur, in which case streams of gas pass completely through the bed of particles. Correct design of the reactor and system can avoid these two effects. The typical size of particles used in coal fired fluidised bed combustion is about 3mm and would not normally exceed 10mm.

2.5.1.2 Coal combustion in fluidised beds

Fluidised beds can bring a number of advantages when used for coal combustion. These are made possible due to the intensive heat and mass transfer and the low combustion temperatures found in FBC. The major advantages over conventional coal fired boilers are:

- Very efficient heat transfer to steam/ water pipes.
- Efficient utilisation of a wide range of coal types and particle size.
- Compact plant/ low capital cost.
- Enables effective use of in-situ sulphur removal by use of limestone/ dolomite sorbents.
- Inherently low NO_x emissions.

The usual temperature range of operation of FBC is between 800°C and 950°C, this is high enough to ensure rapid burnout of the particles and low enough to avoid sintering of the ash contained in the coal. At these temperatures limestone is very effective at absorbing SO₂ from the combustion products and can be injected directly into the bed. The good solids mixing and longer residence times lead to greater absorbent efficiencies when compared to limestone injection in pulverised fuel combustion and compares favourably with pulverised fuel plant with FGD⁴⁶ (see sections 2.4.2.1 and 2.5.3.1). The lower combustion temperatures also mean that the emissions of NO_x are lower compared to pulverised fuel firing; the contribution from 'thermal NO_x' being negligible⁴⁷ (see section 2.3.2.3).

The good solids mixing ensures a uniform bed temperature and efficient heat transfer by direct conduction to heat exchangers whilst the high heat capacity of the bed of solids gives a high degree of thermal stability making FBC more tolerant of fuel quality than traditional pulverised fuel combustion.

The carbon inventory of a FBC is typically as low as 2% (by wt.) of the total bed²¹, with the rest of the bed being made up of inert material, ash particles and sulphur sorbent. Figure 2.19 shows a simplified schematic of a fluidised bed boiler.

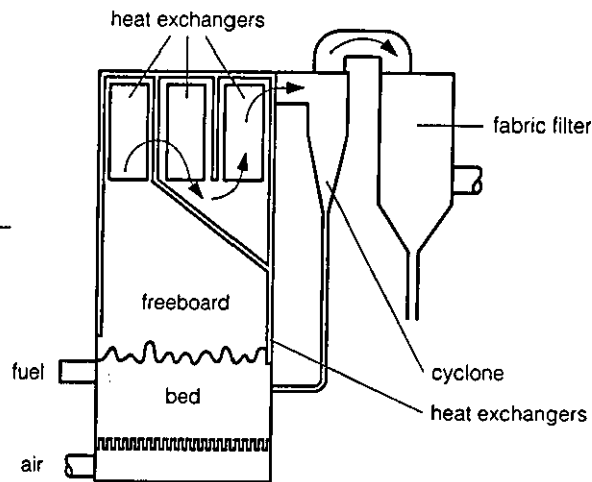


Figure 2.19 A bubbling fluidised bed boiler⁴⁶

2.5.2 INDUSTRIAL FBC PROCESSES

Since the late 1970's fluidised beds have been used to burn coal to generate steam. As the technology has developed FBC plants have been scaled up and now some relatively large plants (between 50 and 175MWe) exist for cogeneration and electricity generation⁴⁶.

FBC's can be operated under two main fluidisation regimes: i) bubbling fluidised bed - moderate fluidisation velocities (typically 1 - 3 m/s) with a well defined bed of solids and area above the bed (freeboard) - substantial part of the heat transfer takes place in the bed. ii) circulating fluidised bed - higher fluidisation velocities (typically 5 - 10 m/s) - most of the heat transfer occurring out of the bed and a high degree of solids recirculation. Both can be operated at atmospheric pressure or elevated pressure.

2.5.2.1 Atmospheric fluidised bed combustion (AFBC)

Bubbling fluidised beds

Atmospheric bubbling fluidised beds are operated at gas velocities low enough to reduce solids entrainment and carry over. Figure 2.19 shows a simple schematic of a bubbling fluidised bed boiler. The gas velocities used in bubbling fluidised bed combustion (BFBC) are typically between 1 and 3 m/s. The reactors are usually designed to give a total gas residence time in the reactor of 6 seconds and typically the effective in-bed residence for the gas is around 0.5 seconds. If the gas velocity is too high then sulphur retention is reduced, if it is too low then oxygen supply is reduced.

BFBC can be operated with shallow or deep beds, with two types of coal firing. Over-bed firing has the coal inserted just above the bed and in in-bed firing the coal enters the bed just above the gas distributor. Over bed firing uses larger coal, but gives poor sulphur retention as the initial combustion products are carried away quickly and do not come into contact with the sorbent. Because the reactions occur mainly in the bed, heat exchangers are placed in the bed to control the combustion temperature. The rest of the heat is removed from the hot gases as in conventional boilers using superheaters and economisers.

Some disadvantages of BFBC are that complex feed systems are needed in the bed to ensure effective bed mixing and the use of in-bed heat transfer surfaces can lead to erosion problems.

Circulating fluidised beds

Circulating fluidised beds use much higher fluidising velocities in the order of 5 - 10m/s. At these fluidising velocities there is no defined upper surface to the bed and heavy duty cyclones are used to recycle the solids back into the bottom of the bed. Figure 2.20 shows the basics of a circulating fluidised bed boiler. Even though gas velocities are higher, the gas-solid contact is greatly increased over that observed in BFBC due to the recirculation of solids.

The increased combustion efficiency of circulating fluidised bed combustion (CFBC) allows lower-grade fuels, those with higher ash and moisture content, to be utilised. Higher combustion efficiency can be achieved in CFBC due to the higher fluidisation rate and the recycling of solids. The heat released inside a CFB boiler is over a larger volume and so more efficient use of the heat exchangers can be made in the upper part of the bed. The circulation of relatively cool solids to the bottom of the bed also removes the need to have heat exchangers in this region to control the combustion temperature.

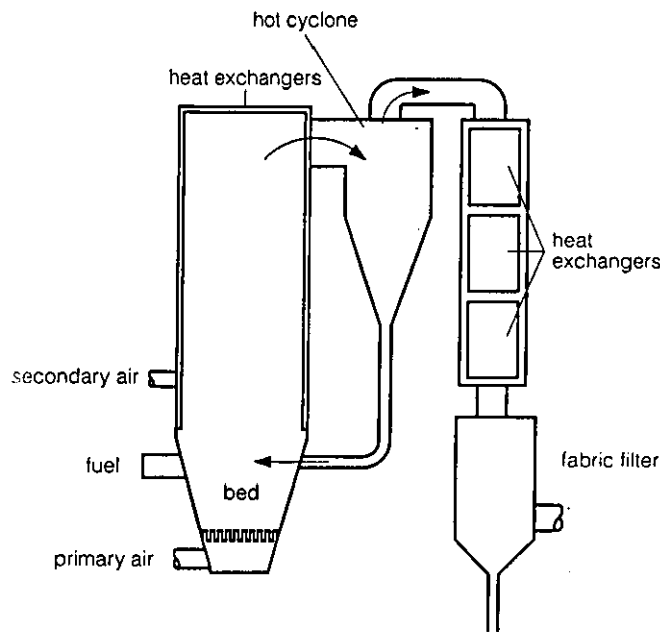


Figure 2.20. The basics of a circulating fluidised bed boiler⁴⁶

Other advantages of CFBC are fewer fuel feed points needed and air staging to control NO_x is more effective than in BFBC. For these reasons, CFBC has become more popular than BFBC, especially for larger plant.

The first commercial CFBC was Ahlström's 20 ton/h steam boiler installed in Finland in 1979. Since then larger boilers have been commissioned which can generate 420 ton/h of steam producing around 110 MWe of electricity⁴⁸. The different types of CFBC differ mainly in their incorporation of external or internal heat exchangers. A CFBC with integral heat exchangers is shown in Figure 2.21, it is typical of the systems used by Ahlström Pyropower. In 1994 there were 120 CFBC plant similar to this design in use world-wide with an estimated total capacity of 13,500 MW_t⁴⁶.

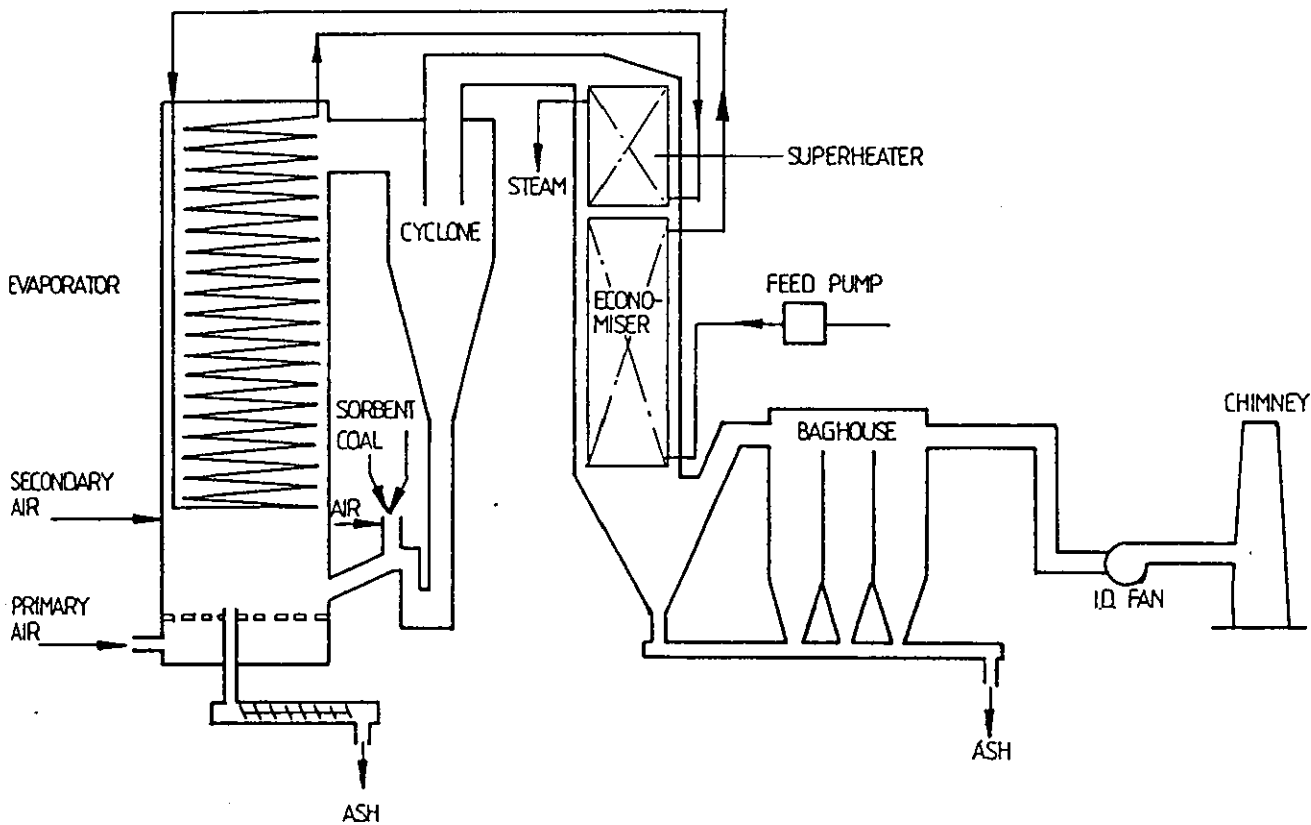


Figure 2.21. CFBC system with integral heat exchanger

2.5.2.2 Pressurised fluidised bed combustion (PFBC)

Pressurised fluidised beds typically operate at pressures between 1 and 2MPa and systems for power generation combine both steam and gas turbines. Steam is generated for the steam turbines similarly to other FBC, but because the combustion gases are pressurised they can be expanded through a gas turbine which drives the compressor for the combustion air and generates additional electricity. Most PFBC boilers are based on bubbling beds and can be kept very compact compared to atmospheric BFBC.

Deeper beds are used in conjunction with lower fluidising velocities; typically beds are between 4 and 4.5m and fluidising velocities are around 1m/s. Deeper beds are possible because the pressure drop across the bed is minimal compared to the reactor pressure and lower fluidising velocities are needed as the gas is much denser. These two factors lead to greatly increased gas-solid contact times not achievable with atmospheric BFBC.

Pressurised CFBC has the potential for even higher heat release rates than pressurised BFBC but is still at pilot plant stage. A disadvantage over pressurised BFBC is more hot gas filtering is required due to the high particulate burden.

Table 2.7 compares plan area heat release rates for various combustors⁴⁶, highlighting the compactness of PFBC.

Table 2.7. A comparison of plan area heat release rates in combustors⁴⁶

COMBUSTOR	HEAT RELEASE, MWe/m ²
Stoker (travelling grate)	1.3 - 2.2
Pulverised coal bituminous	4.4 - 6.3
Bubbling fluidised bed	
- atmospheric	0.7 - 2.1
-pressurised, 1.5MPa	up to 10
Circulating fluidised bed	
-atmospheric	2.8 - 3.3
-pressurised, 1.5MPa	up to 40

2.5.2.3 Hybrid PFBC

Fluidised beds can be used to gasify coal. By introducing steam and a limited oxygen supply as the fluidising gas, a low calorific value gas can be produced consisting mainly of CO and hydrogen. This fuel gas can be then utilised for power and heat generation.

PFBC can be utilised in plants referred to as hybrid combined cycle PFBC or topping cycles. An example of this type of process is the Air Blown Gasification Cycle (ABCG) presently under development in the UK. Essentially coal is partially gasified in a PFBC to produce a low calorific value gas and the char remaining is removed and burnt in an atmospheric CFBC. This optimises both the gas turbine and steam cycles with potential overall efficiencies of up to 46.9% achievable⁴⁹.

Figure 2.22 shows a schematic of the of the ABGC⁵⁰. A pressurised fluidised bed gasifier operating up 1000°C is used to convert 80% of the coal feed to low calorific fuel gas. The process uses a spouted bed which uses an orifice as a gas distributor at fluidising velocities between that of BFBC and CFBC. The fuel gas produced passes through a cyclone, is cooled to 600°C, passes through gas filters to remove finer particulates and condensed alkali metals before being burnt in the gas turbine combustor. This increases the gas temperature at the turbine inlet and increases the gas turbine efficiency. Heat recovered from the exhaust contributes to the steam cycle.

Sulphur sorbent is used in the pressurised fluidised bed gasifier, removing potentially 90% of the SO₂. The char produced in the gasifier is removed from the bottom of the reactor and burnt in an atmospheric CFBC producing further heat for the steam cycle.

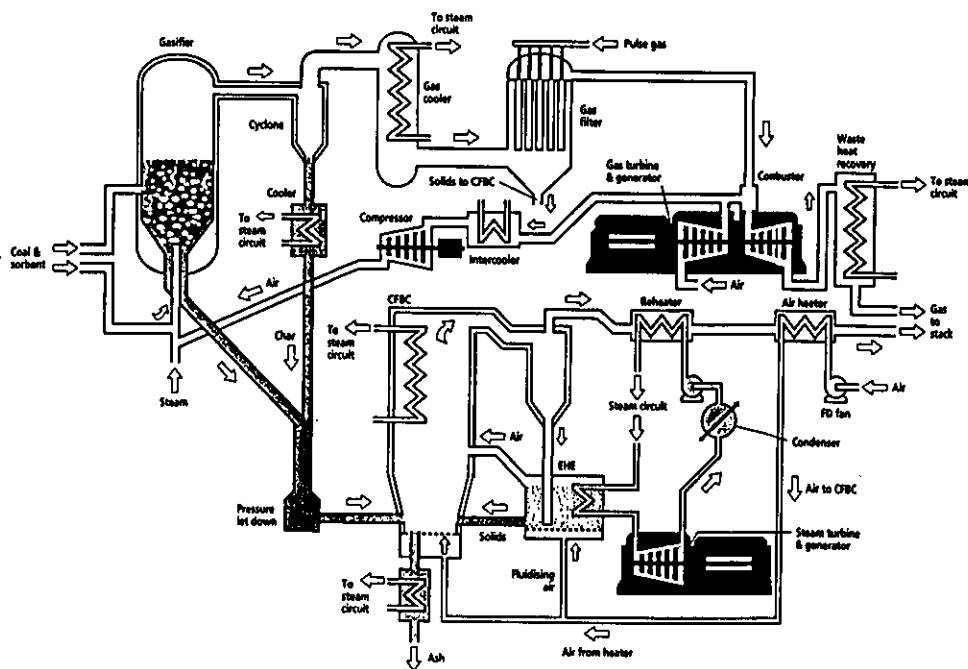


Figure 2.22. A schematic of the Air Blown Gasification Cycle⁵⁰

Advantages of this type of system over other coal combustion and integrated gasification combined cycle processes is based on the use of the pressurised fluidised bed gasifier. These include higher tolerance of coal size and quality, avoidance of tar production, in-situ sulphur retention and efficiency gains from hot gas clean-up.

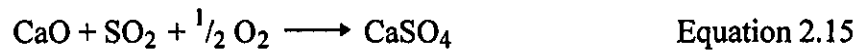
2.5.3 EMISSIONS FROM FBC

2.5.3.1 Sulphur dioxide

At the temperatures found in FBC, limestone or dolomite is very effective at removing SO_2 directly from the combustion products, following equations 2.14 and 2.15 and can be injected directly into the bed along with the coal. This inherent sulphur removal capability significantly reduces the plant size of FBC processes without the need for large retrofitted gas scrubbing equipment.



The calcination reaction Equation 2.14 produces higher porosity in the sorbent particle. The calcium oxide goes on to react with the SO_2 .



The Ca/S molar ratio can be set to give high sulphur retention (a Ca/S molar ratio of 1 is equivalent to a limestone/sulphur mass ratio of 3.12 and a dolomite/sulphur mass ratio of 5.75). Typically, for 90% SO_2 removal, the Ca/S molar ratio for an atmospheric BFBC would be 3 to 5 and would be between 1.5 and 2.5 for PFBC⁵¹. The lower Ca/S ratios for PFBC correspond to the increased gas-solid contact times experienced with deeper beds and lower gas velocities. Increased pressure can change the reactivity of the sorbent; the reactivity of limestone drops because of a delay in the onset of calcination.

Disposal of the large quantities of spent sorbent from fluidised beds is a problem and is one of the biggest draw backs of FBC.

2.5.3.2 Oxides of nitrogen (NO_x)

The low combustion temperature used in FBC boilers means that emissions of NO_x are lower than traditional PF burners. Unlike PF burners, the contribution from thermal NO_x is negligible with essentially all the NO_x originating from the oxidation of the nitrogen

contained in the coal (see section 2.3.2.3). Typical NO emissions from single stage combustion in FBC are between 100 and 150 ppmv.

Nitrogen oxide emissions from fluidised beds can be reduced further; introducing staged combustion can reduce values by up to 50%⁵². Reducing the amount of air passed through the bottom of the reactor produces a fuel rich zone in the bed. Here most of the volatiles are generated and the fuel rich environment promotes reactions leading to the formation of N₂ instead of NO. Introducing secondary air above the bed in the free-board region provides an oxidising region for the rest of the combustion reaction to take place. This is more effective in CFBC where there is a higher homogeneity of the gas and solids; air staging in BFBC can lead to incomplete combustion.

Table 2.8 shows a comparison of NO_x emissions from PF-fired processes and FBC under various control strategies. This highlights the lower NO_x capabilities of FBC.

Table 2.8. NO_x emissions (ppmv) from PF-fired and FBC processes⁴⁶

Method	PF-fired plant	FBC
1. Standard	550 - 800	100 - 150
2. Low excess air	450 - 650	70 - 120
3. (2) + Air staging	300 - 500	50 - 80
4. (2) + Flue gas recirculation	350 - 550	--
5. (3) + Flue gas recirculation	200 - 400	--
6. (5) + Low NO _x burner	150 - 300	--
7. (6) + SNCR or SCR	10 - 50	10 - 50

Unfortunately, FBC produces considerably more N₂O than conventional PF combustion and in AFBC plants it can be as high as 100 ppmv compared to 2 ppmv in PF-fired plant⁴⁶. PFBC typically produces lower N₂O emissions and the ABGC could potentially reduce N₂O further due the higher exhaust temperatures generated before the gas turbine inlet.

CHAPTER 3

PROJECT CONCEPT

3.1 PURPOSE

Coal has been exploited as a fuel for power generation for many years. However, modern environmental legislation governing the emissions of certain pollutants into the atmosphere, such as NO_x and SO_2 , means that traditional pulverised fuel methods of power generation are becoming less attractive. Expensive retrofit technology is required to bring existing coal fired power plants below emission targets. Future utilisation of coal as a fuel requires 'clean coal' technologies to be developed which will be cost effective and fuel efficient.

In the short term in countries like the UK, alternative fuels such as natural gas are replacing coal as a fuel for power generation in new plant. Natural gas is suited to smaller, lower capital cost, gas turbine plants with transportation costs of the fuel being minimal. The fuel also contains negligible amounts of sulphur and nitrogen and therefore contributes less to emissions of SO_2 and NO_x . This is in contrast to the large capital outlay of a traditional pulverised fuel facility with the associated solids handling costs accompanied by fuels with relatively high sulphur and nitrogen contents. However, forecasted depletion of natural gas and oil reserves is much faster than for coal. Coal is by far the major fossil fuel reserve; over five times greater than that of gas and oil and more evenly spread throughout the world⁵³. In the long term, as energy consumption increases with a potential oil and gas price rise, it is essential that cleaner and more efficient methods of burning coal are developed.

Cleaner coal technologies do exist: as retrofit plant, such as low NO_x burners and flue gas desulphurisation or as inherently cleaner technologies such as fluidised bed combustion. As discussed in the Literature Review, fluidised bed combustion offers a solution for efficient combustion with inherently lower emissions of NO_x and SO_2 , albeit on a smaller scale than PF combustion. Many power generating plants now exist which use fluidised bed boilers. There is also scope for the use of coal as a feed stock to produce a gaseous fuel as demonstrated by processes such as the British Gas-Lurgi slagging gasifier.

An emerging technology is the use of fluidised beds in the partial gasification of coal to produce a low calorific value gas that can be burnt in a gas turbine to generate electricity. The residual char produced as part of the process can be burnt in a fluidised bed boiler to raise steam for a steam cycle. These hybrid combined cycles optimise both the steam and gas turbine cycles and have potential overall efficiencies in the order of 45%.

A promising example of this Hybrid Combined Cycle is the Air Blown Gasification Cycle, ABGC, presently under development in the UK (see section 2.5.2.3 for full description). The ABGC uses a pressurised fluidised bed to partially gasify the coal and an atmospheric circulating fluidised bed boiler to burn the residual char for the steam cycle. It was with the ABGC process in mind when the objectives of this research project were drafted.

For effective development of clean coal combustion it is important to understand the processes which govern the formation of pollutants and how these relate to the various properties of the coal used. For processes such as the ABGC the split of sulphur and nitrogen species between the volatile matter and the residual char during gasification has significant operating implications on all of the separate stages of the process. Being able to predict the behaviour of such pollutants under different gasification conditions from known coal properties would be advantageous and result in much wider control of processes such as the ABGC.

As the literature review has shown, coal is a complex fuel varying in calorific value, volatile matter content, heteroatom content and ash content. As coal has had to become more internationally competitive the more likely it will come from a greater number of locations, differing widely in its properties. It is therefore even more important to understand how the more basic properties of coal influence the formation of pollutants. In this way processes like those mentioned above can be optimised cleanly and efficiently.

3.2 APPROACH

3.2.1 OBJECTIVES

As summarised in section 3.1, with the inevitable increase in use of coal as a fuel for fluidised bed combustors or a feedstock for gasification processes, a better understanding of how a coal's differing properties effect pollutant emissions from these processes is needed.

Much of coal combustion research in the laboratory is geared to simulating as closely as possible those conditions found in pulverised fuel boilers. That is, small particle sizes used in conjunction with high heating rates, usually in entrained flow reactors (EFR). As with all laboratory equipment, the EFR is limited in its application to the conditions found in real burner or boiler. Other equipment such as the wire mesh reactor can be used for larger particle sizes, where a heated grid holds a small coal sample under programmed heating conditions. Both are limited in their relevance to fluidised bed combustion or gasification. The EFR can only use small $\sim 75\mu\text{m}$ coal particle sizes and short residence times ~ 1 second and the wire mesh reactor is limited to the grid size and very small coal samples, typically 5mg.

In contrast to the above methods, laboratory fluidised beds are not widely used and pose a different series of drawbacks and limitations. The initial part of the project assessed the suitability of each method of experimental equipment with regard to the general objectives below.

The chief aim of this project was to simulate as closely as possible, in the laboratory, the conditions found in modern industrial fluidised bed combustion/gasification power generating processes. This was to be with reference to the emergence of fluidised beds in hybrid combined cycle processes, in particular the ABGC. The split of nitrogen and sulphur between the char and volatile products during pyrolysis and subsequent gasification could be then investigated under different reaction conditions. The ultimate objective being to gain a better understanding of the processes which govern this split.

3.2.2 PROGRAMME

The proposed project programme fell into two main categories, these were:

1. The design and commissioning of a suitable experimental rig capable of operating under conditions most relevant to fluidised bed combustion/gasification of coal, i.e. sufficiently high heating rates at temperatures of approx. 1000°C.
2. Undertake a programme of experimental studies to generate enough data to determine how the nitrogen and sulphur distributes between char, tar and gas during pyrolysis and oxidation under these conditions.

The novelty of approach would be in the use of a specifically designed experimental rig capable of producing pyrolysis and partially gasified chars under conditions most relevant to hybrid combined cycle processes, in particular the ABGC.

3.2.2.1 Envisaged experimental programme

An experimental programme was proposed to tackle the above two main sections of work with the project objectives in mind.

The first part would involve a feasibility study of the different methods of producing chars representative of industrial fluidised beds, in the laboratory, and of enough quantity for chemical analysis. This would then feed into the design stage, collecting enough theoretical data to allow a proper design to be achieved. The designed rig, once built, would then need appropriate commissioning to allow a satisfactory experimental method to be established. Once this was achieved collection of experimental data could begin.

Although the exact operating principle of the experimental rig was not known at the start of the project, it was envisaged that the experimental programme would focus on three basic operating conditions, these being:

- i) Inert gas in reactor
- ii) Oxidising gas in reactor
- iii) Oxidising gas with sulphur sorbent in reactor

This would enable the behaviour of nitrogen and sulphur species to be studied during coal devolatilisation and gasification/combustion, the latter with or without the presence of a sulphur sorbent such as limestone.

The char and in the case of pyrolysis, tar, would be collected and analysed for ash, carbon, sulphur and nitrogen. The sulphur content would be determined by a method suitable to small quantities of char sample, <1g, and the carbon and nitrogen by micro-elemental analysis. In this way the split of the sulphur and nitrogen between the various products would be established.

It was proposed to concentrate efforts on coals likely to be used in gasification processes although additional coals would be used to extend the rank range of the study. It was expected from this, that the following key topics and their effect on the distribution of coal sulphur and nitrogen between the char, tar and gases could be covered. These are presented as a series of questions which the project aimed to answer.

Reactor temperature

How does the reactor temperature effect the distribution of sulphur and nitrogen between the char and volatiles? In the initial stages of any combustion or gasification process, devolatilisation takes place. Temperature is known to effect volatile yield behaviour but are the quantities of sulphur and nitrogen species released affected and how are they affected in the temperature range and conditions typically found in fluidised bed combustion and gasification?

Residence time

How does the influence of residence time effect the relative shift of sulphur and nitrogen into the gases? How fast or slow are these processes?

Char morphology

Under the high heating rates found in industrial combustion processes, a wide variety of char particle shapes are produced. Could the char morphology be linked to the degree of volatile yield or subsequent char burnout and would this effect the nitrogen and sulphur distribution.

Coal rank

How does the nature of the coal effect the shift of nitrogen and sulphur into the tar and gases on devolatilisation and char burnout? The aromatic carbon content of coal increases with rank, does this or the quantity of volatile matter yielded by the coal on devolatilisation effect sulphur and nitrogen release?

Atmosphere and sorbent material

How does the presence of sorbent material or an increase in oxygen content effect the sulphur and nitrogen distribution? Does the heteroatom content match the carbon loss with char burnout?

Type and quantity of nitrogen and sulphur in the fuel

The quantity and nature of nitrogen and sulphur varies considerably from coal to coal. Could the chemistry of the nitrogen and sulphur in the coals explain the behaviour during devolatilisation and gasification? If so, could this be linked in turn to the nature of the coal, e.g. Rank, volatile matter content etc.?

Although these topics had been explored, some in, detail by other authors the question is always how representative the work is to full scale fluidised bed combustion/gasification conditions. By their nature laboratory investigations never fully simulate these processes it is always a compromise between size/cost and flexibility/applicability. Therefore, the aim of this study was to construct a representative laboratory rig to carry out the above experimental programme and always bearing in mind the applicability of the results to the conditions it was attempting to simulate.

CHAPTER 4

EXPERIMENTAL STUDIES

4.1 INTRODUCTION

This chapter details the work carried out at the beginning of the project to design and construct a system capable of producing coal chars for analytical study. It was important to balance the simulation of industrial combustion/ gasification, the aims of the research project itself and the practicalities of using the designed equipment in the laboratory. From this, an experimental method of producing chars was developed.

The first section details the design approach which led to the adoption of the fluidised bed system used for these studies. Established design equations were then used to develop the concept of producing pyrolysis/gasification chars by injecting coal into a heated fluidised bed and then ejecting them after a desired residence time by increasing the gas flow to that of the terminal flow of the char. A gas cyclone was also designed to remove the char from the gas stream leaving the reactor. Construction of a glass prototype and commissioning studies of the full sized apparatus helped refine the rig design and char production method.

The experimental rig designed and developed was capable of heating coal in a fluidised bed up to 1050°C in an inert or oxidising atmosphere to produce chars of varying degrees of burn-out whilst giving the coal/char a set residence time in the reactor. The chars produced could be collected easily, along with any tar material, for elemental and microscopic analysis. The process developed was able to produce chars with a similar burn-off to that of the gasification stage of the Air Blown Gasification Cycle (ABGC), i.e. approximately 70wt% (daf).

In the final section, the experimental method developed to produce chars from the fluidised bed system for all the coals used in the study, along with the appropriate analysis techniques, is described.

4.2. DESIGN CRITERIA AND ENVISAGED EXPERIMENTAL APPROACH

4.2.1 METHOD OF CHAR PRODUCTION

As outlined in earlier chapters, the main aim of this research project was to gain a better understanding of factors governing the distribution of nitrogen and sulphur between the char, tar and gas during pyrolysis and partial gasification of coal under conditions pertinent to the ABGC.

To obtain relevant data on the distribution of nitrogen and sulphur between the char, tar and gas in the laboratory, certain criteria have to be met. It was necessary to design an experimental system capable of simulating as closely as possible conditions found in an industrial fluidised bed gasifier while providing a safe and practical way of producing representative samples of char for later analysis.

Initially a number of possible methods of char production were considered. They fell into three main categories: wire mesh reactors, entrained flow reactors (EFR) and laboratory scale fluidised bed reactors. These were assessed for their suitability in meeting the above general criteria.

The use of wire mesh reactors to study coal pyrolysis and combustion in the laboratory is widespread. The method heats the coal, placed between two pieces of wire mesh, rapidly to the desired temperature (up to 1500°C) at a reasonably controlled heating rate. Whereas this technique provides the high heating rates that are found in industrial fluidised bed reactors it has the significant disadvantage of only producing a small char sample, usually around 5mg per run. Clearly this introduces implications for later analysis of chars.

EFR or drop-tube furnaces are used extensively to study coal pyrolysis and combustion. The technique involves entraining coal particles into a gas stream which together pass through a reactor at temperatures lower than wire mesh reactors, usually up to 1100°C.

Here a defined residence time can be achieved. The system has an advantage over the wire mesh reactor of being able to produce larger amounts of char for analysis, but has the disadvantage of restricting the coal particle size that can be used to typically $38\mu\text{m}$ - $75\mu\text{m}$. With the short residence times there may also be a question over the actual temperatures achieved by the coal particles. This method, as with wire mesh, is perhaps more pertinent to studying pulverised fuel combustion than fluidised bed combustion/gasification which uses longer residence times and larger particle sizes. A comparison of the two above methods to produce pyrolysis chars is given in a paper by Hindmarsh et al⁵⁴ and highlights the advantages and disadvantages of both systems in simulating industrial combustion processes.

The use of fluidised bed reactors in the laboratory is not as widespread as the other two methods of char production but does have its advantages. Laboratory-scale fluidised beds can produce similar heating rates as their industrial counterparts and can use larger particle sizes than EFR and wire mesh reactors. The introduction and removal of coal and char from the reactor, however, is not as easy as wire mesh or EFR techniques. In addition controlling the residence time of the coal/char in a fluidised bed reactor is difficult; fluidised bed processes tend to be continuous operations.

Whereas it appeared the most difficult technique to implement, it was considered important to adopt a fluidised bed method if possible to best meet the criteria defined earlier. For this, it was necessary to design a process specifically suited for the required studies.

4.2.2. TYPE OF FLUIDISED BED SYSTEM

As discussed above, it was decided that the use of a fluidised bed reactor would best meet the general criteria which, to a certain degree, the aims of the project dictated. It was now necessary to look in more detail at the application of a fluidised bed system to the specific studies. Three types of system were considered:

1. A continuous system
2. A simple batch system
3. An 'injection' batch system

It was important that the chosen system should provide a representative sample of char and tar in sufficient quantities for elemental analysis. Also, because of the nature of the project the system could not be too expensive and could not take too long to design and commission. A brief description of how each system was envisaged and the advantages/disadvantages of each are discussed below.

4.2.2.1. A continuous system

The continuous system envisaged consisted of a fluidised bed reactor constructed in silica surrounded by a tube furnace to provide the heat for the experiment. The fluidising gas could be oxidising or inert. The coal feed into the reactor would be via a screw or vibratory feeder down a central tube into the centre of the bed. The coal would be fed continuously, with the char removal consisting of another screw thread or an overflow tube. Tars could be collected using condensers. The bed material would have to be fed in with the coal at the same rate as its removal with the char/coke. When the products were recovered the char/coke would have to be separated from the sand using perhaps a float-sink process.

The main advantage of this system is that, because of continuous addition/removal of coal/char, the system simulates industrial fluidised bed operations relatively accurately. This system allows steady conditions to be achieved in the reactor for reliable and reproducible results.

The disadvantages are, firstly, it would be fairly difficult to control accurately the feed and product flow rates for mass balance data and secondly, any char sample removed from the reactor would have a distribution of residence times, that is, it would contain chars of varying degrees of burn-out. It would therefore prove difficult to relate sulphur and nitrogen contents of chars to a definite residence time for those chars analysed. In addition, for a continuous system of this nature the equipment is costly.

4.2.2.2. A batch system

This system, again, would consist of a silica fluidised bed reactor surrounded by a tube furnace. The coal feed, however, would have to be loaded with the bed material prior to fluidisation. It was envisaged that the furnace would then heat up the reactor whilst the bed was fluidised, until the correct temperature and residence time had been reached. At this point the furnace would be turned off or removed and cold gas drawn through the bed to quench any reactions. The char and bed material could then be removed and separated by a sieving or float/sink process. The tars could be collected by condensers.

The first advantage of the system is that no expensive or difficult to operate feed equipment is needed. The system has the advantage that a sample of char can be collected which has experienced a definite residence time which aids later analysis of the nitrogen and sulphur distribution between that char and its volatiles.

The disadvantages were deemed to outweigh the advantages. The nature of this system would inevitably mean the chars would experience long residence times and low heating rates which do not accurately represent the industrial, fluidised bed combustion/gasification process. The time taken to produce samples of char would be lengthy. This overall system was seen to be far removed from simulating an industrial fluidised bed combustion/ gasification process.

4.2.2.3. An 'injection' batch system

The basis for this idea came from the operation of circulating fluidised beds. Because they use high gas flow rates, a significant amount of the solids becomes entrained in the gas exiting the reactor and is collected in cyclones and fed back to the reactor. This suggested that in the laboratory system, increasing the gas flow at a defined time could remove char particles from the fluidised bed reactor. The char particles could then be collected in a gas cyclone.

It was envisaged that the central part of this design would be a silica fluidised bed reactor placed inside a tube furnace. In this design the reactor would be brought up to temperature by the furnace and steady conditions reached before feeding in the coal. The coal would be fed into the reactor by injecting the coal into the centre of the bed with a flow of nitrogen or air. When the required residence time was reached the coal would be ejected by increasing the fluidising gas flow to that of the terminal flow of the char particles. This product could then be collected in a gas cyclone. The tars could be collected in a similar way to that envisaged for the first two systems. The potential advantages of this system were as follows:

- A more definite residence time at the desired temperature and conditions.
- A full representative sample that can be collected for analysis.
- The bed material and the char are separated as part of the operation.
- Relatively simple feed and product removal equipment.

A disadvantage of the system was the fact that it was a batch system and therefore did not simulate, as closely as a continuous system would, the industrial fluidised bed combustion/gasification process. It did, however, meet all the design criteria thought to be most important to the research project.

After the decision had been taken to implement the 'injection' batch system, more detailed design work was needed along with further exploration of the theories suggested by such an approach. A glass prototype was therefore commissioned before a full-sized heated version was designed and built.

4.2.3. DESIGN CALCULATIONS

4.2.3.1. Fluidised bed reactor

Gas-solid fluidisation systems do not fluidise smoothly; factors such as gas distributor, reactor dimensions, flow rates and gas/solid properties affect widely the quality of fluidisation achieved. It is important, therefore, when designing a gas-solid fluidised bed system to choose conditions which minimise any adverse effects caused by the above factors.

A basic description of the phenomena of fluidisation is given in section 2.5.1.1. It explains the significance of calculating the minimum fluidisation velocity, U_{mf} . When designing the experimental fluidised bed reactor, it was the value of U_{mf} which formed the basis for setting the operating flow rate of the system. When a fluidising gas had been chosen and the properties of the bed material had been set at nominal values, size range and type, the velocity of gas needed to achieve minimum fluidisation was calculated using equation 2.20⁴⁵. As in most applications involving a bubbling fluidised bed, the operating velocity was taken to be around 4 times this value.

$$U_{mf} = \frac{(\Phi_s \cdot d_p)^2}{150} \cdot \frac{\rho_s - \rho_g}{\mu} \cdot g \left(\frac{\epsilon_{mf}^3}{1 - \epsilon_{mf}} \right) \quad \text{Re} < 20 \quad \text{Equation 2.20}$$

For a particle of a specific size and density the velocity of gas needed to transport that particle out of a bed of fluidised particles into the exiting gas stream is termed its terminal velocity. For the system being designed it was suggested that raising the fluidising gas stream would be an ideal way of both removing the char from the reactor and separating it from the sand in the bed. To calculate the terminal velocity of coal/char of a certain size, equation 2.21 was used⁴⁵.

$$U_{t(spherical)} = \left(\frac{4}{225} \frac{(\rho_s - \rho_g)^2}{\rho_s \mu} \cdot g^2 \right)^{1/3} \cdot d_p \quad 0.4 < \text{Re} < 500 \quad \text{Equation 2.21}$$

Once these two important velocities had been calculated, the diameter of the reactor was chosen to give reasonable flow rates of fluidising gas. Appendix A gives a full description and example of the fluidised bed flow calculations used.

4.2.3.2 The gas cyclone

To remove entrained char particles from the exiting gas stream it was necessary to design a gas cyclone. The gas cyclone adopted used the general design for a high efficiency cyclone, this is shown below in figure 4.1⁵⁵.

For a high efficiency cyclone it is assumed that the entrance velocity of the in coming gas is 15m/s into the inlet duct of the cyclone. The flow rate of the gas leaving the fluidised bed reactor is known from equation 2.21 and therefore the cross sectional area of the inlet duct and the cyclone diameter D_c can be calculated. Once D_c was known the rest of the dimensions were calculated.

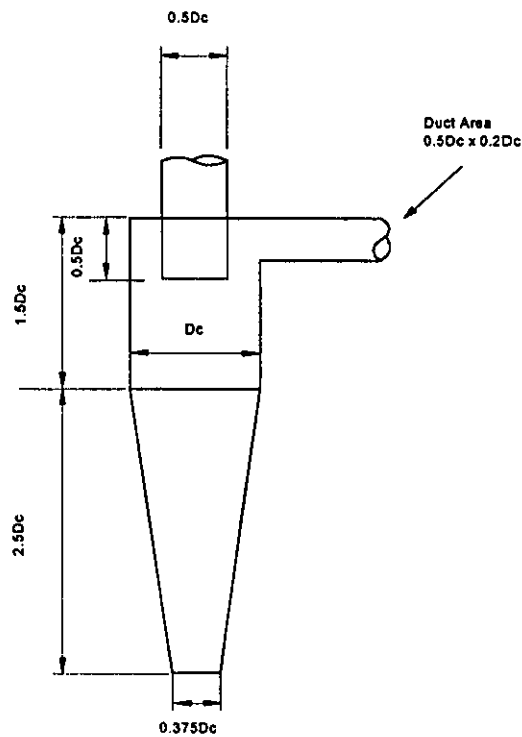


Figure 4.1. The dimensions of a high efficiency cyclone⁵⁵

The efficiency of this cyclone was then checked by comparing it to the standard size cyclone performance curves and the scaling up equation 2.22⁵⁵.

$$d_2 = d_1 \left[\left(\frac{D_{c2}}{D_{c1}} \right)^3 \times \frac{Q_1}{Q_2} \times \frac{\Delta \rho_1}{\Delta \rho_2} \times \frac{\mu_2}{\mu_1} \right]^{1/2} \quad \text{Equation 4.3}$$

Where subscript 1 denotes the properties of the standard size cyclone at the chosen efficiency and 2 denotes the properties of the proposed cyclone. In the above equation d is the mean particle diameter separated by the cyclone, D_c is the cyclone diameter, Q is the flow rate of gas through the cyclone, $\Delta \rho$ is the solid-fluid density difference and μ is the gas viscosity.

Before a full sized heated version of the system was built a prototype was constructed in glass to observe how efficient the split was between the bed sand and the char when ejected at the above flow rate. The design equations detailed above were used to design the prototype. The commissioning of this prototype and the full size apparatus is described in section 4.3.

4.3. COMMISSIONING

4.3.1. PROTOTYPE TESTING

4.3.1.1 Glass prototype

Initially a small glass prototype reactor, feed tube and cyclone were designed to assess whether exploiting the difference in terminal velocities of char and sand would result in an efficient separation. Early tests with the 40mm i.d. reactor, using silica sand for the bed and coal particles injected into the bed confirmed that extremely good separation could be achieved by raising the fluidising gas to the correct level and choosing the correct size range of the bed sand.

The prototype reactor was constructed from glass and contained a small glass sintered disc for gas distribution. The bed consisted of 100g of silica sand and was fluidised with 24 l/min of air at 20°C. To inject coal into this bed, a small fraction of fluidising gas was diverted to coal situated in a U-tube above the reactor. This resulted in the coal particles in the U-tube being flushed down the central feed tube into the centre of the fluidised bed of sand where they became almost instantaneously mixed with sand. The flow rate of the fluidising gas was then increased to 50 l/min and the elutriated particles collected in a small gas cyclone capable of collecting 100% of particles $>30\mu\text{m}$. The cyclone underflow was checked for sand contamination and the sand size range altered accordingly. An optimum sand and coal particle size range was established to carry forward for further testing.

4.3.1.2 Full size reactor

A schematic of the process showing the general system layout is given in Figure 4.3. A detailed description of the system and the larger cyclone designed for it are given after first describing the preliminary experiments, carried out during the first stages of commissioning, assessing various modes of operation and leading to the establishment of standard operating conditions.

Heated fluidising tests were carried out initially using crushed Thoresby coal, in the size range 125 μm - 185 μm , and 300g of 210 μm - 500 μm silica sand for the bed material. The reactor was heated by a tube furnace to a temperature of 950°C and fluidised with 24l/min of nitrogen (at 20°C). Before entering the main reactor, the gas was preheated to 450°C. The gases exiting the reactor passed through the cyclone, through two water-cooled condensers and then through a crude filter (a tube packed with glass wool) in an attempt to capture all the condensable and fine particulate matter.

Pyrolysis

1g of coal was injected down the feed tube into the centre of the fluidised bed as explained in 4.3.1.1, fluidised at 950°C. Upon the coal injection, rapid pyrolysis occurred generating large amounts of volatiles. This resulted in a back pressure being generated causing some of the Quickfit apparatus to blow apart. To combat this, the coal added per injection was reduced to 0.5g and the sand size range was reduced to 250 μm - 355 μm to allow the fluidising flow rate to be reduced to 12 l/min of nitrogen (at 20°C). A flow rate of 45 l.min⁻¹ was found to be the optimum flow rate to eject the coal-char from the bed without sand contamination. The reactor was flushed at this flow rate for a total of 1 minute to ensure all the char had been removed.

The problem of coal sticking in the central coal injection tube was overcome by pre-oxidising the coal to 200°C for 1 hour prior to use.

Filter

The fine particulate matter was found to be passing through the crude quartz wool filter. Too large a pressure drop across various filters tested caused the back pressure problem experienced earlier. Eventually, a polymer filter possessing an electrostatic charge was found to provide the best solution. Five layers of the material removed all visible particulates from the exiting gas stream. With two 300 mm long water-cooled condensers up-stream of the filter, tar exiting the reactor was captured.

Gasification

Using a selected oxygen and nitrogen mixture to fluidise the reactor, gasified chars could be produced in a similar manner to the pyrolysis chars. The best way of controlling the burn-out of a char was found to be by setting the residence of the char in the reactor to 10 seconds before ejection. Differing degrees of char burn-out could then be achieved by varying the oxygen content of the fluidising gas. The target 70wt.% (daf) burn-out was obtained using a 15vol% oxygen/nitrogen mixture at a residence of 10 seconds.

At this stage it was felt that the basic experimental apparatus, procedure and char production methods had been sufficiently well established to enable experimental studies to begin.

4.3.2. ESTABLISHED SYSTEM CONFIGURATION

The following section aims to clarify the previous sections in Chapter 4 by describing the final apparatus and system set-up adopted after design and initial commissioning had been completed. The general process described in part 4.3.2.2 forms the basis of the procedure used in both the pyrolysis and gasification experiments. More detailed descriptions of those procedures are given in later sections. Figure 4.2 shows the main features of the designed fluidised bed reactor.

4.3.2.1. Apparatus

Fluidised bed reactor

The fluidised bed reactor consists of a 70mm i.d. silica tube with an overall length of 1m containing a sintered quartz disc for the purpose of gas distribution across its diameter (450mm from the gas inlet). The reactor is shown in Figure 4.2 (not to scale). It has two thermocouple tubes, one extending deep enough to penetrate the bed of sand the other sited at the gas outlet level. The central tube is open-ended and extends to within 50mm of the quartz, gas distributor, disc. This central tube forms the lower part of the coal injection system. The top part consists of a 6mm diameter coal delivery U-tube connected

to a purging gas stream. The top of the reactor, before the gas cyclone, is lagged. The bed itself consists of 280g of silica sand in the size range $250\mu\text{m}$ to $355\mu\text{m}$.

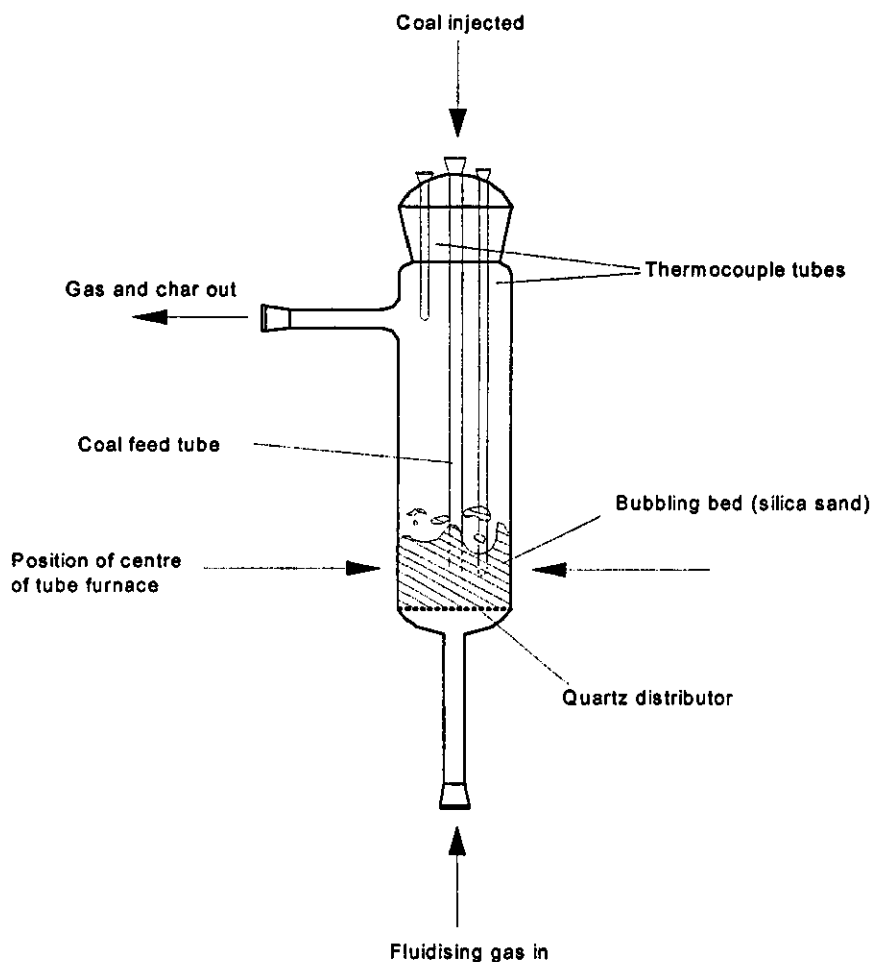


Figure 4.2 A diagram showing the main features of the silica fluidised bed reactor designed for the studies at Loughborough.

Fluidising gas

The fluidising gas may be obtained as compressed air or from pressurised nitrogen and oxygen cylinders. The gas flows are monitored with individual flow meters

Furnace and pre-heater

The reactor is located in a vertical tube furnace of internal diameter 80mm and a height of 720mm. It is placed in such a position that the quartz distributor of the reactor is 50mm below the centre of the furnace. This ensures that during operation the centre of the fluidised bed of sand lies in the hottest part of the furnace. The furnace is capable of heating to a maximum continuous temperature of 1150°C and is controlled by a small programmable controller with touch keypad.

The gas pre-heater consists of a glass vessel 60mm in diameter and 500mm long packed with short glass tubes to increase contact area. It sits in a horizontal tube furnace below the main reactor and operates at 450°C. The pre-heater and main reactor are connected by cone and socket Quickfit joint.

Downstream from the reactor

Connected to the gas exit point of the reactor is the gas cyclone and char collection pot. A pass-over tube connects the over flow of the cyclone to the first of two water cooled condensers. At the bottom of the condensers is fitted the filter body containing layers of electrostatically charged polymer filter.

4.3.2.2. General process description

The layout of the system is shown in Figure 4.3 and Figure 4.4 shows a photograph of the assembled rig. A regulated flow of gas passed from the gas cylinders through flow meters at the appropriate flow rates to make up the desired gas mixture. The mixed gas passed at a flow rate of 12 l/min through the gas pre-heater into the bottom of the main reactor where it passed through the gas distributor and fluidised the bed of sand at around 4 times its minimum fluidisation velocity. The tube furnace controlled the temperature of the reactor at the desired level.

Approximately 0.5g of coal, accurately weighed, in the size range 125µm to 185µm rested in the coal U-tube described above. A small amount of fluidising gas mixture was diverted through a gas bubbler and then into the U-tube where it purged the coal prior to injection. After the coal was completely purged it was injected into the bed by

momentarily diverting more gas mixture through the U-tube. The coal then passed down the central injection tube into the centre of the fluidised bed of sand where it was rapidly mixed.

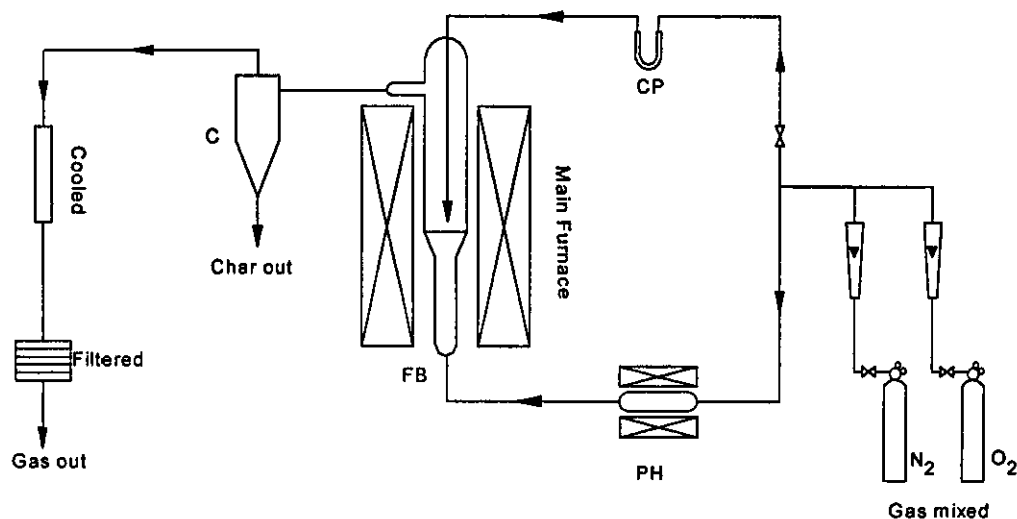


Figure 4.3 A Schematic of the fluidised bed process showing all the main features.
PH - gas pre-heater, FB - heated fluidised bed reactor, CP - gas purged coal feed tube and C - cyclone

After the desired residence time of 10 seconds the char in the reactor was ejected by increasing the fluidising flow rate to a level calculated to blow the char from the reactor out into the gas cyclone leaving the denser sand behind. The char was collected in the under-flow of the cyclone, removed and weighed prior to analysis. The gas from the cyclone over-flow passed into the water cooled condensers and finally through the polymer filter where fine particulates were removed. The tar condensed on the walls of the cyclone and the water cooled condensers can be removed for analysis, the detailed procedure is discussed later.

Using the above apparatus, chars were produced from different coals and by subsequent analysis the sulphur and nitrogen contents of those chars were determined. The conditions to which the coals were subjected were known by precisely controlling the residence time in the reactor more precisely than can be obtained in a continuous process.



Figure 4.4 A photograph of the assembled fluidised bed system.

4.3.3. COMMENTS

Although the design and prototype reactor construction was completed in the expected time scale, the commissioning time of the experimental rig had been under estimated. A considerable amount of time was spent optimising the conditions to allow sufficient char material to be collected without sand contamination. Developing the right filtering technique for the pyrolysis runs along with a suitable method for tar recovery was also time consuming. This commissioning time was, however, necessary and resulted in a minimum of changes needed when the experimental programme began.

4.4 EXPERIMENTAL METHOD

4.4.1. COAL SAMPLE PREPARATION

Seven UK coals were provided by the Coal Research Establishment from their Coal Bank. The coals and some of their properties are shown in Table 4.1. The first five coals were of particular interest to the ABGC project, the last two were chosen to extend the rank range of the coals to be studied.

Table 4.1. Coals used for study (data reproduced from Coal Bank booklet) ⁵⁵

Coal	ISO classification	Vol. matter (dmmf)	Ash, wt.% (db)	Carbon % wt.% (dmmf)	Hydrogen, wt.% (dmmf)	Total sulphur, wt.% (db)	Nitrogen, wt.% (db)
Nadins	801	45.1	8.5	80.1	5.1	2.2	1.9
Kellingley	634	41.6	5.3	85.1	5.9	1.6	2.1
Dawmill	711	40.4	4.7	81.3	4.8	1.4	1.3
Thoresby	634	38.7	5.2	84.3	4.6	2.0	1.8
Longannet	N/A	35.4	11.9	82.9	5.0	0.4	1.6
Cwm	434	22.6	5.9	90.3	4.4	0.8	1.5
Tilmanstone	333	17.2	5.4	92.4	4.5	1.2	1.5

dmmf: Dry mineral matter free

db: Dry basis

The coal samples were prepared by coarsely crushing in a screw fed grinder. The size range 125 μ m to 185 μ m was then sieved out, preoxidised for 1 hour in a muffle furnace at 200°C (this was to prevent the coal from sticking in the reactor feed tube) and stored in a desiccator.

These coal samples in the 125 μ m to 185 μ m size range were ashed, analysed for nitrogen, sulphur and volatile matter content according to the methods discussed in detail in section 4.4.3. - Coal and char analysis.

4.4.2 CHAR PRODUCTION

4.4.2.1 System preparation

A detailed description of the fluidised bed apparatus developed for producing chars is given in section 4.3.2.1. Section 4.3.2.2 describes the general char production process, Figure 4.3 shows a schematic of the fluidised bed system, and Figure 4.4 shows a colour photograph of the rig.

To prepare the fluidised bed rig prior to an experiment, both the reactor furnace and the preheater furnace were warmed up 2 hours in advance and the fluidising air (12 l/min) was switched on 30 minutes before beginning of an experimental to allow full settling of temperatures. The reactor contained around 280g of silica sand in the size range 250 μ m to 355 μ m. Before any pyrolysis/ gasification experimental runs were carried out, the reactor was "blown out" at 950°C with a flow rate of 45 l/min for 15 minutes to remove any fine particulates and any calcination products.

4.4.2.2. Pyrolysis chars

The apparatus was prepared as above. For pyrolysis experiments the reactor was fluidised with nitrogen gas. Coal samples were purged for 15 minutes in the U-tube with nitrogen before they were injected into the fluidised bed.

For a particular individual run, the pyrolysis char was produced by injecting about 0.5g of pre-oxidised coal (accurately weighed) into the fluidised bed reactor for 10 seconds at 950°C then ejecting and collecting the char in the cyclone under-flow as described in section 4.3.2.2.

The outlet gases from the cyclone over flow were cooled in two water cooled condensers in order to condense the tars. Any fine particulate matter remaining in the gas outlet was then removed by passing the gas through layers of the filter polymer. This batch injection was repeated 6 times for each coal to collect enough pyrolysis char for analysis.

After a pyrolysis run the bed material was removed. The method of cone and quartering was used to take duplicate 10g samples, these were ashed to establish char content of the bed material due to agglomeration. The tar was recovered by washing the cyclone, condensers and filter material with a total of 200ml of 4:1 chloroform/methanol solution. The washings were filtered to remove any fine particulate matter and then evaporated at 60°C until concentrated. This residue was then left overnight at 40°C to dry and finally weighed. Appendix B shows in detail how the mass balance was calculated for the pyrolysis experiment.

The above method was repeated, at 950°C, for all seven coals used in this study. The mass balance was calculated for each pyrolysis experiment; volatile matter was calculated by subtraction of tar and char mass (daf) from the original coal mass (daf) added to the reactor. Appendix B details the mass balance calculations for each pyrolysis run. The char and tar samples collected were analysed for ash, sulphur and nitrogen content. These methods are described in full in section 4.4.3 - Coal and char analysis.

To study the effects of sorbent in the bed material, one pyrolysis experiment was carried out, using Nadins, with approximately a 2:1 limestone/ total coal mass added to the bed material. The limestone was prepared in the size range 420µm - 500µm. The pyrolysis chars were produced as above. After the run the bed was removed, sieved and the reacted limestone collected for sulphur analysis by Coal Research Establishment. The char and tar samples were analysed as before.

To study the effects of pyrolysis temperature, pyrolysis chars were collected at 50°C intervals in the range 850°C to 1050°C. The method used to collect these pyrolysis chars was different to that detailed above. For these tests the gasification method was adopted, see below.

4.4.2.3. Gasification Chars

The apparatus was prepared as in section 4.4.2.1. The fluidising gas was mixed from regulated bottles of nitrogen and oxygen in the required proportion. This was done through rotameter flow meters to create the desired volume % mixture of N₂/O₂ at 20°C.

Approximately 0.5g, accurately weighed, of the preoxidised coal was placed in the U-tube. This was then purged with a small proportion of the fluidising mixture 15 minutes prior to injection into the reactor.

For a particular individual run, gasification char was produced by injecting the preoxidised coal from the U-tube into the fluidised bed reactor for 10 seconds at the desired temperature, then ejecting and collecting the char in the cyclone under-flow as described in section 4.3.2.2. Nitrogen was used to eject the char from the reactor to freeze the gasification reaction. This batch injection was repeated 3 times to collect enough material for analysis.

The above method was repeated for all seven coals used in the study at various conditions. Chars were produced at 950°C in 10, 15 and 20 vol.% mixtures of O₂/N₂ for all coals. One coal, Longannet, was used to study the effects of reaction temperature in the range 850°C to 1050°C; chars were produced at 50°C intervals in this temperature range in a fluidising gas mixture of 15 vol.% O₂/N₂.

The char and tar samples collected were analysed for ash, sulphur and nitrogen content. The ash content of the char was used to estimate the degree of burnout the coal had undergone. The coal and char analytical methods are described in full in section 4.4.3

One set of gasification experiments with Nadins coal was carried out with approximately 1% limestone in the bed material. The limestone was prepared in the size range 420µm - 500µm. The gasification chars were produced as above at 950°C in 10, 15 and 20 vol.% mixtures of O₂/N₂. After each run the bed was removed, sieved and the reacted limestone collected for sulphur analysis. The char samples were analysed as before.

4.4.3 COAL AND CHAR ANALYSIS

4.4.3.1. Proximate analysis

The ash contents of the coal and fluidised bed char samples were determined using the British Standard method, BS1016 Part 3⁵⁷. The volatile matter of the coal samples was determined using British Standard method, BS1016 - Part 4⁵⁸.

It is important to note that the amount of fluidised bed char material collected during an experiment did not allow the required 1g of sample to be used for ashing. Apart from this, the ashing method of the char samples followed the British Standard method

4.4.3.2 Total sulphur

For total sulphur analysis, the coal and fluidised bed char samples were further prepared by grinding with a pestle and mortar, passing through a 30µm sieve and storing in a desiccator.

The coals, pyrolysis tars and chars, prepared as above, were analysed using a version of the oxygen flask method, chosen because only small quantities of char and tar material were available for analysis. The basic oxygen flask method is described in Coke Research Report 13⁵⁹ where it is compared to other methods of total sulphur analysis techniques. It is described in more detail by Fritz et al⁶⁰. The apparatus consisted of a 500ml conical flask with a special stopper. The stopper contained a platinum wire with a platinum basket attached to the bottom, see Figure 4.5.

A 25 - 30mg sample of coal or char was weighed into a 25mm² piece of ashless filter paper with a small fuse, folded carefully and placed into the platinum basket with the fuse protruding. 10ml of distilled water along with 10 drops of 30% hydrogen peroxide were added to the flask. The flask was then flushed with oxygen for 20 seconds, the fuse was lit and stopper placed firmly back into the flask.

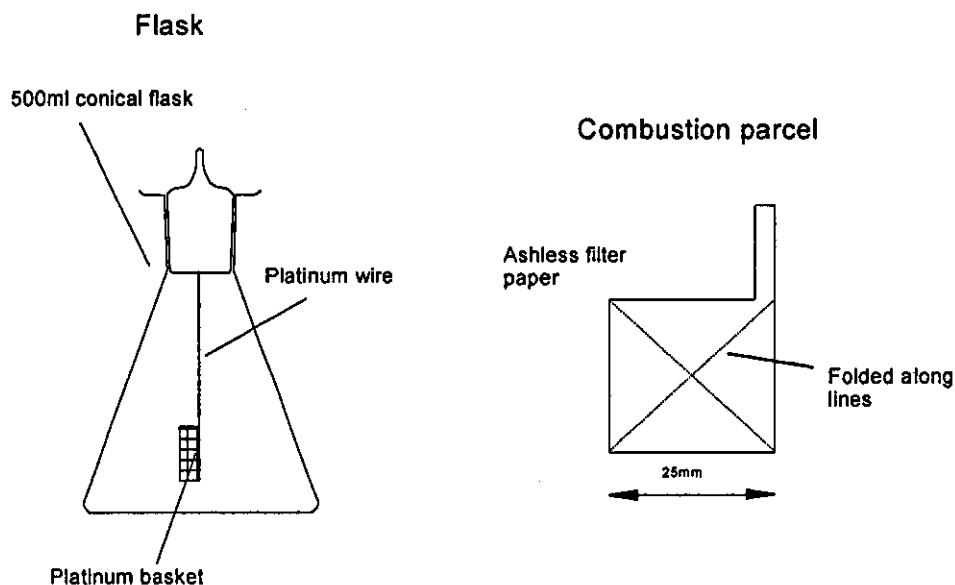


Figure 4.5. Apparatus for Oxygen Flask total sulphur determination

When the combustion of the sample was complete the flask was shaken for 3 minutes. The stopper was then washed with 40ml of propan-2-ol. To this, 8 drops of thorin indicator and 1-2 drops of methylene blue were added. The yellow solution was then titrated against a 80% propan-2-ol/20% aqueous solution of 0.001 molar barium perchlorate. The end point was from yellow through to pale pink. Although the colours were relatively similar, the end-point was sharp and agitation of the solution helped identify the colour change more readily.

The barium perchlorate solution was standardised against a standard H_2SO_4 solution. The thorin and methylene indicators were 0.005 and 0.0005 molar respectively.

4.4.3.3 Nitrogen, carbon and hydrogen

The coals, pyrolysis tars and chars were ground to less than $30\mu\text{m}$ in a pestle and mortar as for total sulphur analysis. They were then analysed for nitrogen, carbon and hydrogen using a *Perkin-Elmer* Model 240 elemental analyser. Duplicate samples were analysed.

4.4.3.4. Char morphology

A sample of each of the pyrolysis chars was mounted on a polished block for reflected light microscopy studies. Four main categories of char particle type were identified i.e.

1. INERT. Particles with unfused angular shape, sometimes bearing small pores often slit-like.
2. SEMI-INERT. Particles which show evidence of rounding of the edges bearing some small to medium sized pores often aligned.
3. HONEYCOMB (NETWORK). Particles which exhibit quite a large degree of particle rounding with at least three large central pores, the pore walls bearing many small rounded pores.
4. CENOSPHERE. Rounded, highly porous particles, usually with one large central pore. The surrounding walls bearing many small to medium sized rounded pores.

The proportion of these char types present in the samples was counted using a point counting method, based on 200 particle counts (4 lots of 50).

CHAPTER 5

RESULTS AND DISCUSSION

5.1. EXPERIMENTAL RESULTS

5.1.1. ANALYSIS OF COALS USED

The analyses of the coals used in this study, pre-oxidised in the size range 125 μ m - 185 μ m, are given in Table 5.1. This analysis differs slightly to the bulk sample data provided by the CRE coal bank⁵⁶, see section 4.4.1 for summary, Appendix C lists the full CRE data on the coals used. The data supplied by the CRE is based on a typical sample and so variations were inevitable between batches dispatched. The particle size range used in the study may well also have had an effect on the weight percent of each component measured.

It was necessary to preoxidise the coals for 1 hour at 200°C prior to experimental runs to reduce the tendency for the samples to become stuck in the coal feed tube to the fluidised bed reactor. The higher ranked coals, Tilmanstone and Cwm, were a particular problem during pyrolysis experiments; readily becoming agglomerated and leading to small amounts of char having to be recovered from the bed material after pyrolysis. This effect was negligible for the other five coals. For all seven coals sticking and agglomeration during gasification was less of a problem, presumably due to the presence of an oxidant in the gas of the reactor feed tube.

Oxidation can lead to the coal becoming less plastic on heating. For this reason, it was recognised that preoxidation of the coal could have a small effect on the char particle size/shape and could possibly reduce the volatile yield of the coal on pyrolysis.

It was considered that the benefits of preoxidation of the coal samples used in the study would outweigh the disadvantages. Rapid injection of the coal sample was required and it was deemed that preoxidation of the coal to achieve this would not excessively effect the split of nitrogen and sulphur between the char and the volatiles.

Table 5.1. Analysis of coals used (125µm to 185µm preoxidised for 1 hour at 200°C)

Coal	ISO Classification	Ash content, wt% (db)	B.S. standard volatile matter, wt% (daf)	Carbon, wt% (daf)	Hydrogen, wt% (daf)	Total sulphur, wt% (daf)	Nitrogen, wt% (daf)
NADINS	801	7.0	40.0	70.5	3.4	2.1	1.5
DAW MILL	711	3.4	38.4	75.2	4.3	1.8	1.3
THORESBY	634	4.5	35.3	77.9	4.3	1.9	1.7
KELLINGLEY	634	4.1	36.6	77.2	4.6	1.4	1.8
LONGANNET	N/A	12.6	33.1	76.0	4.1	0.4	1.7
CWM	434	2.8	27.9	85.4	4.6	1.3	1.5
TILMANSTONE	333	3.6	17.0	88.2	4.1	1.4	1.4

5.1.2. FLUIDISED BED PYROLYSIS

5.1.2.1. Volatile yields

The fluidised bed pyrolysis experiments were carried out on each of the coals using the method described in section 4.4. The weight distribution of each of the pyrolysis products is shown in Table 5.2, in order of decreasing volatile matter yield. The volatile yield measured from the fluidised bed experiment follows a similar trend with coal type as the British Standard method volatile yield. However, yields are higher from the fluidised bed runs, probably due to a higher rate of heating experienced in the fluidised bed than the B.S. analysis⁵⁸. Increased heating rate is generally considered to increase the volatile yield during pyrolysis; increasing the internal mass transfer of the coal particle and therefore reducing the tendency for the volatile matter to undergo recombination reactions forming soot and heavier tars in the pores of the developing char particle²³.

When the B.S. proximate volatile matter is plotted against the fluidised bed volatile matter, see Figure 5.1, the gradient of the linear best fit is 1.05 indicating a 5% higher volatile yield from the fluidised bed runs than the from the proximate analysis. Other work⁶¹ has observed even higher volatile yield ratios in the order of 1.5 for chars produced in entrained flow reactors (particle size 75 μ m, final temp. 1000°C), this also was attributed to high estimated particle heating rates of around 10,000 k/s. Even at lower estimated heating rates (1000 k/s), the fluidised bed volatile yields were still 1.2 times greater than the proximate analysis at pyrolysis temperatures of 800°C and 900°C.

Even though increased heating rate can increase the volatile yield, increased particle size and reactor pressure can reduce the quantity of volatile matter released on pyrolysis. Laughlin et al⁶¹ observed a 16% drop in volatile yield when the pyrolysis pressure was increased from 0.1 MPa to 1 MPa. This is significant when considering pressurised fluidised bed combustion or the gasifier stage of the ABGC which operate at a typical pressures of between 0.2 and 1.5 MPa. The apparatus used in this study did not permit the effects of increased reaction pressure to be investigated.

Table 5.2. Distribution of products after fluidised bed pyrolysis

Parent coal	Weight % of each pyrolysis product (daf)*			
	Char	Gas	Tar	Total FB vol. matter
NADINS	56.4	39.3	4.3	43.6
DAW MILL	57.6	37.4	5.0	42.4
THORESBY	59.1	37.3	3.6	40.9
KELLINGLEY	62.8	32.7	4.5	37.2
LONGANNET	67.0	30.1	2.9	33.0
CWM	75.6	19.9	4.5	24.4
TILMANSTONE	78.6	18.5	2.9	21.4

* Full mass balance calculations in Appendix B

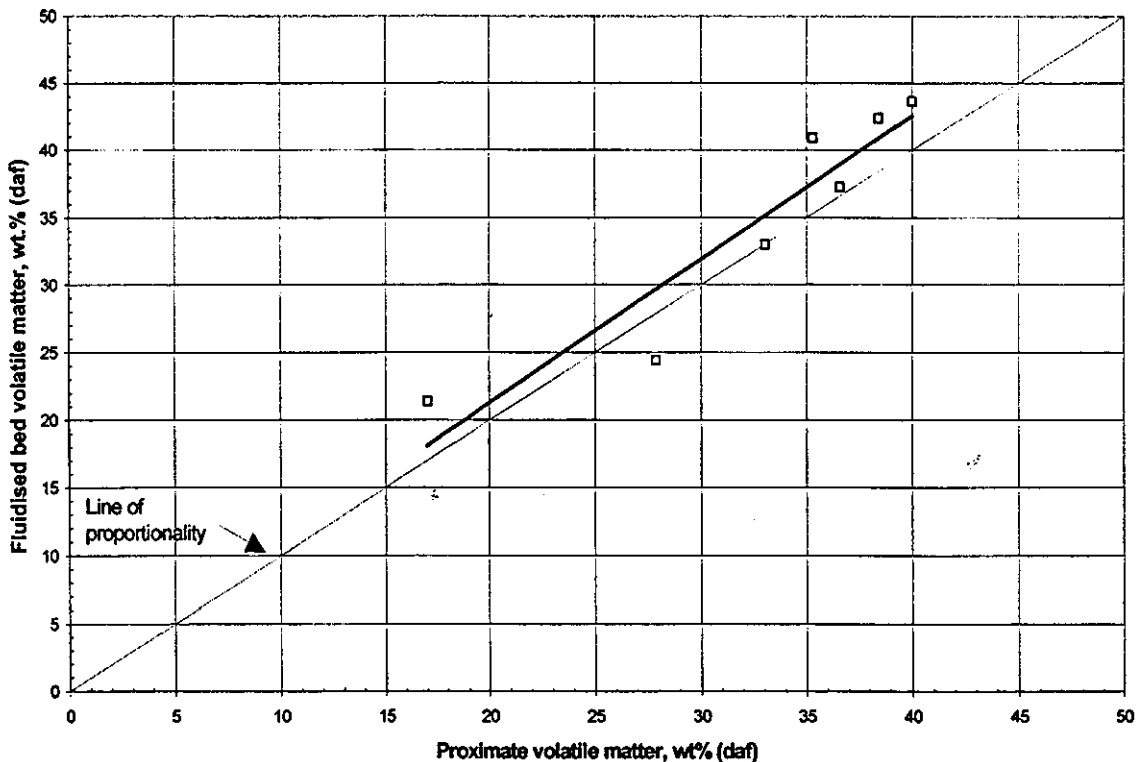


Figure 5.1. Difference in volatile matter yields between FB pyrolysis and proximate analysis.

5.1.2.2 Sulphur and nitrogen distribution

Table 5.3 shows the analysis of the fluidised bed pyrolysis chars and tars collected. In order to establish how closely the sulphur and nitrogen content of the coal is associated with the carbon content the sulphur/carbon and nitrogen/carbon ratios were calculated for the coal and pyrolysis products, as follows:

$$\text{Sulphur/ carbon ratio, } S/C = \frac{Wt.\% S(daf)}{Wt.\% C(daf)} \quad \text{Equation 5.1}$$

$$\text{Nitrogen/ carbon ratio, } N/C = \frac{Wt.\% N(daf)}{Wt.\% C(daf)} \quad \text{Equation 5.2}$$

Once these had been calculated the normalised sulphur/ carbon and nitrogen/ carbon ratios, S'/C and N'/C , were calculated for the pyrolysis products of each coal.

$$\text{Normalised S/C ratio, } S/C' = \frac{S/C_{\text{Product}}}{S/C_{\text{Coal}}} \quad \text{Equation 5.3}$$

$$\text{Normalised N/C ratio, } N/C' = \frac{N/C_{\text{Product}}}{N/C_{\text{Coal}}} \quad \text{Equation 5.4}$$

These ratios give a practical indication of the split of nitrogen and sulphur between the char and volatiles and provide a consistent method of comparing results to the gasification chars whose degree of burn-out was calculated using an "ash tracing" method susceptible to errors from sand contamination. The S/C , N/C , S/C' and N/C' ratios for the pyrolysis chars and tars of the seven coals studied are given in Table 5.4.

Table 5.3. Elemental analysis of the fluidised bed pyrolysis products

PARENT COAL	PYROLYSIS CHAR					PYROLYSIS TAR			
	Ash, wt% (db)	S, wt% (daf)	N, wt% (daf)	H, wt% (daf)	C, wt% (daf)	S, wt% (daf)	N, wt% (daf)	H, wt% (daf)	C, wt% (daf)
NADINS	12.0	1.5	1.6	0.7	93.0	1.8	1.7	5.7	86.1
DAW MILL	6.3	1.5	1.3	0.8	90.9	1.6	1.4	5.5	83.4
THORESBY	8.0	1.5	1.7	0.7	87.4	1.5	1.8	5.0	84.4
KELLINGLEY	7.7	1.3	1.9	0.7	91.6	1.2	2.6	5.6	80.0
LONGANNET	19.9	0.4	1.8	0.8	94.2	1.2	1.7	5.7	84.1
CWM	7.0	1.0	1.1	0.7	76.	1.5	1.2	5.5	84.1
TILMANSTONE	5.3	1.1	1.1	0.7	81.2	1.9	1.6	6.0	77.6

Table 5.4 Sulphur/ carbon and nitrogen/ carbon ratios of pyrolysis products.

PARENT COAL	PYROLYSIS CHAR				PYROLYSIS TAR			
	S/C	N/C	S/C'	N/C'	S/C	N/C	S/C'	N/C'
NADINS	0.016	0.017	0.54	0.80	0.021	0.02	0.70	0.94
DAW MILL	0.016	0.014	0.70	0.84	0.019	0.017	0.82	1.01
THORESBY	0.017	0.019	0.70	0.82	0.018	0.022	0.74	1.01
KELLINGLEY	0.014	0.021	0.74	0.89	0.014	0.032	0.77	1.37
LONGANNET	0.004	0.019	0.72	0.86	0.014	0.02	2.53	0.91
CWM	0.013	0.015	0.82	0.86	0.018	0.015	1.17	0.85
TILMANSTONE	0.013	0.013	0.86	0.84	0.024	0.02	1.58	1.29

Generally in Table 5.4 the N/C' ratios tend to be higher than the S/C' ratios in both the char and the tar. This implies that more sulphur species become concentrated in the gaseous phase than do nitrogen species. It is also clear that both the S/C' and the N/C' ratios are less than 1 in all pyrolysis chars indicating that both sulphur and nitrogen are released preferentially into the volatiles. The normalised ratios of nitrogen and sulphur in the tar display a larger degree of scatter.

The normalised ratios, S/C' and N/C' are plotted against carbon content of the parent coal in Figure 5.2. The nitrogen is shown to increase very slightly with increasing coal rank up to about 80 wt.% C (daf), and possibly decreasing slightly above this. Five of the data points show a linear effect, but with the two higher ranked coals not following this trend, this leads to a slight curvature in the trend. What is certain is that the N/C' ratio is less than 1 for all the pyrolysis chars indicating a preferential release of nitrogen to the volatiles on pyrolysis.

Figure 5.2 also shows, for the seven coals studied, that as coal rank increases there is a trend for the sulphur to become less preferentially released into the volatiles. Again this implies that as rank increases the sulphur in the coal is becoming associated with more thermally stable compounds. The S/C' ratios for all but one of the coals, Tilmanstone, is lower than the N/C' ratios indicating that on pyrolysis sulphur is more readily released into the volatile products than nitrogen.

To investigate whether the change in S/C' ratio was attributable to the pyritic content of the coal, the S/C ratios of the pyrolysis chars are plotted against the proportion of pyritic sulphur/ total sulphur, wt.% (daf) of the parent coals according to the original CRE data (appendix C) in Figure 5.3. From this graph it can be argued that the proportion of pyritic sulphur in the coal has no significant effect on the resulting S/C' ratio of the pyrolysis chars produced.

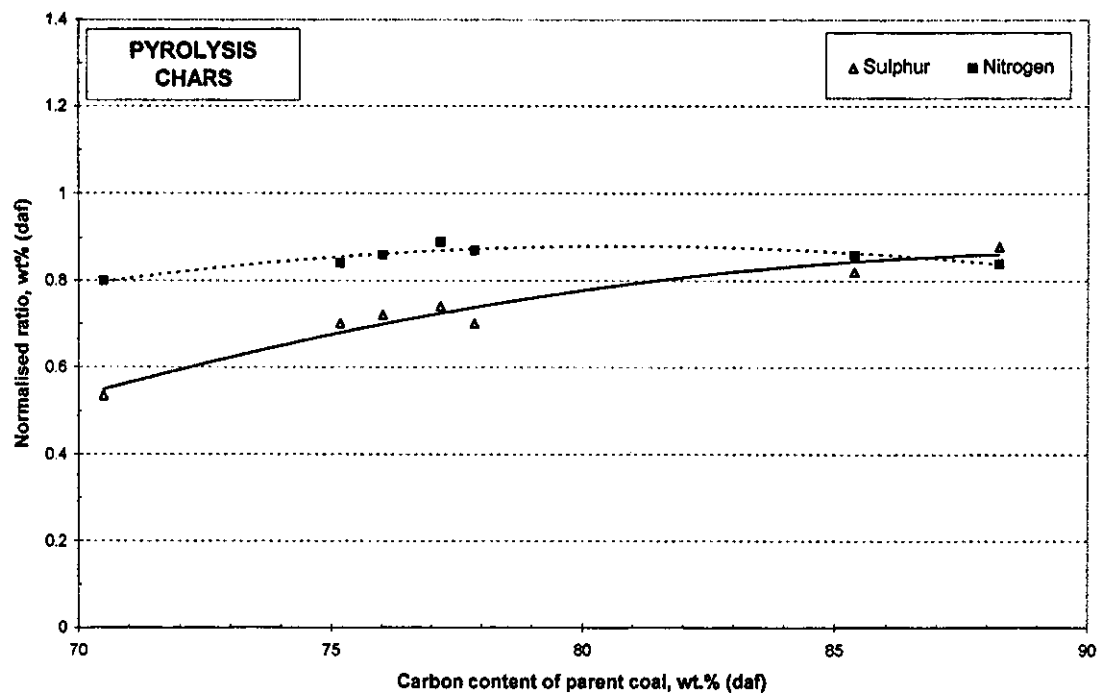


Figure 5.2. Change of S/C' and N/C' of pyrolysis char with coal rank

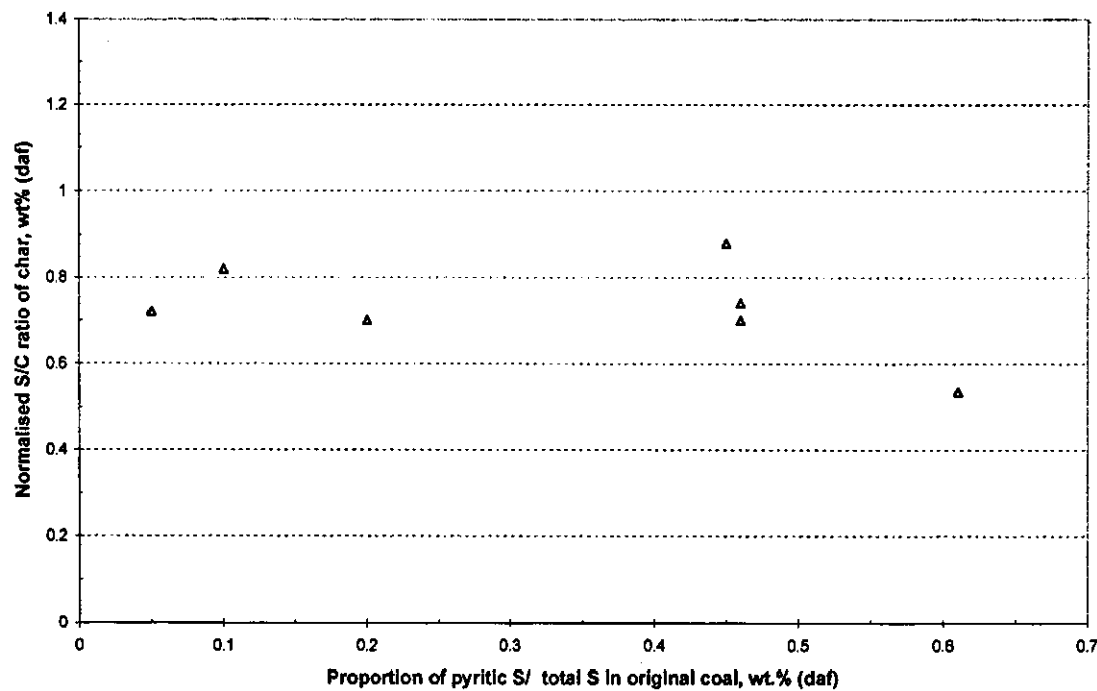


Figure 5.3. Effect of increased pyritic sulphur content of parent coal on S/C' ratio of pyrolysis chars.

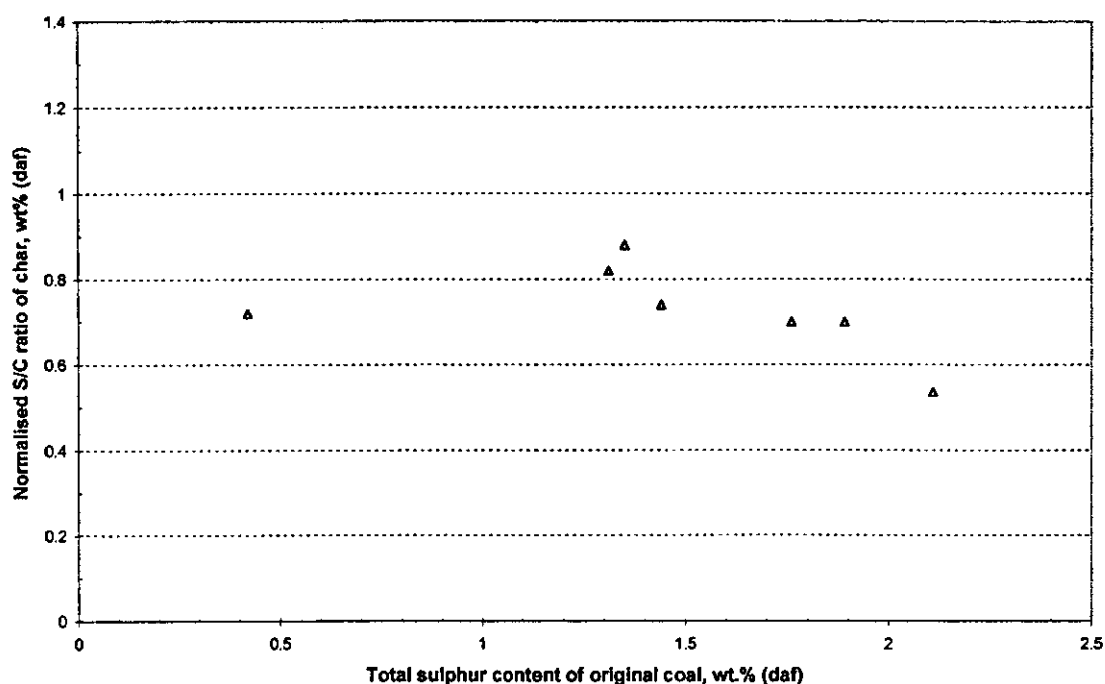


Figure 5.4. Effect of total sulphur content of parent coal on S/C' ratio of pyrolysis chars

The S/C' ratio of the pyrolysis chars was also plotted against the total sulphur content of the parent coals in Figure 5.4. Although slight, the plot shows a weak trend for sulphur to become more preferentially released into the volatiles with increased total sulphur content of the parent coal.

As a further indication of the effect of rank on the split of sulphur and nitrogen into the char and volatiles, the S/C' and N/C' ratios of the pyrolysis chars were plotted against volatile matter yield collected during the fluidised pyrolysis runs. Figure 5.5 again indicates a link between the rank of the coal and the corresponding degree of concentration of sulphur into the volatile matter. The ratios remain essentially constant until a volatile yield of around 39 wt.% (daf) and then drop off with a further increase in volatile matter yield. The trend is similar but less pronounced for nitrogen.

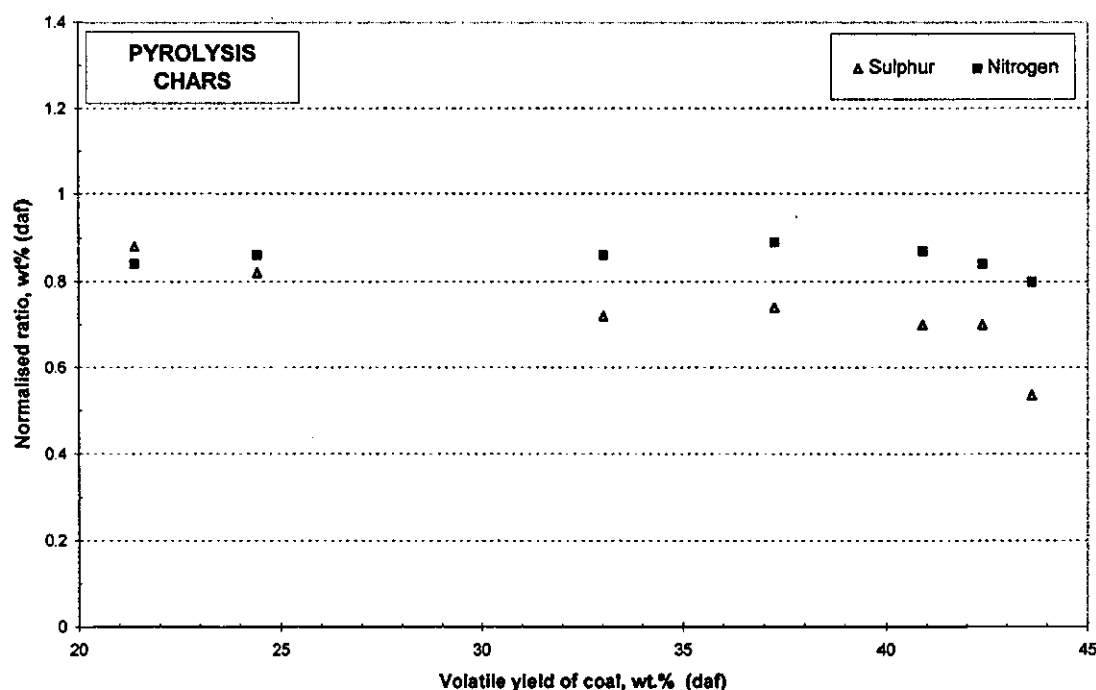


Figure 5.5. Change of S/C' and N/C' with increased volatile matter content.

The quantities of sulphur and nitrogen reporting to the tar constituent of the volatile matter is represented in Figure 5.6. Generally higher proportions of nitrogen were observed in the pyrolysis tar but the data shows a high degree of scatter. This is thought to be due larger errors associated with the relatively small quantities of tar material recovered for analysis. For this reason it would be difficult to deduce anything significant from the tar analysis, but there seems to be a general tendency for the N/C' ratio to be closer to 1 for the pyrolysis tars than for the chars. If so, this would agree with a number of studies reporting nitrogen contents of pyrolysis tars^{28,29,34,62}.

It is known that pyrolysis temperature can affect the proportion of nitrogen released into the volatiles. Increased pyrolysis temperatures have been shown to lead to an increased shift of the nitrogen into the gaseous phase, ultimately leading to negligible quantities of nitrogen being left in pyrolysis chars at 1800°C²². To see if temperature had a significant effect on the split of nitrogen or sulphur between the volatiles and the char in the typical fluidised bed reactor operating range, pyrolysis runs were carried out at temperatures in the range 850°C to 1050°C using the Longannet coal sample. The results are shown in Figure 5.7, the data indicates no significant effect of pyrolysis temperature on the nitrogen and sulphur contents of the char in the temperature range studied.

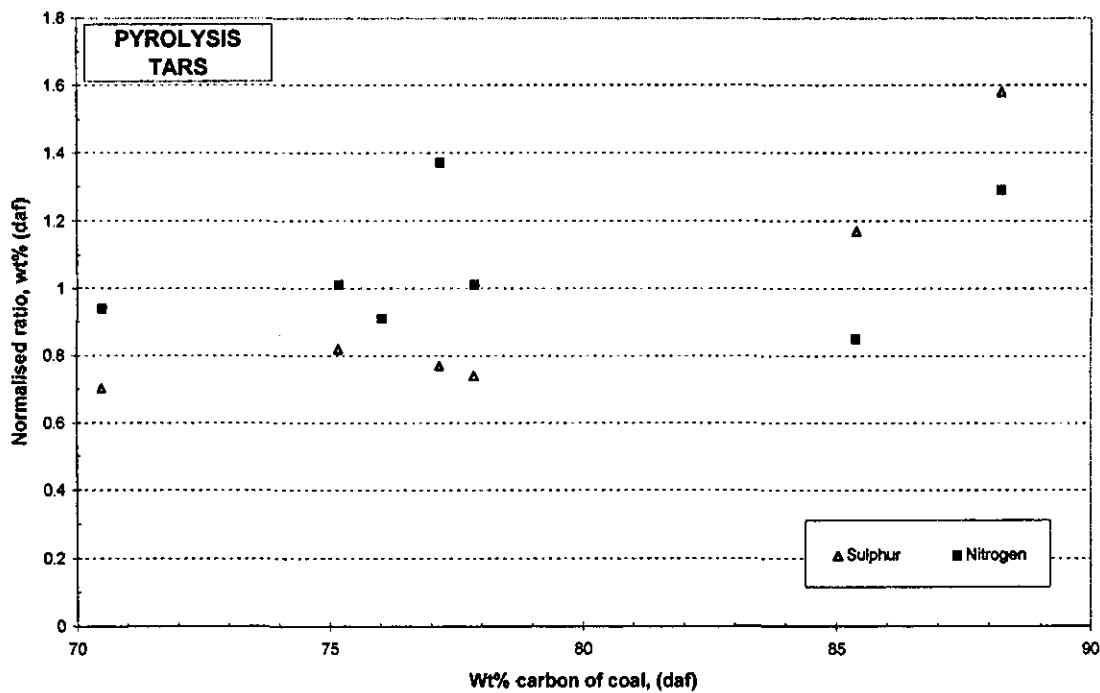


Figure 5.6. Variation of S/C' and N/C' of the tar with carbon content of parent coal.

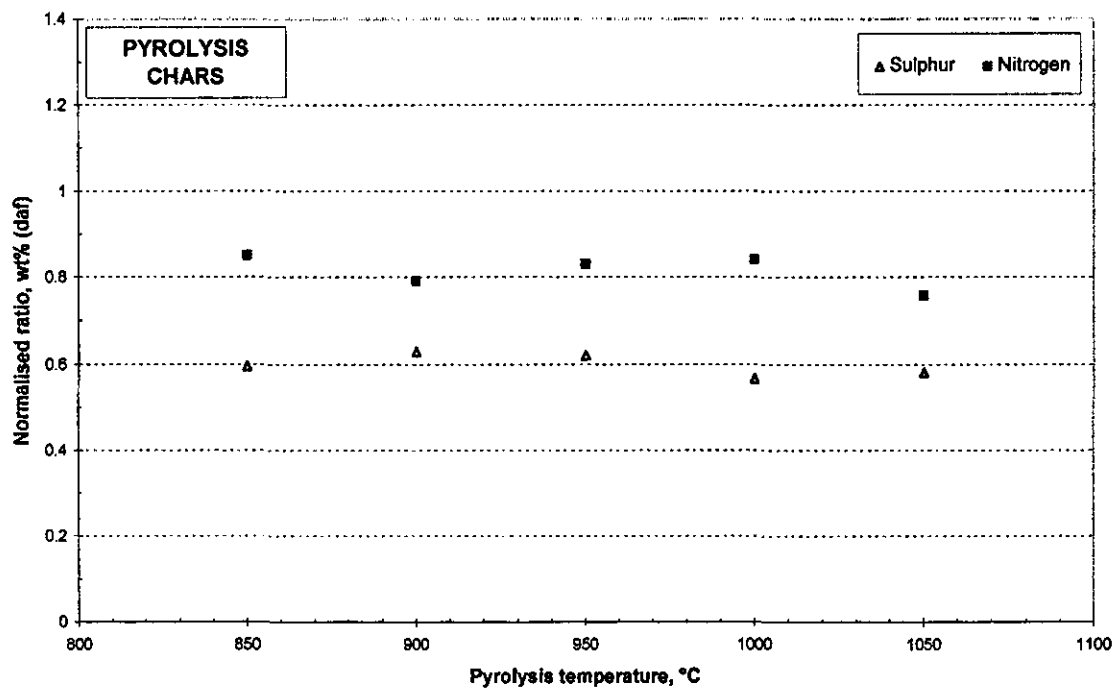


Figure 5.7. Effect of pyrolysis temperature on S/C' and N/C' of chars

5.1.2.3 Char morphology

Samples of pyrolysis chars from five of the coals were examined under the microscope to establish the type and relative number of char particle shapes produced during devolatilisation in the fluidised bed. Table 5.5 shows the occurrence of each of the particle shape types. The results appear in descending order of carbon content of parent coal sample, as measured for this study, with highest C wt% (daf) at the top. The particle counting method is given in Section 4.4.3.4 of the Experimental Method.

Table 5.5. The occurrence of four main char particle types during pyrolysis

COAL	<u>Char particle types observed, %</u>			
	Inert	Semi-inert	Honeycomb	Cenosphere
THORESBY	9	22	44	25
KELLINGLEY	5	20	43	32
DAWMILL	6	19	61	14
NADINS	12	23	60	5
LONGANNET	12	35	52	1

The most common particle shape in all the chars is the honeycomb (or network) - particles which exhibit a large degree of particle rounding with at least three central pores, the pore walls bearing small rounded pores. Chars from the higher ranked coals contain a higher proportion of the cenosphere-type shape.

Micrographs of the four types of char particle shapes observed are shown in Figures 5.8 - 5.11. The char produced from the Nadins coal was used for the photographs.

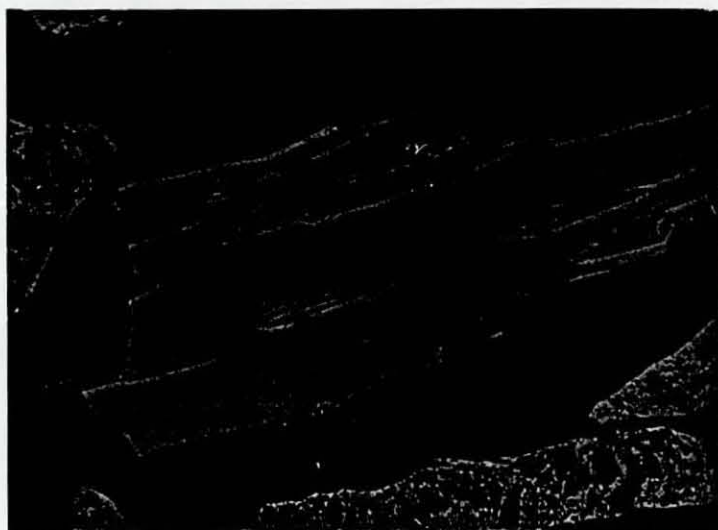


Figure 5.8. Inert type char particle type (400 \times magnification)

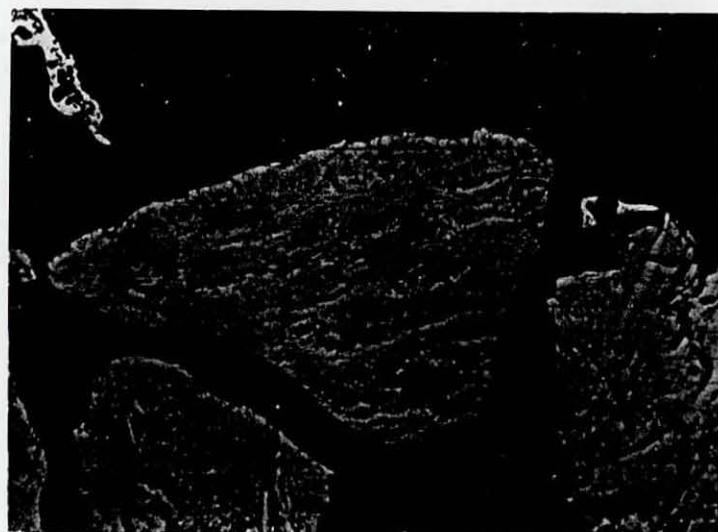


Figure 5.9. Semi-inert char particle type (400 \times magnification)

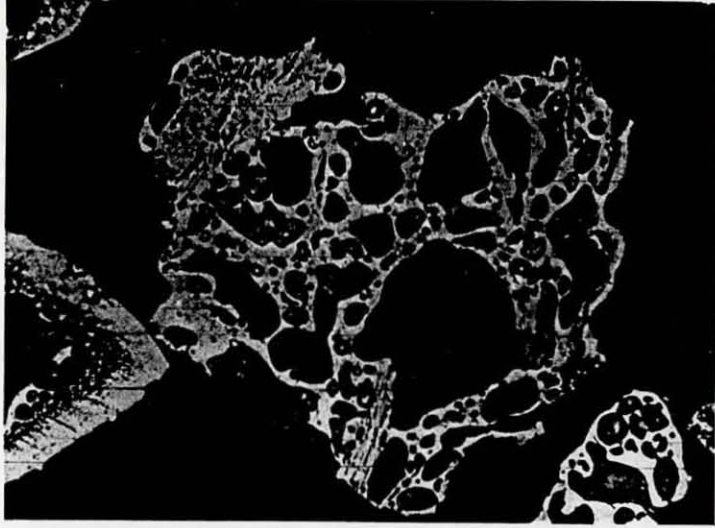


Figure 5.10. Honeycomb char particle type (400 × magnification)

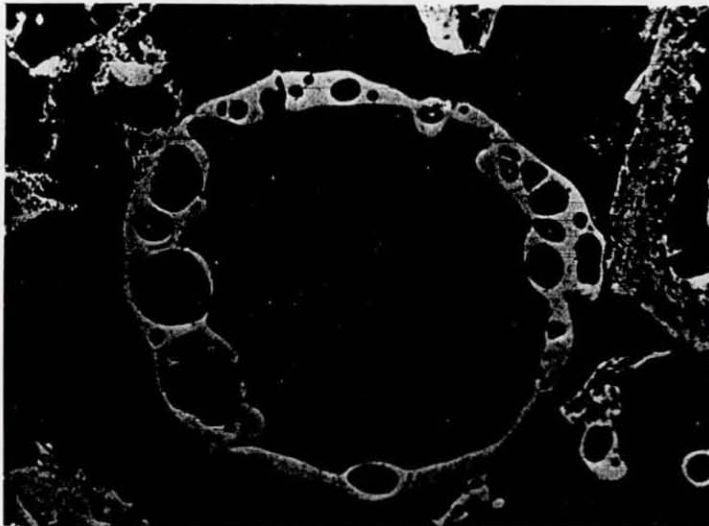


Figure 5.11. Cenosphere char particle type (400 × magnification)

5.1.3. FLUIDISED BED GASIFICATION

The fluidised bed gasification experiments were carried out using the method described in 4.4. Varying degrees of burnout were achieved by increasing the oxygen content of the reactor gas and keeping the residence time constant. The wt.% (daf) gasified was calculated from the residual ash content of the char collected. The method of calculation is given in Appendix B, but essentially the following equation was used, where the weight percent coal substance gasified (daf) is given by G:

$$G = 1 \times 10^4 \cdot \frac{(A_{char} - A_{coal})}{A_{char}} \cdot \frac{1}{(100 - A_{coal})} \quad \text{Equation 5.5}$$

and where A_{coal} and A_{char} are the wt.% (db) ash contents of the parent coal and the gasification char respectively.

Using G from Equation 5.5 and the carbon analysis of the chars, the carbon mass lost during gasification, L, could be calculated from:

$$L = \frac{1 \times 10^2 \cdot C_{coal} - (100 - G) \cdot C_{char}}{C_{coal}} \quad \text{Equation 5.6}$$

where C_{coal} and C_{char} are the carbon contents, wt.% (daf), of the coal and char respectively.

It is clear from Eqn. 5.5 that the wt.% gasified calculated relies on the accuracy of the char collection method and would be greatly affected by bed-sand contamination of the sample. Even though dry runs, without coal, never yielded significant amounts of sand carry-over, sand contamination of the char samples could not be 100% ruled out. For this reason the yields on gasification are less reliable than the pyrolysis yields calculated from the mass balance but still allow sufficient accuracy to track the trends observed in the split of sulphur and nitrogen between the char and gases.

The results of the partial gasification runs are given in Table 5.6. The wt% (daf) gasified at each run, C₁₀, C₁₅, and C₂₀, are shown. The subscript numbers correspond to the vol.% oxygen concentration in the O₂/N₂ fluidising gas mixture. Data from the pyrolysis chars, C₀, is also included. The wt.% gasified at any one oxygen concentration differs from coal to coal and is dependent on volatile yield during initial pyrolysis and subsequent reactivity of the char formed.

Table 5.6. Burnout of chars with increasing vol.% oxygen in fluidising gas

Parent coal	Char type	Ash, wt.%(db)	wt.% gasified, % (daf)	C, wt.% (daf)	S, wt.% (daf)	N, wt.% (daf)
NADINS	C ₀	12.0	43.5	93.0	1.5	1.6
	C ₁₀	21.2	72.2	80.0	1.4	1.4
	C ₁₅	40.3	88.9	94.8	1.8	1.5
	C ₂₀	45.7	91.1	82.8	1.8	1.6
DAW MILL	C ₀	6.3	42.3	90.9	1.5	1.3
	C ₁₀	9.5	65.9	93.9	1.3	1.4
	C ₁₅	11.6	73.0	92.5	1.1	1.2
	C ₂₀	14.0	78.1	94.1	1.0	1.3
THORESBY	C ₀	8.0	40.8	87.4	1.5	1.7
	C ₁₀	14.2	71.3	90.9	1.3	2.0
	C ₁₅	14.8	72.6	91.7	1.2	1.9
	C ₂₀	17.5	77.6	91.7	1.1	1.9
KELLINGLEY	C ₀	7.7	36.9	91.6	1.3	1.9
	C ₁₀	10.1	62.0	86.0	0.9	1.8
	C ₁₅	13.7	73.1	89.1	0.9	2.0
	C ₂₀	17.5	79.9	87.7	0.9	2.1
LONGANNET	C ₀	19.9	32.4	94.2	0.4	1.8
	C ₁₀	33.9	72.0	83.3	0.3	1.8
	C ₁₅	43.2	81.1	90.6	0.4	2.0
	C ₂₀	52.2	86.8	89.1	0.4	1.6
CWM	C ₀	7.0	23.8	76.0	1.0	1.1
	C ₁₀	25.4	91.5	91.8	1.0	1.5
	C ₁₅	22.5	90.1	91.7	1.0	1.6
	C ₂₀	30.4	93.4	90.0	1.1	1.5
TILMANSTONE	C ₀	5.3	21.3	81.22	1.09	1.1
	C ₁₀	13.4	75.9	93.50	0.97	1.3
	C ₁₅	20.0	85.1	93.38	1.04	1.5
	C ₂₀	20.2	85.3	94.27	0.93	1.3

5.1.3.1 Sulphur and nitrogen distribution

The wt.% (daf) sulphur and nitrogen contents of each char is also shown in Table 5.6. The normalised ratios, S/C' and N/C' , were calculated using Equations 5.1 - 5.4 and are shown in Table 5.7 below.

Table 5.7. The S/C' and N/C' ratios for each of the chars

Parent coal	Char type	Carbon mass loss, wt. %	S/C'	N/C'	Parent coal	Char type	Carbon mass loss, wt. %	S/C'	N/C'
NADINS	C ₀	25.5	0.53	0.78	LONGANNET	C ₀	16.2	0.79	0.87
	C ₁₀	68.4	0.57	0.79		C ₁₀	69.3	0.70	0.96
	C ₁₅	85.1	0.64	0.76		C ₁₅	77.5	0.72	1.02
	C ₂₀	89.5	0.73	0.92		C ₂₀	84.6	0.81	0.83
DAW MILL	C ₀	30.2	0.70	0.84	CWM	C ₀	32.1	0.82	0.86
	C ₁₀	57.5	0.60	0.86		C ₁₀	90.9	0.72	0.92
	C ₁₅	66.7	0.50	0.81		C ₁₅	83.4	0.74	1.03
	C ₂₀	72.6	0.45	0.84		C ₂₀	93.0	0.82	0.94
THORESBY	C ₀	33.5	0.70	0.87	TILMANSTONE	C ₀	27.5	0.88	0.84
	C ₁₀	66.5	0.57	1.0		C ₁₀	74.4	0.68	0.92
	C ₁₅	67.7	0.53	0.94		C ₁₅	84.2	0.73	1.04
	C ₂₀	73.6	0.51	0.96		C ₂₀	84.2	0.64	0.91
KELLINGLEY	C ₀	25.1	0.74	0.89		C ₀			
	C ₁₀	57.6	0.57	0.86		C ₁₀			
	C ₁₅	68.9	0.53	0.92		C ₁₅			
	C ₂₀	77.1	0.51	1.02		C ₂₀			

As with the pyrolysis experiments, the S/C' and N/C' ratios give an indication of how the sulphur and nitrogen has split between the char and the gases. From Table 5.7 the split can be monitored at increasing degrees of burnout of the char to indicate whether the sulphur or nitrogen is removed preferentially to the C atoms in the coal or in the same proportion. Again, consistent with the pyrolysis experiments, the S/C' ratios were lower than the N/C' ratios for the gasification chars.

The ratios, S/C' and N/C' , were plotted against the degree of carbon mass loss from the char for all the coals used, the results are shown in Figures 5.12 - 5.18. The figures are in order of increasing carbon content (wt.% daf) of parent coal, measured from the individual elemental analysis. There is not as clear a relationship with rank as found with pyrolysis chars. Certainly the sulphur does not appear to follow any clear rank related trend in the gasification chars.

On closer inspection the nitrogen behaves consistently throughout the coals studied in that it drops initially on pyrolysis and remains constant or rises very slightly as the degree of burnout of the char increases. As the rank of the coal increases the N/C' becomes closer to 1 in the C_{15} and C_{20} chars of the higher ranked coals. This may be due to the N/C' starting at a higher value after pyrolysis. The main observation is that the N/C' ratio for the gasification chars is around 1 or just below, indicating no further preferential shift of nitrogen into the gas phase after pyrolysis. It could be argued that in the higher ranked coals, the nitrogen remaining in the char after pyrolysis becomes slightly concentrated in the carbonaceous part of the char with increased burnout because of the more significant change in gradient of the best fit line i.e. the gradient becomes more positive.

The sulphur behaves differently from the nitrogen showing no particular consistent relationship of S/C' ratio with coal type. For the Daw mill, Kellingley and Thoresby chars there is a clear continued drop in the S/C' ratio with increasing char burnout for those coals. This implies that as burnout proceeds for these three coals the sulphur continues to be removed at a higher proportion than the carbon atoms into the gas phase.

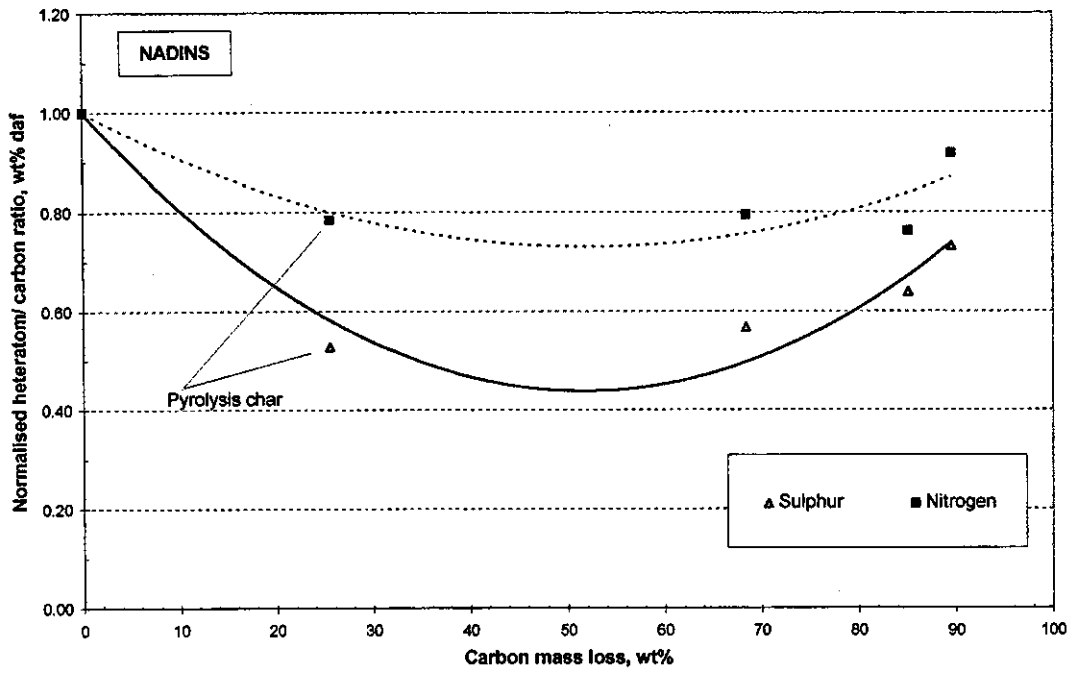


Figure 5.12. Change of S/C' and N/C' with increased char burnout - NADINS

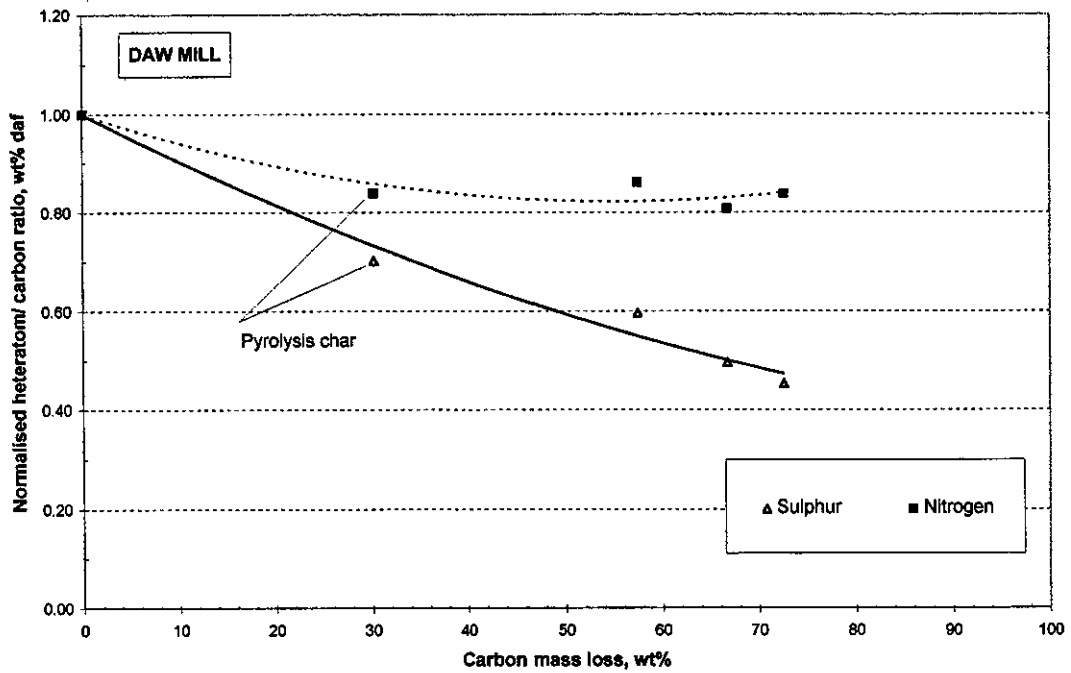


Figure 5.13. Change of S/C' and N/C' with increased char burnout - DAW MILL

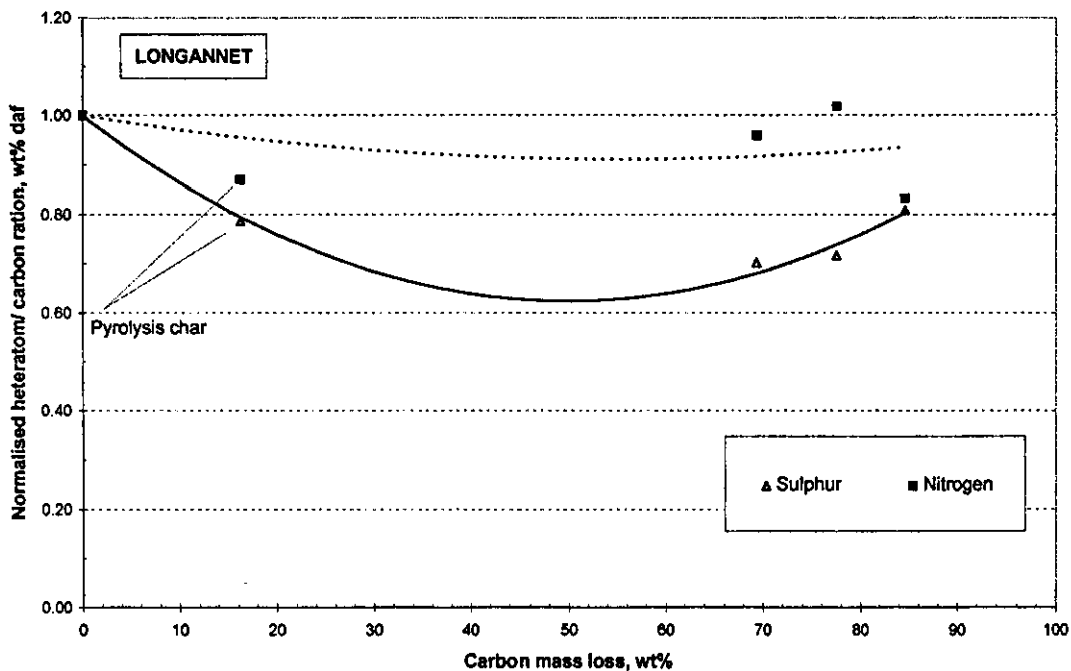


Figure 5.14. Change of S/C' and N/C' with increased char burnout - LONGANNET

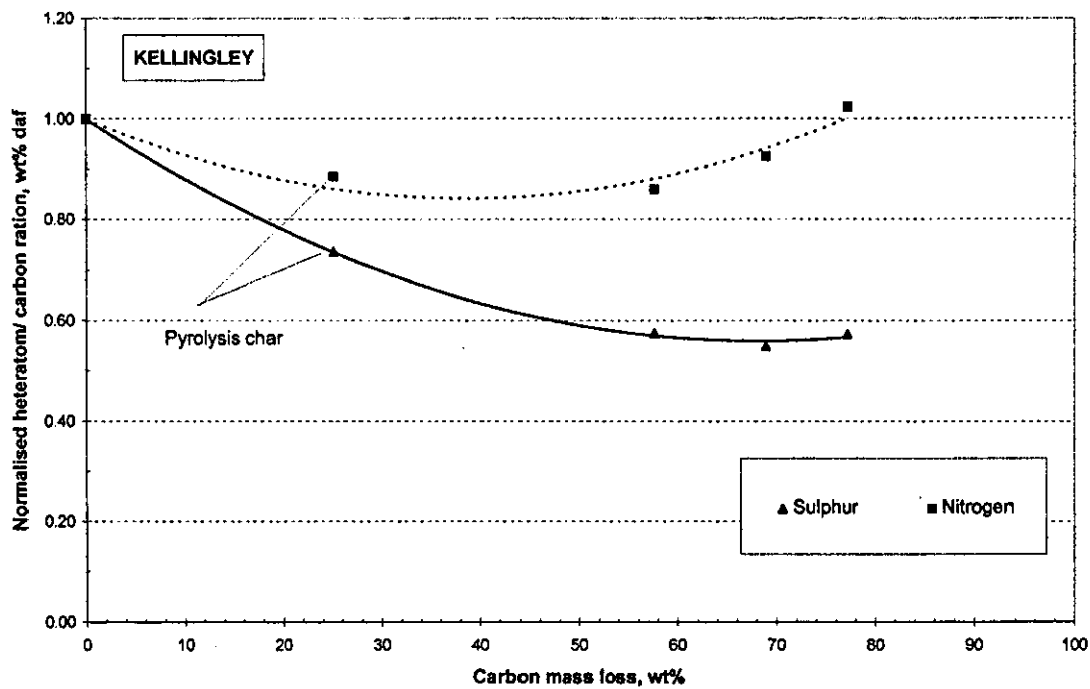


Figure 5.15. Change of S/C' and N/C' with increased char burnout - KELLINGLEY

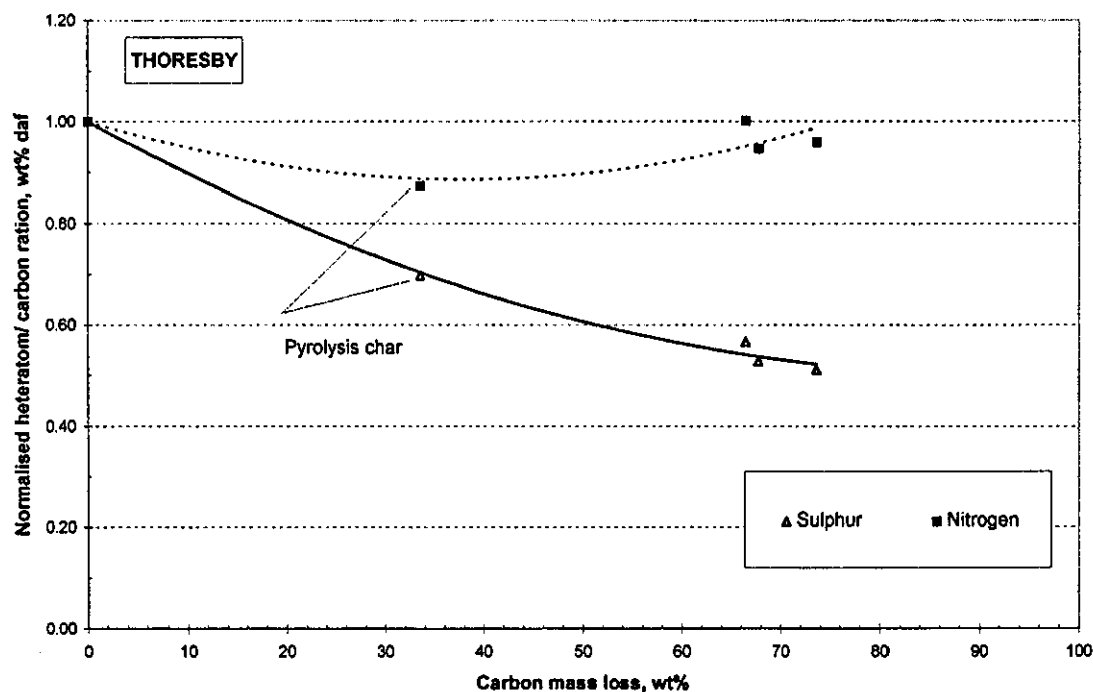


Figure 5.16. Change of S/C' and N/C' with increased char burnout - THORESBY

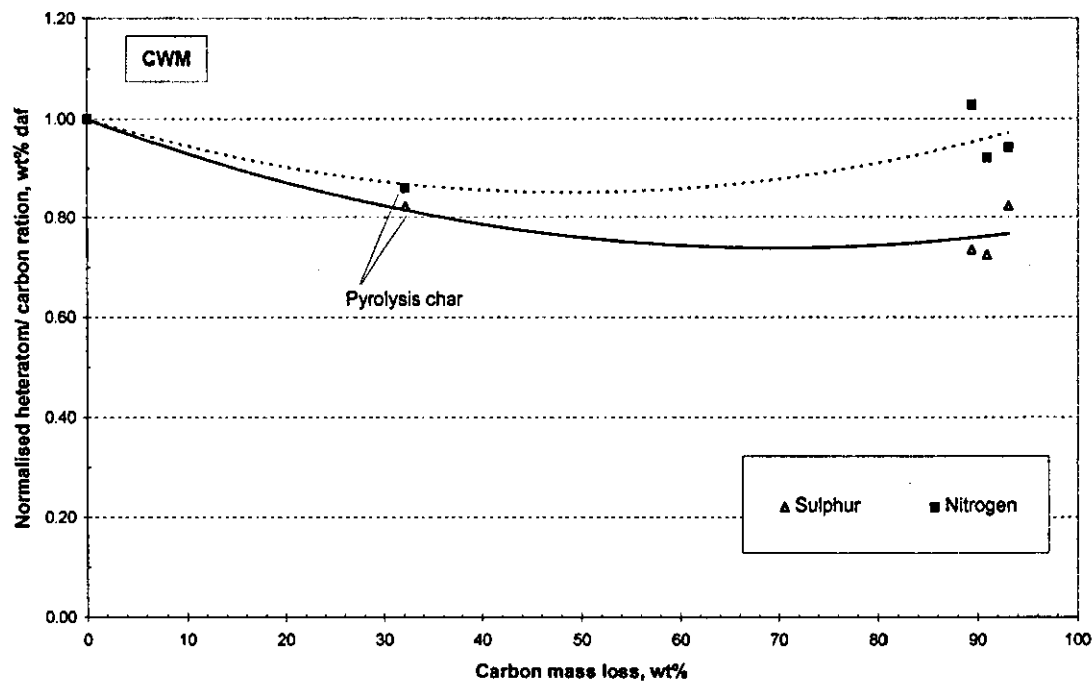


Figure 5.17. Change of S/C' and N/C' with increased char burnout - CWM

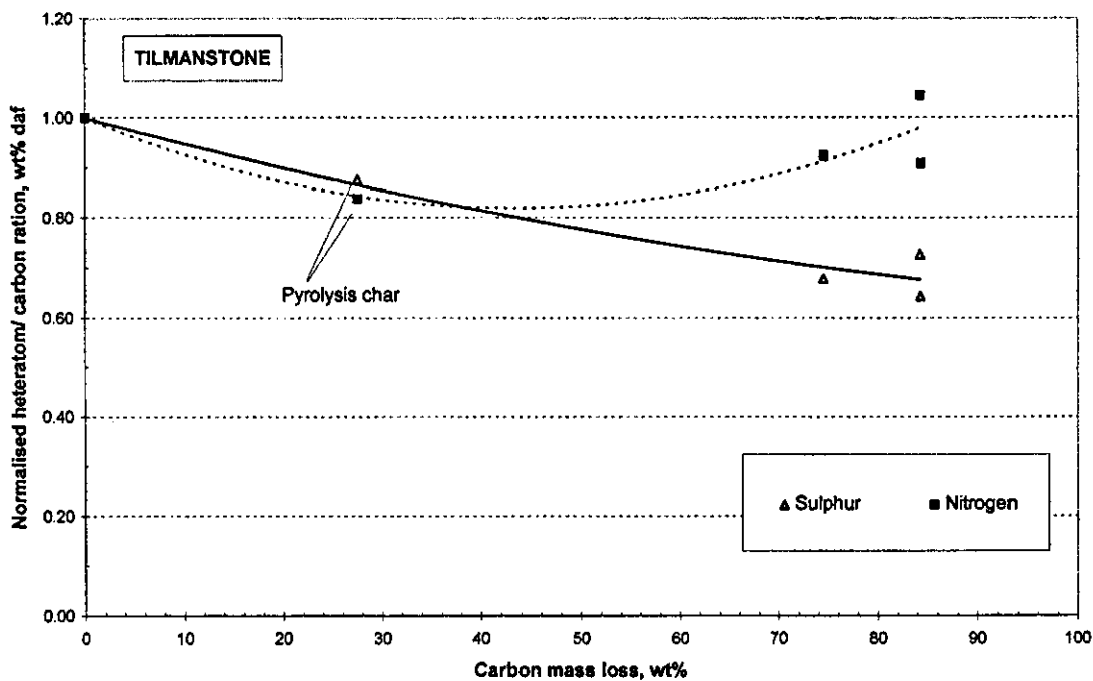


Figure 5.18. Change of S/C' and N/C' with increased char burnout - TILMANSTONE

It was noted, however, that the three coals Daw mill, Kellingley and Thoresby produced relatively low burnouts in their C₁₅ and C₂₀ chars. To see if this was significant Figure 5.19 was plotted including the data from all the coals on S/C' and N/C' against wt.% gasified. It can be seen from this plot that the degree of gasification, or burnout, has an effect on S/C' ratios and for the coals studied the S/C' is lower than those for the pyrolysis chars and then begins to rise again after about 70% wt.% (daf) gasified. The general trend of all the coals for nitrogen is also shown in Figure 5.19. The nitrogen tends not to change as much with increased char burnout, perhaps a small trend for it to rise above the N/C' ratio of the pyrolysis char. The best fit for the nitrogen data has also been included on the plot for reference, but its R² value is poor at 0.4, suggesting further that generalising the nitrogen distribution in this way may not be possible.

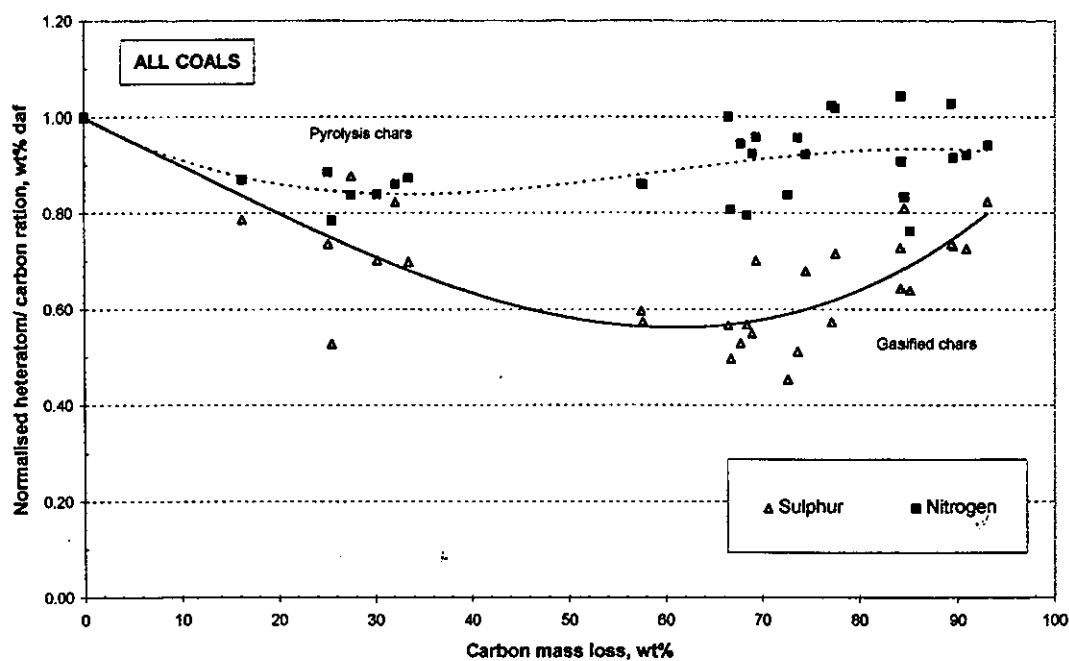
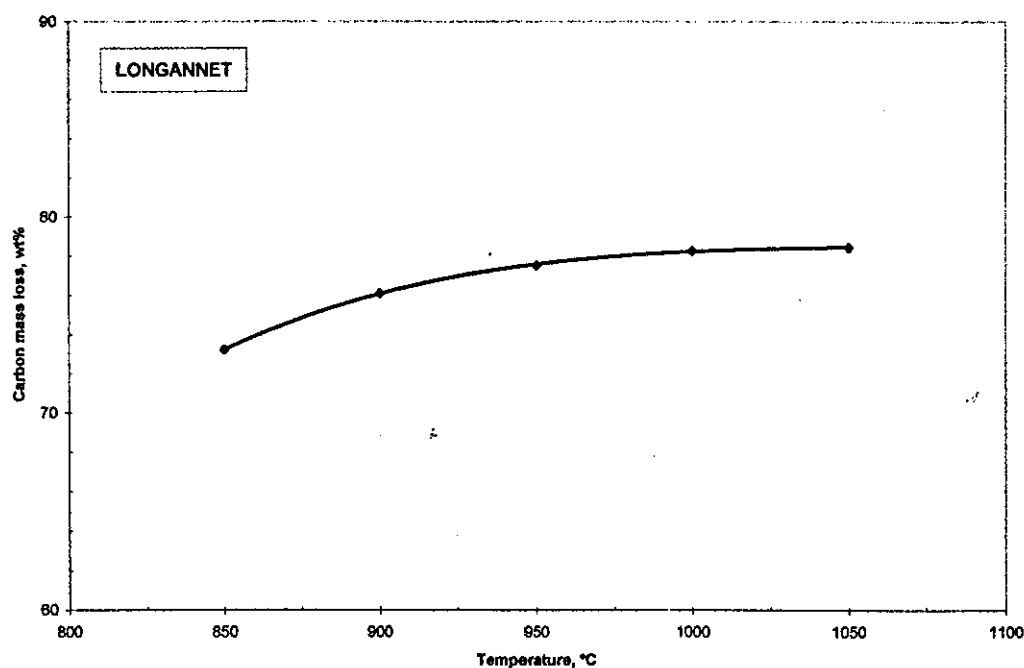


Figure 5.19. Change of S/C' and N/C' with increased burnout for all coals.

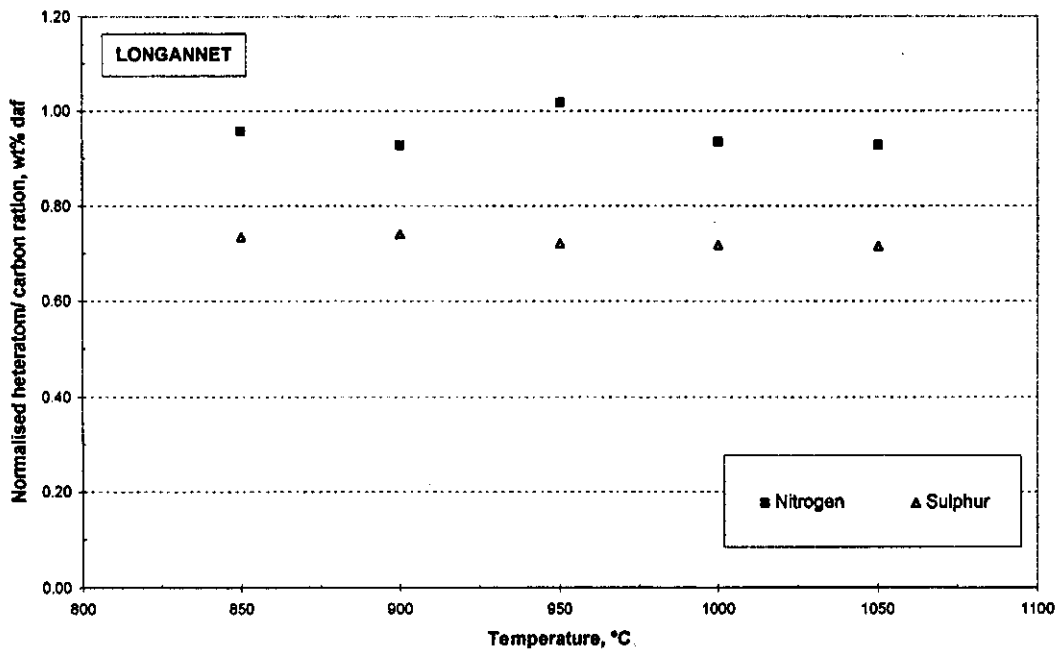
To study the effects of temperature, Longannet coal was chosen and gasified in 15 vol.% O_2/N_2 fluidising gas, residence time 10 seconds, at varying reactor temperatures in the range 850°C to 1050°C. Figure 5.20 shows the effect on reaction temperature on the carbon lost from the char with increased temperature. The carbon loss increases with increased temperature, this can be expected from the Arrhenius expression, i.e. the carbon oxidation reaction rate increases with increased temperature. The increased carbon loss is not great with increased temperature and it is likely that the conditions are in the pore diffusion controlled region; Zone II kinetics³⁵ (see also Section 2.3.2.1 of Literature Review).

The effects on the sulphur and nitrogen content of the C_{15} chars with increased temperature is shown in Figure 5.21. Both the N/C' and the S/C' for the coal studied are unaffected by the reaction temperature in the range 850°C to 1050°C. This implies that, for the coal and temperature range studied, the sulphur and nitrogen are lost from the char in the same proportion as the carbon as the temperature is increased.



Coal used - Longannet, residence time 10 seconds and fluidised with 15 vol.% oxygen/nitrogen mixture

Figure 5.20. The effect of temperature on the carbon mass loss from the C_{15} gasification chars

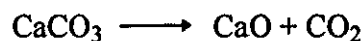


Coal used - Longannet, residence time 10 seconds and fluidised with 15 vol.% oxygen/nitrogen mixture

Figure 5.21. The effect of temperature on the nitrogen and sulphur contents of the C₁₅ gasification chars

5.1.4. EXPERIMENTAL RUNS WITH LIMESTONE SORBENT

Runs using limestone as a sulphur sorbent in the fluidised bed were only partly successful. The method detailed in Section 4.4 was successful in retrieving the spent sorbent for analysis, with negligible quantities being lost to attrition in the bed. The reduced mass collected was explained by the calcination reaction, Equation 2.14 below.



The sulphur contents of the spent sorbent were outside the guaranteed scope of the CRE analysis technique and difficulties were encountered in the analysis of the chars for sulphur. The titration involved in the oxygen flask method seemed to be affected by the presence of traces of sorbent in the char samples. As a result the colours of the indicators changed and the end point of the titration was masked hence rendering it undetectable. Without the char and tar sulphur contents not much could be deduced from the results. All sorbent experimental data is listed in Appendix D for both pyrolysis and gasification.

5.2. DISCUSSION

5.2.1. PYROLYSIS

It could have been expected that the fluidised bed pyrolysis experiments would yield more wt.% (daf) volatiles over the proximate analysis (B.S. standard) method than was actually obtained. It may have been that the preoxidation of the coal samples reduced the sensitivity of the coal to differences in particle heating rate by changing its plastic properties on heating. As mentioned in Section 5.1.2.1, the figure of 1.05 times greater volatile yield over the proximate analysis was lower than other reported work such as Laughlin et al⁶¹ who reported as high as 1.5 times greater. However, along with a much higher residence time of 100 seconds, their values of volatile yield were calculated from the ash content of the pyrolysis char which may over predict if the char samples are contaminated with bed material. This was overcome in the Loughborough experiments by retrieving almost all the char produced, the mass balance was then adjusted to accommodate the whole char content retained in the bed after each pyrolysis experiment (see Appendix B for the detailed mass balance calculations).

Averaging at around 4 wt.% (daf) of the total pyrolysis products, the tar yields of the pyrolysis products were low. Cracking of the primary volatiles and secondary reactions occurring before the tars could be condensed was unavoidable in the upper part of the fluidised bed apparatus. The gases could not be cooled before entering the gas cyclone and so the volatiles were subjected to the high temperatures of the top of the reactor (~500°C) and the walls of the cyclone (~350°C) before they were cooled by the condensers. This was believed responsible for the low quantities of tar collected in these experiments.

Whereas the trend for nitrogen to be preferentially released into the volatiles on pyrolysis is consistent with other work carried out under similar conditions.^{20,40,61}, to establish whether the increase of N/C' with increasing rank for the majority of the coals is a trend and not scatter, further data points were needed. The N/C' ratios of pyrolysis chars calculated from other similar studies, along with those obtained in this study, were

plotted in Figure 5.22. The fluidised bed pyrolysis results presented in this thesis lie close to the best fit line, five data points lie above the line and the two higher ranked coals, Cwm and Tilmanstone lie below it. The additional data confirms the trend for the nitrogen in coal to be released preferentially into the volatiles during pyrolysis at temperatures in the region 900°C - 950°C. It further shows that the nitrogen becomes less preferentially released into the volatiles with an increase in rank and that, as the carbon content of the parent coal increases above 90% wt.% (daf) C, the trend line suggests that nitrogen becomes concentrated in the carbonaceous component of the char. These results point to the nitrogen in coal becoming linked to more thermally stable organic compounds as coal rank increases.

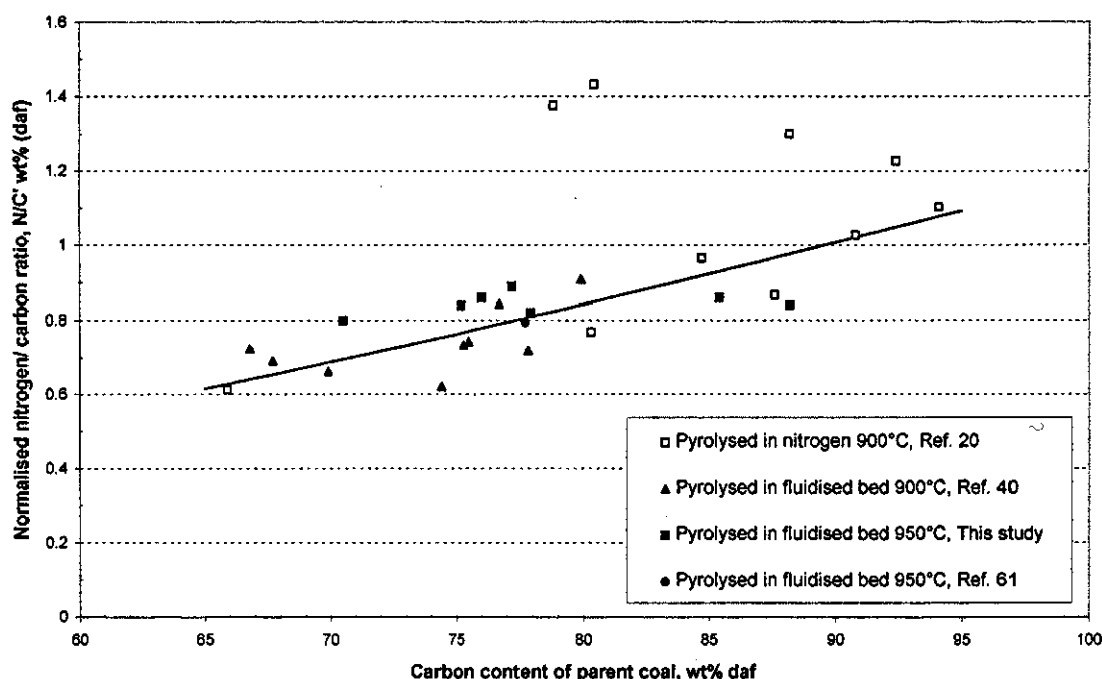


Figure 5.22. Comparison of pyrolysis char N/C' with other studies

The best fit of the line for the N/C' for the pyrolysis chars for the 27 data points in Fig. 5.22, assuming the line would pass through zero at 0 wt% (daf) C, was:

$$\frac{N}{C}' = 1.1 \times 10^{-3} C_{coal}^{1.52} \quad \text{Equation 5.7}$$

Where C_{coal} is the carbon content of the parent coal, wt% (daf).

The trend observed for nitrogen to become less preferentially released into the volatiles on pyrolysis with increased coal rank would seem to be consistent with the reported chemistry of nitrogen in coal (see section 2.2.3.3 of Literature Review); generally as coal rank increases so does the proportion of the more thermodynamically stable pyridinic nitrogen¹⁸.

As the pyrolysis results of all the seven coals show, the normalised ratio N/C' is below 1 and this has been shown to be consistent with a number of similar studies mainly on chars produced in fluidised beds at a similar pyrolysis temperature. However, other studies, in particular Wanzl et al^{28,29} and Solomon et al³⁴, have reported the proportion of the nitrogen in the pyrolysis char to be comparable to that of the parent coal and in some cases slightly concentrated in the char i.e. $N/C' > 1$. Solomon et al³⁴ concludes that the initial release of nitrogen species during pyrolysis was similar in nature and proportional to the amount of tar evolved and that at higher temperatures $> 1000^{\circ}\text{C}$ further release of nitrogen occurred from the char in the form of gaseous nitrogen species. However, both authors concentrated their work mainly at pyrolysis temperatures lower than 900°C . Chen et al³³, in a pyrolysis study of 6 coals, reports that at temperatures above 900°C the nitrogen carries on being released into the volatiles after the formation of char has finished. This suggests that there is a kinetic element to the loss of nitrogen during heating at high temperatures, $>900^{\circ}\text{C}$, therefore increased residence time at a particular temperature could have an effect.

The S/C' ratios plotted against C wt% (daf) of the coal in Figure 5.2 show a definite increase with increased coal rank but tend to be lower than the corresponding N/C' ratios. This is not unexpected as the chemistry of coal-sulphur means that the sulphur is more likely to be released into the gaseous phase on heating of the coal, especially in lower ranked coals where more of sulphur is present as aliphatic compounds. The majority of organic sulphur in high rank coals is generally present in more thermally stable aromatic, thiophenic compounds¹³ (see Section 2.2.3.2 of Literature review). It would seem logical, as with the nitrogen results, to suggest that this move to more thermally stable aromatic compounds explains the increase of the S/C' ratio of the pyrolysis char with rank.

However, the exact make-up of the organic sulphur of the parent coals was not known for these experiments. Deductions could only be made on the basis of the split of the total sulphur between the char, tar, and gas. The proportion of the total sulphur present as pyrite in the parent coal was known. As reported in the results Section 5.1, Figure 5.3, the plot of S/C' ratio of the char versus proportion of sulphur as pyrite in the coal proved inconclusive showing no significant change over the range of coals studied. It might have been expected that as the proportion of pyrite to organic sulphur in the coal increased so would the tendency for the sulphur associated with it be released into the gaseous phase. Decomposition of pyrite to ferrous sulphide (FeS) begins at temperatures as low as 330°C. The Nadins char, which had highest pyritic/ total sulphur ratio and lowest corresponding char S/C', implied a higher shift of sulphur into the volatiles because of its pyrite content. However, if the other points on Figure 5.3 are taken in isolation they varied little with increased pyrite content. It can not therefore be concluded from this study that higher proportions of pyritic sulphur in coal produce higher yields of sulphur in the volatiles on pyrolysis.

A possible explanation for this is that on the decomposition of pyrite, iron sulphide is produced (FeS) which is more stable than some of the organic sulphur contained in less stable aliphatic compounds. FeS does not decompose until higher temperatures around 1000°C are reached. Some of this sulphur released as H₂S could react with coal matrix³¹.

The sulphur and nitrogen contents of the tar showed no trend with rank or volatile matter and generally showed a high degree of scatter. It could be tentatively suggested that the N/C' ratios were closer to 1 than for the chars and this indicates that nitrogen species released in to the tar are of a similar nature to those found in the parent coal. This indicates further that the reduction of the N/C' ratio of the char was due to a shift of nitrogen species into the gaseous species. The S/C' ratios of the tars were also generally higher than the pyrolysis char, but lower than the parent coals, with the exception of the two higher ranked coals which had S/C' ratios >1.

It would be difficult to conclude anything of any significance from the tar results. Studies^{28,29} have found the sulphur concentration of the pyrolysis tars to be significantly

reduced compared to the parent coal ($S/C' < 0.5$) and that this could be greatly affected by reactor pressure and atmosphere. It is difficult to compare the tar results from this thesis to those of Wanzl et al^{28,29} because they collected much higher tar yields. The apparatus quickly quenches the volatiles close to the pyrolysis sample. It is likely that the tars collected in the fluidised bed apparatus used in this thesis study undergo further pyrolysis and are not representative of the primary devolatilisation products, but are perhaps more typical of those products produced in the reactors of actual combustion/ gasification applications. It is possible that on initial release in the fluidised bed reactor, the tar S/C' and N/C' ratio is different from that measured in the tar collected.

The above discussion reasonably explains the results obtained for sulphur and nitrogen distribution between char and volatiles on pyrolysis under the given experimental conditions. Some generally accepted observations, however, have not been reproduced in this study, in particular the effect of pyrolysis temperature on nitrogen release i.e. for nitrogen concentrations in the pyrolysis chars to progressively decrease with an increase in pyrolysis temperature^{22,28,29,61}. An explanation for this could be that the temperature range studied, 850°C to 1050°C, was small but this was chosen primarily to represent the typical operating temperature of fluidised bed combustors/gasifiers. The results may have been more conclusive if a wider temperature range had been studied. However, lowering the reaction temperature increased the flow of gas at ambient conditions, 20°C, needed to eject the pyrolysis char from the bed and supplying sufficient nitrogen under these conditions proved difficult (see Appendix A). There was also a limit on higher reaction temperature due to doubts over the integrity of the upper part of the fluidised bed apparatus at temperatures above 1100°C.

5.2.1.1 Char morphology

The results of the microscopic examination of the pyrolysis chars showed the presence of all the char types identified in the classification system used. Although the numbers of each char particle type varied between coals studied, the predominant particle shape was the honeycomb shape. It has been shown in work with density separated fractions of coal²⁵ that the lighter density fractions, concentrated in exinite and vitrinite, produced chars with the highest internal surface area typical of the honeycomb (network). See

Section 2.3.1.2 of the Literature Review. It is therefore to be expected that the most common char particle shape observed would be the honeycomb-type because of the coals natural predominance of vitrinite.

The inert and inert-like char particles originate mainly from the inertinite and mineral matter of the coal. The results in Table 5.5 show the two coals producing the highest proportion of semi-inert and inert-type char particles to be the Nadins and Longannet samples. These notably have the highest ash content of the coals used in the study. The results also show the chars from the higher ranked coals to contain a higher proportion of cenosphere particles. This is probably due to these coals, in particular Thoresby and Kellingley, being relatively high swelling coals coupled with an inherently low ash content. The presence of significant numbers of cenosphere-type particles indicates that the preoxidation of the coal samples does not seem to have greatly affected the plastic properties of the coal during heating in the fluidised bed.

Looking at the maceral distribution of the parent coal samples as analysed by CRE, see Appendix C, no direct link can be made with the char particle types produced on pyrolysis. Although it is recognised that this is not truly representative of the maceral distribution of the coal size range used in the studies, but is used merely as a guide.

5.2.2. GASIFICATION

The differing degrees of burnout of the gasification chars produced at 10, 15 and 20vol.% oxygen in nitrogen (chars C₁₀, C₁₅ and C₂₀) were considerably different depending on parent coal and did not seem to depend on the amount of volatiles generated during devolatilisation. It was thought that this effect could be attributable to the reactivity of the chars produced during devolatilisation. The reactivities of five of the fluidised bed pyrolysis chars produced in this study were measured in a thermogravimetric analyser (TGA) at the Northern Carbon Research Laboratories⁶³ as part of their investigation into the behaviour of sulphur and nitrogen during coal gasification. Data for the Cwm and Tilmanstone chars was not available. Table 5.8 shows the reactivities of the fluidised bed

pyrolysis chars obtained by isothermal combustion tests, $\text{g.g}^{-1}.\text{s}^{-1}$ in 20% O_2/Ar mixture @ 1050°C. Also included is the wt% (daf) gasified for the C_{20} chars from Table 5.6.

Table 5.8 A comparison of wt.% gasified versus reactivity of pyrolysis chars

Coal type	Pyrolysis char reactivity at 1050°C, $\text{g.g}^{-1}.\text{s}^{-1} \times 10^{-3}$	Wt.% carbon lost for fluidised bed C_{20} char
DAWMILL	4.8	72.6
NADINS	4.7	89.2
THORESBY	4.7	73.6
KELLINGLEY	4.1	77.1
LONGANNET	3.7	84.6

No relationship can be seen between the reactivity of the pyrolysis chars and the degree of burnout of the C_{20} chars. This is unexpected and may have occurred for several reasons, the reactivity was measured at a higher temperature than the fluidised bed gasification runs although the same trends should apply to both temperatures, 950°C and 1050°C. This difference could also be due to the pyrolysis chars produced in 100% nitrogen being different in nature to the chars formed after devolatilisation in an oxidising atmosphere perhaps due to possible higher particle temperatures experienced if oxygen reaches the particle surface. What is more likely is that the method of calculating the wt.% gasified for the C_{20} is not as accurate as a true mass balance and so small errors are introduced due mainly to traces of bed contamination in the gasification char samples collected.

The mean error for mass of individual char samples collected during gasification was ± 4.0 wt%. What was not known was how the ash contents of the individual char samples varied as runs were bulked together to produce a large enough sample and then ashed, and hence the errors are not known. It is likely that the lower the ash content of the parent coal the higher the effects sand contamination would have on calculated gasification yields. This was one of the main reasons for using the $\text{S/C}'$ and $\text{N/C}'$ ratios

to indicate heteroatom split between char and volatiles as it is largely independent of errors in calculated gasification yields, it also allows consistent comparison to the pyrolysis chars whose volatile yields were calculated slightly differently.

The gasification results reported in Section 5.1.3 suggest that the sulphur and nitrogen continue to behave differently to each other during burnout of the char after pyrolysis; the sulphur being more affected by char burnout than nitrogen. Figures 5.12 to 5.18 show that for the lowest ranked coals the nitrogen follows more or less the same proportional loss as the carbon from the char during gasification (N.B. after devolatilisation where there is a preferential shift to the volatiles). As coal rank is increased, the N/C' ratio increases slightly from that of the pyrolysis char in the C₁₅ and C₂₀ chars. The plot of all the coals N/C' ratio with char burnout, Figure 5.19, displays a general trend, that if anything the nitrogen content of the char increases slightly from that of the pyrolysis char with increasing char burnout. This implies that somehow the nitrogen is being lost at a lower rate than the carbon during the later stages of char burnout. Considering that coal nitrogen is not associated with the mineral matter of the coal it implies that the nitrogen remaining after significant char burnout is associated with more refractory aromatic compounds. This is more noticeable in some of the individual higher rank coals than considering all coals to behave similarly as in Figure 5.19, this explains the poor R² fit of the nitrogen best fit line hence not plotted on the graph.

This observation has been seen in other studies. In experiments using a novel radiant flow reactor⁶⁴, coals were subjected to various heating rates applicable to pulverised coal combustion and chars with increasing burnout were produced by increasing the oxygen content of the reactor gas from 14% to 40% (vol.). It was observed for four low to medium volatile coals, 22wt% - 36wt% (daf) vol. matter, that an initial preferential release of the coal nitrogen into the volatiles on devolatilisation was then made up by increased rate carbon conversion during burnout.

Hampartsoumian et al⁶⁵ in a study of five coals, three bituminous, one sub-bituminous coal and an anthracite observed that, for four of the coals, with increased carbon burnout of the char the nitrogen content of the char remained fairly similar to that of the parent

coal. In a graph of carbon mass loss plotted against nitrogen mass loss the nitrogen loss was in the main slightly higher than the carbon loss. The notable exception was an Indonesian sub-bituminous coal whose nitrogen mass loss was much higher at 1.2-2 times more than the carbon loss during burnout. The tests were carried out at 1000°C. Although generally closer to the parent N/C ratio, these results seem to be fairly consistent with the gasification char results presented in this thesis.

The behaviour of the sulphur with increased coal rank during gasification of all the coals is less clear. It appeared that the S/C' ratio of the char through increasing degrees of burnout during gasification was very much dependent on the individual coal and not on rank. For some coals, particularly Dawmill, Kellingley and Thoresby the S/C' continues to drop with increased wt.% gasified. For the other coals the S/C' ratio begins to rise again after a drop in the pyrolysis and C₁₀ chars. As shown in Figure 5.19, the results of all the coals suggests that the drop in the S/C' ratio happens at lower carbon burnout and then begins to rise significantly at further char burnout of >70% carbon mass loss. The fit of this line in Figure 5.15 was better than the nitrogen fit with an R² value of 0.82. The equation of the sulphur statistical best fit curve for the 28 data points, during pyrolysis and progressive gasification, was:

$$\frac{S}{C}' = 1 \times 10^{-6} \cdot L^3 - 1.3 \times 10^{-5} \cdot L^2 - 1 \times 10^{-2} \cdot L + 1 \quad \text{Equation 5.8}$$

Where S/C' is the normalised sulphur/carbon ratio of the char from Eqn. 5.3 and L is the carbon loss wt% of the char from Eqn. 5.6.

This rise in the curve indicates that the sulphur remaining in the char at high degrees of burnout is somehow more difficult to remove. It is known that the mineral matter of the coal can act as a sorbent for the sulphur released during combustion of coal and this rise of relative sulphur content of the char with burnout may be due some of the sulphur being contained in the ash content and hence implying the char will have a small sulphur component even at 100% carbon mass loss. If this were the case for these coals then the sulphur plot in Figure 5.19 should be asymptotic as the carbon mass loss of 100% is approached. This is not the case as the best fit line tends to an S/C' ratio of 0.9 at 100%

C burnout, although extending it further than experimental data, this indicates no concentration of sulphur in the ash after all the carbon has been lost. It has been shown⁶⁶ that there is a correlation between the calcium content of the ash and its sulphur retaining properties. The calcium content of the mineral matter of the coals used varied from 1.8 to 12% (wt.% expressed as CaO) and does not seem to correlate with any of the data plotted in Figures 5.12 - 5.19.

It is therefore likely that the sulphur remaining in the char in the latter stages of burnout is organically bound. This can be explained by the capture of sulphur, in the form of H_2S , in the coal matrix forming stable thiophenic structures⁶⁷.

The results showing the effects of reactor temperature show that in the range 850°C to 1050°C the sulphur and nitrogen oxidation rate is affected in identical manner to the carbon oxidation. That is, as the carbon mass loss from the C_{15} char is increased slightly with reaction temperature so is the S and N, hence the S/C' and N/C' remain constant over this temperature range. This suggests that at in the temperature range typical of fluidised bed combustion and gasification, after devolatilisation, the only way to remove the sulphur and nitrogen from the char is by oxidation and that this removal will be equal to the carbon loss as the temperature is increased from 850°C to 1050°C.

5.2.3 SUMMARY

During fluidised bed pyrolysis runs, the volatile yields were found to be higher than the proximate analysis yields by a factor of 5%. This can be explained by the higher heating rates associated with the fluidised bed reactor as well as the higher end temperatures experienced in the reactor. The tar yields, typically 4 wt%, were low due to further thermal decomposition and secondary reactions occurring before sufficient quenching could be applied to the volatiles.

Both the nitrogen and sulphur were preferentially released into the volatiles during pyrolysis in the fluidised bed, the sulphur more so than the nitrogen. For five of the coals studied the normalised nitrogen/carbon ratio, N/C' , showed a tendency to increase with

rank. When plotted with data from other similar studies this trend was confirmed, see Figure 5.22. The S/C' ratio of the pyrolysis chars for the coals studied was also shown to rise with coal rank. This seems to be in agreement with the reported chemistry of sulphur and nitrogen in coal; that a greater proportion of thermally stable aromatic heteroatom compounds are associated with higher ranked coals.

No definite link between the pyrite content of the coal and the amount of sulphur released into the volatiles was found. This could be due to the recombination of some of the sulphur from pyrite decomposition into the coal matrix.

The distribution of sulphur and nitrogen in the pyrolysis tar was difficult to interpret due to the high degree of scatter. Generally the S/C' and N/C' ratios of the tar were higher than the pyrolysis char. The N/C' ratios for the tars were generally nearer to 1 indicating close relationship between the nitrogen species contained in the coal and those released into the tar.

During partial gasification the nitrogen distribution is less affected by burnout of the char than sulphur; after pyrolysis nitrogen mass loss more or less matches the loss of carbon from the char. There is perhaps a small trend in the higher ranked coals for the carbon mass loss of the char to be at a higher rate than the nitrogen loss during the latter stages of char burnout, increasing the N/C' ratio. However, nitrogen never really becomes significantly concentrated in the char. This is consistent with other work referenced in the text.

The sulphur behaviour during partial gasification is different, the general trend for all the coals is that during the early stages of burnout the sulphur carries on being released preferentially into the gases. At later char burnout (> 70 wt% C loss) the sulphur remaining becomes more difficult to remove from the char and the S/C' rises slightly. This is not thought to be due to the sulphur being associated with the ash component of the char with no evidence of the S/C' becoming >1 after all carbon has been removed. The results therefore imply that the alkali metal content of the ash mineral does not capture any of the sulphur released during the gasification process. Either the sulphur

remaining in the latter stages of burnout is more stable or some of the sulphur released as H_2S has become bound into the coal matrix as more stable thiophenic compounds.

For both the pyrolysis and gasification runs, the S/C' and N/C' ratios are unaffected by an increase in reaction temperature in the range 850°C to 1050°C . In the gasification runs the carbon mass loss does increase with increased temperature but this is matched by the sulphur and nitrogen loss.

5.2.4. GENERAL

The general trend shown by the majority of the coals in this study, backed up by Figure 5.22, for the nitrogen in coal to become less associated with the pyrolysis char with decreased rank, is important for fluidised bed combustors which typically operate in the temperature region of 850°C to 1000°C . It is known that nitrogen species contained in the volatile matter readily oxidise to form oxides of nitrogen (NO_x). As a result, NO_x control strategies generally try to create a fuel rich region in the area of the reactor where the volatile matter of the coal is released. This promotes reactions leading to the formation of N_2 and NH_3 . If the conversion of volatile nitrogen can be controlled effectively, an increased shift of nitrogen into this volatile phase could be advantageous in reducing NO_x emissions and could help in the choice of fuel.

The pyrolysis results for nitrogen would also seem relevant to the choice of fuel for the gasifier stage of the ABGC. Unlike fluidised bed combustion, gaseous nitrogen species formed during the gasification stage of the ABGC are not released into the atmosphere but go on to be burnt in the combustion chamber of a gas turbine where they could be subsequently oxidised to NO_x . But it may be advantageous for the char that is removed and burnt in the CFB stage (around 20 - 25 wt% (daf) of original coal) to have a reduced concentration of nitrogen, as NO_x formed from char-N is particularly difficult to reduce. However, the gasification results suggest that as gasification of the char proceeds in the gasifier, the carbon in the higher ranked coals may be lost at higher rate than the nitrogen, hence making up for the initial loss of nitrogen to the volatiles. This would mean that the

mean that the char entering the CFB stage is likely to have a very similar N/C ratio to that of the parent coal.

Of course, the gasifier stage of the ABGC is pressurised to around 20 bar and these experiments were conducted at atmospheric pressure. Work has shown, however, that reaction pressure, in the range 0-20 bar, does not significantly effect the proportion of N released into the volatiles during pyrolysis⁶¹, therefore not affecting the N/C' ratio. What pressure does do is reduce the quantity of volatiles produced, the same study showing it to drop by 16% from a rise in reaction pressure of 0 to 20 bar.

So the results presented are considered relevant to the ABGC gasifier stage for nitrogen as far as the N/C' ratios are concerned. Actual volatile yields are likely to be lower due to i) the ABGC gasifier pressure at approx. 20 bar (gauge) and ii) the larger particle sizes used in the bed at approx. 2mm. In the ABGC approximately 70-75wt%(daf) of the coal is gasified before the char is removed and fed into the CFB combustor. The results suggest that the partially gasified char will have a very similar N/C ratio to the pyrolysis char, and that the higher coal rank the closer the N/C ratio of this char will be to the parent coal.

The results showing the sulphur becoming more difficult to remove from the char as the gasification proceeds (>70 wt.% C mass loss from char) is significant when considering the sorbent loading of the gasifier and CFB stages of the ABGC, especially as this effect is likely to increase with increased pressure⁶⁷. Under the gasifier conditions the limestone decomposes to CaO and then reacts with the sulphur released to produce CaS and is fed at the ratio which gives the desired sulphur retention. This partially spent sorbent along with the partially gasified char are removed and feed the atmospheric CFB, if sufficient sulphur remains in the char at this stage further fresh sorbent may be required in the CFB to keep SO₂ emissions low enough. It would seem from these results that after 70 wt% of the total carbon loss from the char, sulphur release to the gas phase is less significant. Hence increasing the residence time further, whilst increasing the amount of coal gasified, may not have as large a requirement of the sulphur sorbent present in the gasifier. They do imply however that if excessive sorbent loading of the gasifier is to be

avoided fresh sorbent feed to the CFB is needed as the feed-char is likely to contain a certain amount of organically bound sulphur even after the 70-75 wt.% (daf) coal gasified.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

1. The experimental rig designed and commissioned for the studies proved an effective way of producing pyrolysis chars, tars and gasification chars in the temperature range 850°C to 1050°C. The batch addition of the coal and the novel method of char removal provided close control over the residence time of particles, whilst the fluidised bed of sand produced rapid mixing conditions and high heating rates similar to large scale combustion processes.

2. On devolatilisation of the seven coals at 950°C, both the sulphur and nitrogen were found to shift preferentially into the volatile matter leaving the char reduced in S and N concentration with respect to the parent coal. Pyrolysis temperature in the range 850°C and 1050°C was found to have no effect on this shift. The following was observed:

2.1 The sulphur shifted more into the volatiles than nitrogen on devolatilisation. The normalised sulphur/carbon ratio, S/C' , of the pyrolysis chars was generally lower than the normalised nitrogen/carbon ratio, N/C' , which was closer to 1. This effect cannot be completely explained by the quantity of pyritic sulphur occurring in the parent coal.

2.2 Both the S/C' and N/C' ratios of the pyrolysis chars were found to increase with increasing coal rank. This is explained by the tendency for nitrogen and sulphur to occur in a higher proportion of more thermally stable compounds as the coal itself becomes more aromatic in nature.

2.3 The nitrogen/carbon content of the pyrolysis tar was close to that of the parent coal, the S/C' ratio was also generally higher in the tar than in the char.

- 2.4 The most common char particle type observed in reflected light microscopic examination of the pyrolysis chars was the honeycomb (or network) type shape. No direct link could be made with these observations and the maceral distribution of the parent coal or sulphur and nitrogen split between char and volatiles on devolatilisation.
3. On gasification at 950°C of the seven coals studied, the sulphur and nitrogen behaved slightly differently.
- 3.1 The nitrogen loss with gasification remained closely matched to the carbon loss with progressive burnout of the char for all seven coals. The N/C' ratios of the chars produced from the higher ranked coals moved slightly closer to 1 with increased burnout than the lower ranked coals.
- 3.2 The sulphur loss with amount of gasification appeared independent of coal rank. A single relationship was found to explain the sulphur behaviour with progressive char burnout for all seven coals. The S/C' drops in early stages of char burnout and then increases again with increased total carbon mass loss from the char above 70wt%.
- 3.3 There was no evidence found in this study for the sulphur to become concentrated in the mineral matter of the gasification char produced.
- 3.4 Whilst increasing the gasification temperature from 850°C to 1050°C increased the degree of carbon mass loss from the char with constant residence time, it did not effect the S/C' or N/C' ratio of the char produced. This indicates that the rate of sulphur and nitrogen oxidation has the same dependence on temperature as the carbon oxidation in the range studied.

4.0 The conclusions drawn from this study were found to be relevant to the choice of fuel for fluidised bed combustion and gasification where NO_x reduction strategies rely on an understanding of how the fuel and the nitrogen bound in it will behave on devolatilisation. Also the behaviour of the coal sulphur with progressive gasification are considered particularly relevant to the sorbent loading of the two stages of the ABGC.

6.2 RECOMMENDATIONS FOR FUTURE WORK

Whilst this study addressed most of the questions posed at the beginning of the project, certain areas of work could not be covered by the experimental programme due to time scale and physical limitations of the designed apparatus. The apparatus developed remains a useful tool for studying the heteroatom distribution in chars produced under atmospheric fluidised bed combustion/gasification conditions but is limited to a relatively narrow particle size range necessary for the elutriation of char particles and, without analysis of the combustion products, quantifying actual emissions of pollutant species is difficult. Further work is required to optimise the sulphur analysis techniques when using sorbents such as limestone in the bed.

It is recommended that further work with a pressurised fluidised bed reactor is undertaken to study the effects of pressure on the retention of sulphur and nitrogen in gasification chars. Coupled with gas analysis, this would also provide valuable information on effects such as the suppression of volatile yields during devolatilisation and the influence of char reactivity on NO_x emissions likely to be observed in industrial PFB combustion and gasification. It is felt this is needed to make closer the link between laboratory experimental results and the performance of pilot or full scale operations.

There also seems to be limited published work on the effect using larger coal particle sizes, typically 2 - 5mm, used in industrial FBC. If future work could incorporate the ability to accept larger coal particles, this could provide very useful experimental data on effects such as particle fragmentation and attrition likely from larger particles and longer residence times.

APPENDICES

APPENDIX A - FLUIDISED BED FLOW CALCULATIONS

Below is a brief example of the type of calculation used to establish the operating conditions for the heated fluidised bed system. The data used below is applicable to the parameters which were arrived at after the initial "cold" runs were completed with the glass prototype. At the nominal conditions below, assuming atmospheric pressure,

Reactor temperature = 950°C

$d_p(\text{sand}) = 425 \mu\text{m}$

$\rho_s(\text{sand}) = 2500 \text{ kg/m}^3$

$\phi_s = 0.86$

$\rho_g(\text{nitrogen}) = 0.28 \text{ kg/m}^3 @ 950^\circ\text{C}$

$\epsilon_{mf} = 0.49$

$\mu = 4.7 \times 10^{-5} \text{ Pa}\cdot\text{s} @ 950^\circ\text{C}$

$g = 9.81 \text{ m/s}^2$

the theoretical minimum fluidisation velocity of the system can be calculated from Equation 2.20.

$$U_{mf} = \frac{(\Phi_s \cdot d_p)^2}{150} \cdot \frac{\rho_s - \rho_g}{\mu} \cdot g \left(\frac{\epsilon_{mf}^3}{1 - \epsilon_{mf}} \right) \quad \text{Re} < 20 \quad \text{Equation 2.20}$$

The figures of ϵ_{mf} and ϕ_s were taken to be those values typical of a sand possessing rounded particles⁴⁵.

Using the above data this gives a minimum fluidising velocity, $U_{mf} = 0.11 \text{ m/s}$. When this is combined with the reactor diameter, in this example 70 mm, the theoretical flow rate needed for minimum fluidisation, Q_{mf} , is 12.5 l/min. As described in the Literature Review, a bubbling fluidised bed operates at approximately four times this value. This gives an operating flow rate, Q_{op} , of approx. 50 l/min at 950°C.

Now to calculate the velocity of gas needed to eject a char particles out of the reactor, the theoretical terminal velocity of the particle needs to be calculated using equation 2.21⁴⁵. Here ρ_s is taken to be 1000 kg/m³ and the char particle size, d_p , to be 185 μm .

$$U_{t(spherical)} = \left(\frac{4 (\rho_s - \rho_g)^2}{225 \rho_g \mu} \cdot g^2 \right)^{1/3} \cdot d_p \quad 0.4 < Re < 500 \quad \text{Equation 2.21}$$

For the above conditions, $U_t = 0.93 \text{ m/s}$ and assuming the same reactor diameter to be 70 mm, $Q_t = 215 \text{ l/min}$

The gases are metered at nominally 20°C and can be converted back to equivalent flow rates at this temperature, therefore parameters were chosen to give manageable gas flow rates at 20°C . Table A below lists the values for Q_{mf} , Q_{op} and Q_t for different conditions of reactor temperature and three reactor diameters. This was compiled using the equations and data detailed on the previous page. Shown also in Table A is the correction for the flow rate seen at the rotameter (assuming 20°C ambient conditions).

A reactor diameter chosen too small introduces the risk of wall effects known as slugging and too large a diameter makes it difficult to supply enough gas flow for Q_t

Table A. Key fluidisation flow rates calculated for various configurations

Reactor diameter, mm	Reactor Temp., $^\circ\text{C}$	N ₂ flow rates @ reactor temp., l/min			N ₂ flow rates @ rotameter (20°C), l/min		
		Q_{mf}	Q_{op}	Q_t	Q_{mf}^{20}	Q_{op}^{20}	Q_t^{20}
60mm	800	10.1	40.3	157	2.8	11.0	42.9
	950	9.2	37.7	159	2.2	8.0	38.1
	1100	8.4	34.6	161	1.8	7.2	34.3
70mm	800	13.7	54.9	214	2.8	15.0	58.4
	950	12.5	49.9	217	3.0	12.0	51.9
	1100	11.4	45.8	218	2.4	9.8	46.6
80mm	800	17.9	71.7	279	4.9	19.6	76.3
	950	16.3	65.2	282	3.9	15.6	67.7
	1100	14.9	59.8	285	3.2	12.8	60.9

APPENDIX B - PYROLYSIS MASS BALANCE CALCULATIONS

Involved in each pyrolysis experiment was a full mass balance to account for the char remaining in the bed due to agglomeration and tar collected in the condensers, cyclone walls and filter material. The daf figures for the char yield quoted in the results section corresponds to figures corrected for the ash content of the char and may differ slightly from true "coal-ash" daf figures, this corrects for sand contamination

Coal type - Nadins
 Fluidising gas - Nitrogen
 Temperature of bed - 950°C
 Residence time - 10 seconds

Elutriated char

Run	Wt. coal injected, g	Wt. of char recovered in cyclone, g
1	0.522	0.278
2	0.523	0.284
3	0.520	0.284
4	0.520	0.291
5	0.522	0.285
6	0.525	0.289
Total	3.132	1.710

Ash content of char, wt% 12.0

Weight of char collected in filters, g 0.113

Char in bed material

Weight of bed material, g 280.8

Weight % of bed lost on ashing 0.013

Weight of bed lost on ashing, g 0.037

Mass of char in bed material corrected
for char ash content, g 0.041

Total char

Elutriated char, g 1.823

Char in bed, g 0.041

Total char, g 1.865

Tar

Weight of tar collected, g 0.126

Pyrolysis mass balance (as analysed - db)

CHAR, WT%	59.5 %
TAR, WT%	4.0 %
GASES, WT%	36.5 %

Coal type - **Dawmill**

Fluidising gas - Nitrogen

Temperature of bed - 950°C

Residence time - 10 seconds

Elutriated char

Run	Wt. coal injected, g	Wt. of char recovered in cyclone, g
1	0.523	0.262
2	0.528	0.271
3	0.532	0.244
4	0.522	0.259
5	0.525	0.268
6	0.531	0.281
Total	3.161	1.586

Ash content of char, wt% (db) 6.3

Weight of char collected in filters, g 0.158

Char in bed material

Weight of bed material, g 279.8

Weight % of bed lost on ashing 0.043

Weight of bed lost on ashing, g 0.120

Mass of char in bed material corrected
for char ash content, g 0.128

Total char

Elutriated char, g 1.743

Char in bed, g 0.128

Total char, g 1.872

Tar

Weight of tar collected, g 0.151

Pyrolysis mass balance (as analysed - db)

CHAR, WT%	59.2 %
TAR, WT%	4.8 %
GASES, WT%	36.0 %

Coal type - **THORESBY**

Fluidising gas - Nitrogen

Temperature of bed - 950°C

Residence time - 10 seconds

Elutriated char

Run	Wt. coal injected, g	Wt. of char recovered in cyclone, g
1	0.523	0.197
2	0.510	0.185
3	0.524	0.190
4	0.515	0.191
5	0.527	0.191
6	0.521	0.213
Total	3.119	1.165

Ash content of char, wt% (db) 8.0

Weight of char collected in filters, g 0.097

Char in bed material

Weight of bed material, g 269.3

Weight % of bed lost on ashing 0.22

Weight of bed lost on ashing, g 0.592

Mass of char in bed material corrected
for char ash content, g 0.644

Total char

Elutriated char, g 1.262

Char in bed, g 0.644

Total char, g 1.906

Tar

Weight of tar collected, g 0.105

Pyrolysis mass balance (as analysed - db)

CHAR, WT%	61.1 %
TAR, WT%	3.4 %
GASES, WT%	35.5 %

Coal type - **Kellingley**

Fluidising gas - Nitrogen

Temperature of bed - 950°C

Residence time - 10 seconds

Elutriated char

Run	Wt. coal injected, g	Wt. of char recovered in cyclone, g
1	0.527	0.192
2	0.525	0.210
3	0.523	0.252
4	0.530	0.223
5	0.546	0.228
6	0.523	0.209
Total	3.173	1.313

Ash content of char, wt% 7.7

Weight of char collected in filters, g 0.127

Char in bed material

Weight of bed material, g 268.0

Weight % of bed lost on ashing 0.21

Weight of bed lost on ashing, g 0.563

Mass of char in bed material corrected
for char ash content, g 0.610

Total char

Elutriated char, g 1.440

Char in bed, g 0.610

Total char, g 2.050

Tar

Weight of tar collected, g 0.136

Pyrolysis mass balance (as analysed - db)

CHAR, WT%	64.6 %
TAR, WT%	4.3 %
GASES, WT%	31.1 %

Coal type - **LONGANNET**

Fluidising gas - Nitrogen

Temperature of bed - 950°C

Residence time - 10 seconds

Elutriated char

Run	Wt. coal injected, g	Wt. of char recovered in cyclone, g
1	0.530	0.335
2	0.532	0.343
3	0.520	0.347
4	0.522	0.343
5	0.527	0.341
6	0.528	0.351
Total	3.159	2.060

Ash content of char, wt% 19.9

Weight of char collected in filters, g 0.041

Char in bed material

Weight of bed material, g 263.0

Weight % of bed lost on ashing 0.05

Weight of bed lost on ashing, g 0.132

Mass of char in bed material corrected
for char ash content, g 0.164

Total char

Elutriated char, g 2.101

Char in bed, g 0.164

Total char, g 2.265

Tar

Weight of tar collected, g 0.080

Pyrolysis mass balance (as analysed - db)

CHAR, WT%	71.7 %
TAR, WT%	2.5 %
GASES, WT%	25.8 %

Coal type - Cwm
 Fluidising gas - Nitrogen
 Temperature of bed - 950°C
 Residence time - 10 seconds

Elutriated char

Run	Wt. coal injected, g	Wt. of char recovered in cyclone, g
1	0.503	0.028
2	0.504	0.027
3	0.504	0.023
4	0.506	0.026
5	0.508	0.033
6	0.506	0.029
Total	3.030	0.167

Ash content of char, wt% (db) 7.0

Weight of char collected in filters, g 0.126

Char in bed material

Weight of bed material, g 268.5

Weight % of bed lost on ashing 0.585

Weight of bed lost on ashing, g 1.571

Mass of char in bed material corrected
for char ash content, g 1.689

Total char

Elutriated char, g 0.293

Char in bed, g 1.689

Char in tube, g 0.347

Total char, g 2.329

Tar

Weight of tar collected, g 0.129

Pyrolysis mass balance (as analysed - db)

CHAR, WT%	76.9 %
TAR, WT%	4.3 %
GASES, WT%	18.8 %

Coal type - **Tilmanstone**

Fluidising gas - Nitrogen

Temperature of bed - 950°C

Residence time - 10 seconds

Elutriated char

Run	Wt. coal injected, g	Wt. of char recovered in cyclone, g
1	0.519	0.038
2	0.512	0.050
3	0.513	0.055
4	0.510	0.056
5	0.522	0.023
6	0.521	0.054
Total	3.097	0.277

Ash content of char, wt% (db) 5.3

Weight of char collected in filters, g 0.092

Char in bed material

Weight of bed material, g 270.2

Weight % of bed lost on ashing 0.646

Weight of bed lost on ashing, g 1.746

Mass of char in bed material corrected
for char ash content, g 1.843

Total char

Elutriated char, g 0.369

Char in bed, g 1.843

Char in tube, g 0.250

Total char, g 2.463

Tar

Weight of tar collected, g 0.087

Pyrolysis mass balance (as analysed - db)

CHAR, WT%	79.5 %
TAR, WT%	2.8 %
GASES, WT%	17.7 %

APPENDIX C - CRE COAL BANK DATA

The following seven pages are reproduced from the CRE Coal Bank data sheets⁵⁶. The information applies to the coal samples as sampled by CRE and is presented here to highlight the differing properties of the parent coals used in the study. Some of the data is used in Chapter 5 - Results and Discussion as useful reference material.

COAL: NADINS
GRADE: SINGLES
SEAM: OPENCAST
BCC COAL RANK CODE: 902
ECE / ISO CLASSIFICATION: 801
PROXIMATE ANALYSIS

(% a.d.)

Moisture	13.3
Ash	7.4
Volatile matter	34.9
Fixed carbon	44.4
Volatile matter (dmmf)	

CAKING PROPERTIES

Swelling Index	0.5
Gray-King Coke Type	B

CALORIFIC VALUE

kJ / kg (daf)	32420
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ASH FUSION RANGE (°C) *

Deformation temp.	1100
Hemisphere temp.	1120
Flow temp.	1240

ULTIMATE ANALYSIS (%)

Carbon (dmmf)	80.1
Hydrogen (dmmf)	5.1
Oxygen (dmmf)	12.0
Nitrogen (dmmf)	1.90

Organic sulphur (db)	0.82
Sulphate as S (db)	0.08
Pyritic sulphur as S (db)	1.34

Chlorine (db)	0.03
Carbon dioxide (db)	0.84
Mineral matter (db)	10.78

MACERAL ANALYSIS

(% by volume, mmf)

Vitrinite	76
Exinite	10
Inertinite	14

ASH ANALYSIS

(% on ash)

Na ₂ O	0.3
K ₂ O	2.4
CaO	8.7
MgO	2.8
Fe ₂ O ₃	27.5
Al ₂ O ₃	17.1
SiO ₂	31.5
SO ₃	7.1
TiO ₂	0.6
Mn ₃ O ₄	0.4
P ₂ O ₅	0.8

 *Test atmosphere: reducing (50% CO₂ / 50% H₂)

This analysis is typical of this specially selected sample, but there may be slight variations between the data given above and that of the actual sample supplied.

ad: as analysed

db: dry basis

daf: dry, ash free

dmmf: dry, mineral matter free

mmf: mineral matter free

COAL: DAW MILL

GRADE: SINGLES

SEAM: THICK COAL

BCC COAL RANK CODE: 802

ECE / ISO CLASSIFICATION: 711

PROXIMATE ANALYSIS

(% a.d.)

Moisture	6.1
Ash	4.4
Volatile matter	35.7
Fixed carbon	53.8
Volatile matter (dmmf)	40.4

CAKING PROPERTIES

Swelling Index	1.0
Gray-King Coke Type	C

CALORIFIC VALUE

kJ / kg (daf)	32820
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ASH FUSION RANGE (°C) *

Deformation temp.	1240
Hemisphere temp.	1270
Flow temp.	1320

ULTIMATE ANALYSIS (%)

Carbon (dmmf)	81.3
Hydrogen (dmmf)	4.8
Oxygen (dmmf)	11.5
Nitrogen (dmmf)	1.28

Organic sulphur (db)	1.12
Sulphate as S (db)	<0.1
Pyritic sulphur as S (db)	0.28

Chlorine (db)	0.21
Carbon dioxide (db)	0.45
Mineral matter (db)	5.84

MACERAL ANALYSIS

(% by volume, mmf)

Vitrinite	66
Exinite	13
Inertinite	21

ASH ANALYSIS

(% on ash)

Na ₂ O	1.5
K ₂ O	0.5
CaO	12.0
MgO	2.5
Fe ₂ O ₃	11.2
Al ₂ O ₃	23.9
SiO ₂	36.8
SO ₃	12.9
TiO ₂	1.1
Mn ₂ O ₄	0.4
P ₂ O ₅	<0.3

*Test atmosphere: reducing (50% CO₂ / 50% H₂)

This analysis is typical of this specially selected sample, but there may be slight variations between the data given above and that of the actual sample supplied.

ad: as analysed

db: dry basis

daf: dry, ash free

dmmf: dry, mineral matter free

mmf: mineral matter free

COAL : THORESBY

GRADE: SINGLES

SEAM: PARKGATE

BCC COAL RANK CODE: 502

ISO RANK CODE: 634

PROXIMATE ANALYSIS

(% a.d.)

Moisture	5.6
Ash	4.9
Volatile matter	34.2
Fixed carbon	55.3
Volatile matter (dmmf)	38.7

CAKING PROPERTIES

Swelling Index	5.5
Gray-King Coke Type	G5

CALORIFIC VALUE

kJ/kg (daf)	34680
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ASH FUSION RANGE (°C) *

Deformation temp.	1060
Hemisphere temp.	1090
Flow temp.	1220

ULTIMATE ANALYSIS (%)

Carbon (dmmf)	84.3
Hydrogen (dmmf)	4.6
Oxygen (dmmf)	7.9
Nitrogen (dmmf)	1.83

Organic sulphur (db)	1.12
Sulphate as S (db)	<0.1
Pyritic sulphur as S (db)	0.91

Chlorine (db)	0.67
Carbon dioxide (db)	0.10
Mineral matter (db)	6.48

MACERAL ANALYSIS

(% by volume, mmf)

Vitrinite	82
Exinite	7
Inertinite	11

ASH ANALYSIS

(% on ash)

Na ₂ O	5.9
K ₂ O	1.4
CaO	3.3
MgO	0.7
Fe ₂ O ₃	26.3
Al ₂ O ₃	23.8
SiO ₂	34.3
SO ₃	3.1
TiO ₂	0.9
Mn ₂ O ₄	<0.2
P ₂ O ₅	<0.2

*Test atmosphere: reducing (50% CO₂/50% H₂)

This analysis is typical of this specially selected sample, but there may be slight variations between the data given above and that of the actual sample supplied.

ad: as analysed

db: dry basis

daf: dry, ash free

dmmf: dry, mineral matter free

mmf: mineral matter free

COAL: KELLINGLEY
GRADE: SINGLES
SEAM: SILKSTONE
BCC COAL RANK CODE: 502
ECE / ISO RANK CODE: 634
PROXIMATE ANALYSIS

(% a.d.)

Moisture	4.7
Ash	5.0
Volatile matter	37.1
Fixed carbon	53.2
Volatile matter (dmmf)	41.6

CAKING PROPERTIES

Swelling Index	4.5
Gray-King Coke Type	G6

CALORIFIC VALUE

kJ/kg (daf)	35440
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ASH FUSION RANGE (°C) *

Deformation temp.	1040
Hemisphere temp.	1080
Flow temp.	1110

ULTIMATE ANALYSIS (%)

Carbon (dmmf)	85.1
Hydrogen (dmmf)	5.9
Oxygen (dmmf)	5.7
Nitrogen (dmmf)	2.12

Organic sulphur (db)	0.84
Sulphate as S (db)	<0.1
Pyritic sulphur as S (db)	0.73

Chlorine (db)	0.41
Carbon dioxide (db)	0.11
Mineral matter (db)	6.31

MACERAL ANALYSIS

(% by volume, mmf)

Vitrinite	69
Exinite	19
Inertinite	12

ASH ANALYSIS

(% on ash)

Na ₂ O	4.2
K ₂ O	1.5
CaO	12.5
MgO	0.6
Fe ₂ O ₃	23.2
Al ₂ O ₃	17.6
SiO ₂	31.4
SO ₃	2.6
TiO ₂	0.6
Mn ₂ O ₄	0.1
P ₂ O ₅	6.6

 *Test atmosphere: reducing (50% CO₂/50% H₂)

This analysis is typical of this specially selected sample, but there may be slight variations between the data given above and that of the actual sample supplied.

ad: as analysed
 db: dry basis
 daf: dry, ash free
 dmmf: dry, mineral matter free
 mmf: mineral matter free

COAL: LONGANNET

GRADE: SPECIAL

SEAM: HIRST

BCC COAL RANK CODE: N/A

ECE / ISO CLASSIFICATION: N/A

PROXIMATE ANALYSIS

(% a.d.)

Moisture	9.2
Ash	10.8
Volatile matter	28.0
Fixed carbon	52.0
Volatile matter (dmmf)	35.4

CAKING PROPERTIES

Swelling Index	2.5
Gray-King Coke Type	C

CALORIFIC VALUE

kJ/kg (daf)	32940
-------------	-------

ASH FUSION RANGE (°C) *

Deformation temp.	> 1500
Hemisphere temp.	> 1500
Flow temp.	> 1500

ULTIMATE ANALYSIS (%)

Carbon (dmmf)	82.9
Hydrogen (dmmf)	5.0
Oxygen (dmmf)	10.0
Nitrogen (dmmf)	1.63

Organic sulphur (db)	0.33
Sulphate as S (db)	0.02
Pyritic sulphur as S (db)	0.02

Chlorine (db)	0.12
Carbon dioxide (db)	0.13
Mineral matter (db)	12.98

MACERAL ANALYSIS

(% by volume, mmf)

Vitrinite	89
Exinite	4
Inertinite	7

ASH ANALYSIS

(% on ash)

Na ₂ O	0.2
K ₂ O	0.4
CaO	1.8
MgO	0.6
Fe ₂ O ₃	1.6
Al ₂ O ₃	40.3
SiO ₂	51.1
SO ₃	0.6
TiO ₂	1.5
Mn ₂ O ₄	< 0.1
P ₂ O ₅	1.3

*Test atmosphere: reducing (50% CO₂/50% H₂)

This analysis is typical of this specially selected sample, but there may be slight variations between the data given above and that of the actual sample supplied.

ad: as analysed

db: dry basis

daf: dry, ash free

dmmf: dry, mineral matter free

mmf: mineral matter free

COAL: CWM

GRADE: TREBLES

SEAM:

BCC COAL RANK CODE: 301A

ECE / ISO CLASSIFICATION: 434

PROXIMATE ANALYSIS

(% a.d.)

Moisture	0.7
Ash	5.9
Volatile matter	20.9
Fixed carbon	72.5
Volatile matter (dmmf)	22.6

CAKING PROPERTIES

Swelling Index	9
Gray-King Coke Type	G6

CALORIFIC VALUE

kJ / kg (daf)	36400
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ASH FUSION RANGE (°C) *

Deformation temp.	>1500
Hemisphere temp.	>1500
Flow temp.	>1500

ULTIMATE ANALYSIS (%)

Carbon (dmmf)	90.3
Hydrogen (dmmf)	4.4
Oxygen (dmmf)	3.0
Nitrogen (dmmf)	1.51

Organic sulphur (db)	0.74
Sulphate as S (db)	0.02
Pyritic sulphur as S (db)	0.08

Chlorine (db)	0.02
Carbon dioxide (db)	0.26
Mineral matter (db)	6.80

MACERAL ANALYSIS

(% by volume, mmf)

Vitrinite	86
Exinite	0
Inertinite	14

ASH ANALYSIS

(% on ash)

Na ₂ O	0.3
K ₂ O	0.2
CaO	2.7
MgO	0.9
Fe ₂ O ₃	4.0
Al ₂ O ₃	38.3
SiO ₂	46.1
SO ₃	1.9
TiO ₂	1.7
Mn ₂ O ₄	0.1
P ₂ O ₅	3.0

*Test atmosphere: reducing (50% CO₂/50% H₂)

This analysis is typical of this specially selected sample, but there may be slight variations between the data given above and that of the actual sample supplied.

ad: as analysed

db: dry basis

daf: dry, ash free

dmmf: dry, mineral matter free

mmf: mineral matter free

COAL: TILMANSTONE
GRADE: SPECIAL
SEAM: KENT No.6
BCC COAL RANK CODE: 204
ECE / ISO CLASSIFICATION: 333
PROXIMATE ANALYSIS

(% a.d.)

Moisture	0.7
Ash	5.4
Volatile matter	16.0
Fixed carbon	77.9
Volatile matter (dmmf)	17.2

CAKING PROPERTIES

Swelling Index	8
Gray-King Coke Type	G3

CALORIFIC VALUE

kJ / kg (daf)	36500
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ASH FUSION RANGE (°C) *

Deformation temp.	1090
Hemisphere temp.	1120
Flow temp.	1160

ULTIMATE ANALYSIS (%)

Carbon (dmmf)	92.4
Hydrogen (dmmf)	4.5
Oxygen (dmmf)	0.9
Nitrogen (dmmf)	1.45

Organic sulphur (db)	0.67
Sulphate as S (db)	0.02
Pyritic sulphur as S (db)	0.54

Chlorine (db)	0.08
Carbon dioxide (db)	0.34
Mineral matter (db)	6.53

MACERAL ANALYSIS

(% by volume, mmf)

Vitrinite	89
Exinite	0
Inertinite	11

ASH ANALYSIS

(% on ash)

Na ₂ O	0.9
K ₂ O	2.2
CaO	3.9
MgO	1.1
Fe ₂ O ₃	15.9
Al ₂ O ₃	30.3
SiO ₂	40.8
SO ₃	3.0
TiO ₂	0.7
Mn ₂ O ₄	0.1
P ₂ O ₅	0.5

 *Test atmosphere: reducing (50% CO₂/50% H₂)

This analysis is typical of this specially selected sample, but there may be slight variations between the data given above and that of the actual sample supplied.

ad: as analysed
 db: dry basis
 daf: dry, ash free
 dmmf: dry, mineral matter free
 mmf: mineral matter free

APPENDIX D - UNREPORTED RESULTS

LIMESTONE IN-BED PYROLYSIS

Coal type -	Nadins		
Fluidising gas -	Nitrogen	Limestone sorbent	6.00g
Temperature of bed -	950°C	sorbent recovered	3.30g
Residence time -	10 seconds		

Elutriated char

Run	Wt. coal injected, g	Wt. of char recovered in cyclone, g
1	0.503	0.275
2	0.503	0.277
3	0.507	0.278
4	0.507	0.280
5	0.506	0.274
6	0.511	0.273
Total	3.037	1.658

Ash content of char, wt% 13.0

Weight of char collected in filters, g 0.031

Char in bed material

Weight of bed material, g 272.0

Weight % of bed lost on ashing 0.027

Weight of bed lost on ashing, g 0.072

Mass of char in bed material corrected
for char ash content, g 0.083

Total char

Elutriated char, g 1.689

Char in bed, g 0.083

Total char, g 1.772

Tar

Weight of tar collected, g 0.092

Pyrolysis mass balance (as analysed - db)

CHAR, WT%	58.4 %
TAR, WT%	3.0 %
GASES, WT%	38.6 %

Analysis - Nadins with limestone in bed

	<i>Pyrolysis char</i>	<i>Pyrolysis tar</i>
Ash, wt% (db)	13.0	N/A
Total sulphur, wt% (daf)	Not available	1.2
Total nitrogen, wt% (daf)	1.7	1.4
Carbon content, wt% (daf)	88.7	84.1
Sulphur content of spent sorbent, wt.% (ad)	0.46	

LIMESTONE IN-BED GASIFICATION**Analysis - Nadins coal 3.00g of limestone added to bed**

Char type	Ash, wt.% (daf)	Wt% gasified, (daf)	C, wt% (daf)	S, wt% (daf)	N, wt% (daf)	S content of sorbent, wt% (ad)
C ₁₀	16.4	61.8	90.5	-	1.7	0.44
C ₁₅	25.6	78.0	91.9	-	1.9	0.32
C ₂₀	34.9	86.0	89.4	-	1.6	0.36

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