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GASEOUS NITROGEN AND SULPHUR EMISSIONS FROM COAL GASIFICATION

RESEARCH REPORT 59

Authors:

S J Day¹
P F Nelson²
D C Park¹

¹ **CSIRO Energy Technology**
² **Macquarie University, Graduate School of the Environment**

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QCAT Technology Transfer Centre, Technology Court
Pullenvale Qld 4069 AUSTRALIA
Telephone (07) 3871 4400 Facsimile (07) 3871 4444
Email: Administration@ccsd.biz

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Curtin University of Technology	Prof Linda Kristjanson
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The University of Queensland	Prof Don McKee

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*Cooperative Research Centre for
Coal in Sustainable Development*
QCAT Technology Transfer Centre
Technology Court
Pullenvale, Qld 4069
Telephone: (07) 3871 4400
Fax: (07) 3871 4444

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CONTEXT STATEMENT

CCSD Project 3.1: Gaseous Nitrogen and Sulphur Emissions from Coal Gasification Final Report - Task 5

This report summarises the work performed, as part of the CRC for Coal in Sustainable Development program in gasification, to examine gaseous emissions from coal gasification. Most of the experimental results presented here are the work of Dongchan Park, the PhD student appointed to the project in February 2000, who has since been awarded his degree from the University of Newcastle. Apart from his thesis there have also been other publications arising from his work (Park *et al.*, 2003; Park *et al.*, 2005). Detailed descriptions of the experimental procedures and results are provided in these publications.

The original aim of the project was to study the effect of coal quality on the gaseous nitrogen and sulphur emissions produced during coal gasification in the CSIRO PEFR facility. However, commissioning problems with PEFR necessitated that the program be modified to include a large component of experimental work on a small scale, fixed-bed reactor at the CSIRO's North Ryde laboratories. The specific aims of the revised experimental program were:

- To identify and quantify the gaseous N and S containing compounds produced during coal and char gasification.
- To determine the effect of gasification temperature and residence time on the emission of these compounds.
- To determine the effect of the gasifying medium on N and S emissions.

The major outcomes of this work are an improved understanding of the type and amount of nitrogen and sulphur compounds produced during gasification, and how emissions of these compounds are affected by process conditions. Data of this type are necessary for process modelling and when designing emission control systems.

Summary

Increasing community concern about atmospheric pollution and the effects of greenhouse gas emissions from coal combustion has led to increased interest in developing more efficient power generation technologies. Among these advanced technologies is integrated gasification combined cycle (IGCC) which can potentially deliver significantly higher generation efficiencies and lower greenhouse gas emissions than the best conventional combustion systems currently available. However, there are few large scale IGCC plants operating in the world and hence emissions of potentially adverse compounds from these processes are not well understood.

To widen the amount of information available on the nature of gaseous emissions from gasification processes, this project was developed with the specific aims of:

- Identifying and quantifying the gaseous N and S containing compounds produced during coal and char gasification.
- Determining the effect of gasification temperature and residence time on the emission of these compounds.
- Determining the effect of the gasifying medium on N and S emissions.

Emissions of nitrogen and sulphur compounds from a Queensland bituminous coal were measured under O₂ gasification conditions in the PEFR at 1100 and 1400 °C. Two chars, prepared from Queensland coals, were studied in the bench scale fixed bed reactor to examine the effects of pressure, temperature and gasification medium on emissions.

The main findings of the project were:

- During O₂ gasification of a Queensland bituminous coal using the PEFR, HCN and NH₃ were the only nitrogen products observed (although N₂ was also likely to have been produced under some conditions). The distribution of products depended upon the temperature of the reaction. Hydrogen sulphide was the main sulphur species with lesser amounts of COS also produced. The PEFR runs showed that about 50 percent of coal N was released as HCN and NH₃ under these conditions. Approximately 50 percent of the S in the coal was released during the PEFR reaction at 1100 °C whereas at 1400 °C, essentially all of the S was released.
- The experimental program identified the main gaseous sulphur and nitrogen products from char gasification in a fixed bed reactor. In relation to nitrogen, the species produced were N₂, NH₃, NO and HCN depending on the reactant gas. With O₂ gasification, N₂ and NO were produced whereas in CO₂, N₂ was the dominant product with very high selectivity over a wide range of pressures and CO₂ concentrations. Steam gasification produced mainly HCN, NH₃ and N₂.
- Pressure was found to have little effect on the nitrogen compounds produced from char in either O₂ or CO₂ gasification, however, with H₂O as the reactive medium, increasing pressure resulted in a greater proportion of NH₃ at the expense of N₂.
- In the fixed bed reactor, SO₂ was the only sulphur compound identified. With O₂, the evidence suggested that this was the only compound produced, however, in CO₂, mass balance deficiencies indicated that other compounds, possibly H₂S and/or COS may also have been produced. Analytical difficulties prevented this from being confirmed.
- The large matrix of experiments performed enabled mechanistic pathways for the formation of the various nitrogen and sulphur compounds in the effluent gas to be

postulated. The transformation routes were proposed for nitrogen and sulphur species. An important finding with respect to nitrogen emissions is that with appropriate control of the gasification conditions, most of the coal nitrogen which is initially released as NH_3 and HCN can be ultimately converted to N_2 within the reactor itself. This will benefit designers of gasification technology since it greatly simplifies the emission control system required to meet environment standards.

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1 Introduction

The work presented in this report was performed as part of the CRC for Coal in Sustainable Development program in gasification. The project came about as a result of a detailed study (Duffy and Nelson, 1997) which identified major areas in which information relating to emissions from gasification processes was lacking. Coal gasification will be central to advanced IGCC systems so the focus of the project described here was to investigate the transformational behaviour of coal-bound nitrogen and sulphur under gasification conditions.

Most of the experimental results presented here are the work of Dongchan Park, the PhD student appointed to the project in February 2000, who has since been awarded his degree from the University of Newcastle. Apart from his thesis there have also been other publications arising from his work (Park *et al.*, 2003; Park *et al.*, 2005).

Since the results of the project have been described in detail in other publications, the purpose of this report is to provide an overview of the work which was performed and to highlight the key outcomes rather than to repeat what has been written elsewhere. Readers who require more detail are directed to those publications, which are listed in the References section of this report.

1.1 Background

Increasing community concern about atmospheric pollution and the effects of greenhouse gas emissions from coal combustion has led to increased interest in developing more efficient power generation technologies. Among these advanced technologies is integrated gasification combined cycle (IGCC) which can potentially deliver significantly higher generation efficiencies than the best conventional combustion systems currently available. However, there are few large scale commercial IGCC plants operating in the world and the nature of potentially adverse emissions from these plants is not yet completely understood.

Emissions from conventional coal combustion processes, where coal is burnt in excess air, are predominantly CO₂ and water with the primary gaseous species of environmental concern being NO_x and SO₂ along with volatile trace elements and some organic compounds. Gasification, on the other hand, operates under oxygen lean conditions to produce a fuel gas of predominantly CO and H₂ but with smaller amounts of CH₄, CO₂ and steam also present. Under these conditions, the pollutant emissions would generally be in a reduced state and may include H₂S, COS, NH₃, and HCN along with trace elements similar to those associated with conventional combustion. Table 1.1 compares the forms in which trace species of interest are released during combustion to those that may form during gasification.

Table 1.1 Comparison of gaseous emissions from combustion and gasification processes

Species	Combustion	Gasification
S-containing	SO ₂ , traces of SO ₃	H ₂ S, COS, CS ₂ , mercaptans, thiophene
N-containing	NO, NO ₂ , N ₂ O	NH ₃ , HCN, sulphocyanide
Halogens	As acids (e.g. HCl)	As acids (e.g. HCl)
Trace elements	Partition between bottom and fly ash and gas phase depending on the volatility	Similar to combustion although reducing atmosphere will have an effect on speciation and hence partitioning; alkalis have deleterious effects on turbine life.

From an emissions control perspective it is important to understand the nature of the pollutant species because the technologies needed to control them are likely to be quite different from those used in conventional combustion systems. It is possible, for example, that IGCC may have some advantages over normal combustion processes because the reduced sulphur and nitrogen species listed in Table 1.1 are substantially more soluble than the oxides and, at low temperatures at least, are potentially easier to remove. Gas cleaning at high temperatures, which will increase the overall efficiency of the IGCC, requires the development of new high temperature gas cleaning technology and is still the subject of research around the world.

1.2 IGCC and Coal Gasification

The basic layout of an IGCC system is illustrated schematically in Figure 1.1.

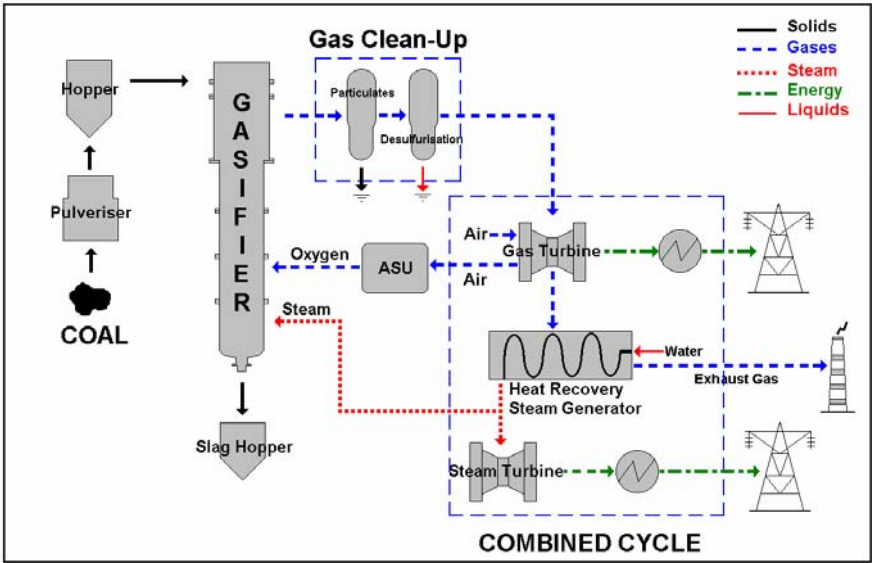


Figure 1.1 Schematic layout of an IGCC system showing the major components

The system includes the gasifier, a reactor typically operated at 2 to 4 MPa, in which coal is reacted with a limited amount of oxygen and steam (or CO₂) to produce a fuel gas containing carbon monoxide, carbon dioxide and hydrogen. This fuel gas, after cleaning, is fired directly in a gas turbine. The gas clean-up system is required to protect the turbine from particulate matter and to remove nitrogen and sulphur compounds. Heat recovered from cooling the fuel gas prior to the clean-up stage and from the turbine exhaust is used to raise steam, which is then used to generate power in a conventional steam turbine cycle and to recirculate back to the gasifier as a gasifying medium.

Air may also be used as the gasifying medium, which does away with the air separation unit (ASU), but increases the volume of the fuel gas which must be cleaned.

The different gasifier designs, operating principles and the development status of the various technologies have been described comprehensively in the literature (for details, see Duffy and Nelson, 1997; Park, 2004, and the references cited therein). However, the majority of the technologies can be broadly classified into three main gasifier types: fixed bed, fluidised bed and entrained flow reactor systems. The facility located at the CSIRO Pinjarra Hills laboratories is of the entrained flow design.

The gasification of the coal itself comprises two separate processes: pyrolysis (devolatilisation) and gasification. Pyrolysis is the first stage of the reaction and yields gaseous and liquid products and a solid carbon-rich residue (char). This stage of the reaction usually occurs before significant amounts of gasification or combustion occurs.

Gasification is the process of heterogeneous reactions which occur with the char produced from pyrolysis and generally begins at temperatures above about 700 °C. There is a range of individual reactions, both endothermic and exothermic, which take place during this process ultimately yielding CO, CO₂, CH₄ and water.

The production of compounds of environmental concern may be produced during both phases of the coal gasification process.

1.3 Aims of Project

Prior to the commencement of this project, the release of potentially harmful compounds from coal under gasification conditions and their speciation had not been extensively studied. This was confirmed by the results of an extensive literature survey (Duffy and Nelson, 1997) which reviewed the published work relevant to high pressure gasification and combustion. The review identified significant deficiencies in our knowledge of the effects of coal quality and characteristics on the formation of gaseous and particulate phase pollutants from coal gasification processes. Accordingly, this project was developed to address this lack of knowledge, particularly in relation to the effects of coal type on emissions of N and S containing pollutant gases as a function of temperature, particle heating rates, pressure and gasification atmosphere relevant to IGCC and related gasification processes.

The bulk of the experimental program envisaged for the project was to be performed on the Pinjarra Hills PEFR facility. However, there were significant problems associated with commissioning this system which resulted in long delays to the original work program. As a consequence, the program was modified to include a large component of experimental work on a small scale, fixed-bed reactor at the CSIRO's North Ryde laboratories. In this program, experiments designed to measure emissions from the gasification of coal chars were conducted under a very broad range of conditions of temperature, pressure and gasification media. The specific aims of the revised experimental program were:

- To identify and quantify the gaseous N and S containing compounds produced during coal and char gasification.
- To determine the effect of gasification temperature and residence time on the emission of these compounds.
- To determine the effect of the gasifying medium on N and S emissions.

The reduced scope of the program performed on the PEFR meant that it was not possible to achieve the original aim of examining the effect of coal type on emissions. Instead, mechanistic pathways for some of the main nitrogen and sulphur reactions were studied in detail. Fundamental information of this type will be crucial for developing models which can effectively simulate coal behaviour under gasification conditions.

2 Literature Review

As a first stage in the project, a comprehensive review of literature relating to environmental emissions from IGCC and other gasification processes was undertaken by Duffy and Nelson (1997). This review examined the effects of gasifier operating conditions (i.e. gasification

medium, temperature, pressure and coal characteristics) on the chemical/physical forms and concentrations of pollutant species in the direct gasifier effluent.

Very briefly, the main findings of the review in relation to nitrogen and sulphur releases are summarised below.

- **Effect of Temperature**

In general, most studies found that increasing heating rate and temperature led to increased amounts of volatile (tar and gaseous) nitrogen released. It was also found that the ratio of HCN to NH₃ formed during pyrolysis increased with increasing temperature and heating rate. Sulphur release also increased with increasing heating rate and temperature and was released mainly as H₂S.

- **Effect of Pressure**

Pressure was generally found to have little effect on the total amount of nitrogen or sulphur released from the coal, however, the distribution of these elements in the product phases was affected to varying degrees by pressure.

- **Effect of Gasifying Medium**

There have been conflicting results as to whether the release of fuel nitrogen from the coal is influenced by the oxygen to coal ratio in the gasifying medium. However, there is general agreement that increased levels of oxygen causes a decrease in both HCN and NH₃ and an increase in NO emissions. Some work has shown that higher steam/coal ratios result in decreased levels of HCN and H₂S.

The results of this review highlighted a number of areas in which more research was required to understand the nature of emissions from coal gasification and, as noted above, formed the basis of determining the scope of the current project.

3 Experiments at VTT Energy

3.1 Background

Because the project was commenced before the pressurised entrained flow reactor at Pinjarra Hills was operational, the Technical Research Centre of Finland (VTT) was commissioned to perform a series of gasification experiments on an Australian coal and analyse the resulting gaseous emissions. These experiments were performed during April 1999 at VTT's Energy Research Laboratories in the city of Jyväskylä about 300 km north of Helsinki.

The reactor operated by VTT is a pressurised entrained flow system very similar in design to the facility at Pinjarra Hills. The main difference is that the Finnish reactor is designed to operate under isothermal conditions and therefore uses much lower fuel feed rates (maximum of about 100 g hr⁻¹ compared to several kg hr⁻¹ at Pinjarra Hills) and higher dilution than the CSIRO PEFR system. A complete description of the Finnish reactor can be found in Hämäläinen and Aho, (1996). The details of the work undertaken by VTT for this project are provided in their report (Aho et al., 1999) but the results are briefly described in the following section.

3.2 Experimental

A sample of a Hunter Valley high volatile bituminous coal, which had been screened to a particle size range of 110 - 130 µm, was run under gasification conditions in the VTT reactor at 1000 °C and a stoichiometry of 0.4. The pressure and residence times were varied between 0.15 - 1.2 MPa and 0.1 – 2 seconds respectively. Continuous measurements of CO₂, CO, NO,

and O₂ concentrations in the reactor off-gas were made during the course of each experiment. As well, the nitrogen species, NH₃ and HCN, and the trace elements, Na, K, Hg, Se and Cd were measured by absorption into appropriate reagent solutions. Char samples were collected during each condition to determine mass loss and were analysed for C, H, N and S as well as trace elements. It was not possible at the time the experiments were conducted to measure gaseous sulphur emissions.

3.3 Results

Table 3.1 summarises the results of the nitrogen species measurements for each residence time and pressure combination.

Table 3.1 Concentration of carbon oxides and nitrogenous species in reactor off-gas

Pressure (MPa)	Residence Time (s)	CO ₂ (ppm)	CO (ppm)	NO (ppm)	HCN (ppm)	NH ₃ (ppm)
0.15	0.1	2100	5170	165	200	48
0.15	0.5	7200	7680	134	300	68
0.15	1.71	5400	>3600	18	235	39
0.5	0.5	4000	6000	40	127	21
1.2	0.1	2670	4690	267	120	22
1.2	0.5	4000	9750	96	145	28
1.2	2	8000	5000	30	100	17

To allow comparison of the results, the relative abundances of NO, HCN and NH₃ present at each condition were calculated by normalising their concentrations to the sum of the corresponding CO₂ and CO concentrations (i.e. the extent of gasification). The relative abundance curves are plotted in Figures 3.1 and 3.2.

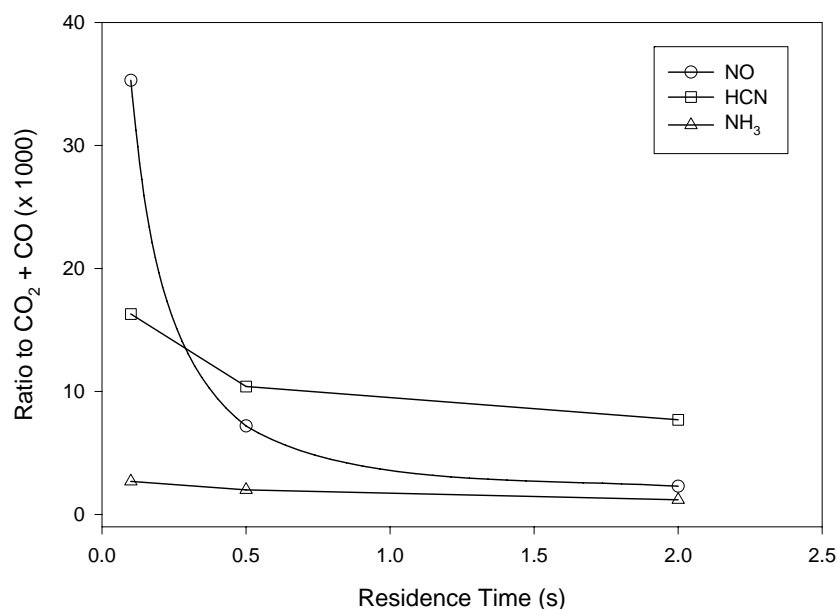


Figure 3.1 Effect of residence time on the release of nitrogenous species

Figure 3.1 shows the effect of residence time (at a reactor pressure of 1.2 MPa) on the release of the nitrogenous species. At low residence times, NO was the dominant species but the relative concentration rapidly decreased with increasing residence time and HCN became the main component. Production of NH₃ remained relatively constant over the range of residence times investigated.

The effect of pressure is shown in Figure 3.2. The residence time for these data was 0.5 seconds in each case. Here, HCN was the most abundant species over the entire pressure range with highest emissions occurring at lowest pressures. NO and NH₃ concentrations were relatively constant over this pressure range.

It is interesting that in all cases, the concentration of HCN was consistently higher than that of NH₃. This is in contrast to the results which were subsequently obtained on the CSIRO PEFR at comparable temperatures (Section 4.1). In those experiments (conducted at 1100 °C compared to 1000 °C on the VTT system), the dominant N species was NH₃.

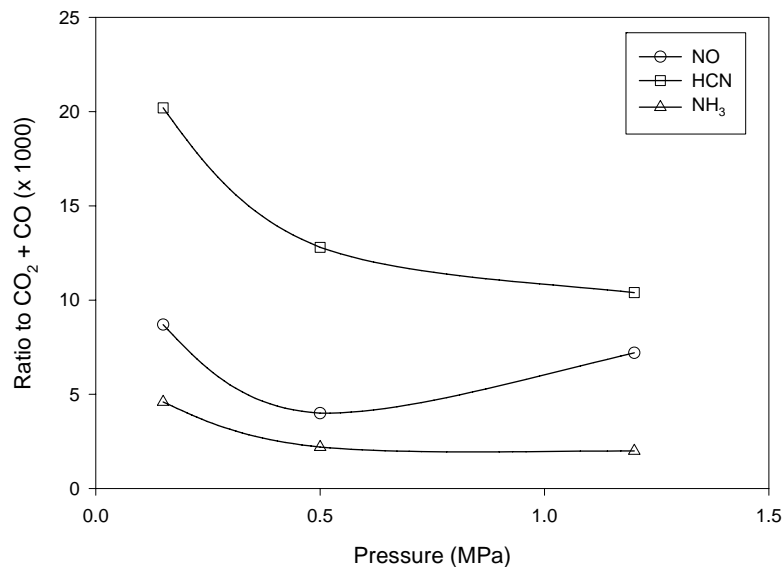


Figure 3.2 Effect of pressure on the release of nitrogenous species

Analyses of the char samples from each condition enabled the fraction of N and S released as a function of both residence time and pressure to be estimated. These results are plotted in Figures 3.3 and 3.4 respectively.

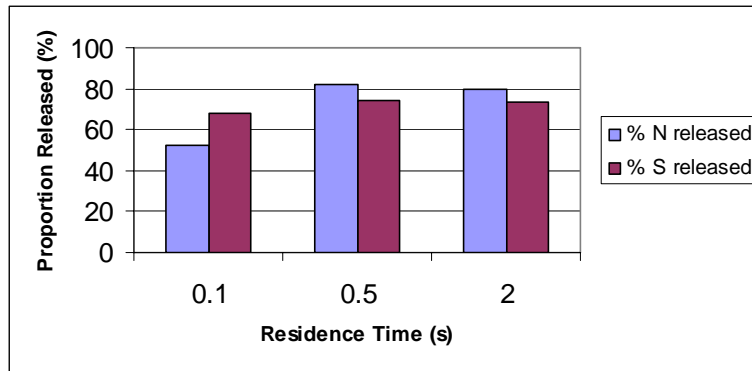


Figure 3.3 Effect of residence time on the fraction of S and N released from the coal

Figure 3.3 indicates that most of the nitrogen and sulphur in the coal was released very rapidly. After 0.1 seconds, more than 50 percent of the total nitrogen and about 70 percent of the sulphur present in the feed coal was released. Increased residence times, however, resulted in only slightly increased release of N and S.

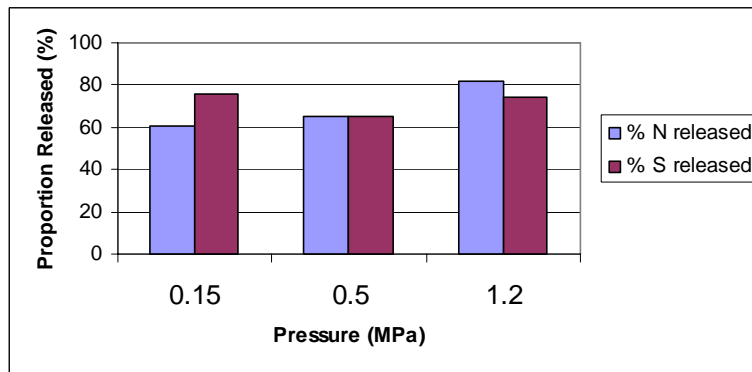


Figure 3.4 Effect of pressure on the fraction of S and N released from the coal

The effect of pressure on the release of nitrogen and sulphur from the coal was much less pronounced as shown in Figure 3.4. Both nitrogen and sulphur release under these conditions were essentially independent of pressure.

In Figure 3.5 the experimental results at all conditions of residence time and pressure have been combined to produce a plot of conversion (i.e. the amount of carbon released) versus the nitrogen and sulphur release. For nitrogen there is a direct linear relationship between conversion and the fraction of the total nitrogen released. In the case of the sulphur there is also a linear relationship, however, the slope of the line is significantly less than the nitrogen curve suggesting that sulphur is more readily evolved at lower conversions than nitrogen. This may be a consequence of sulphur, unlike nitrogen, being distributed between both organic and inorganic (pyrite) phases in the original coal. It may be, for example, that the rate of release of the pyritic sulphur is greater than the organic component so that a large proportion of the sulphur is released in the early stages of gasification.

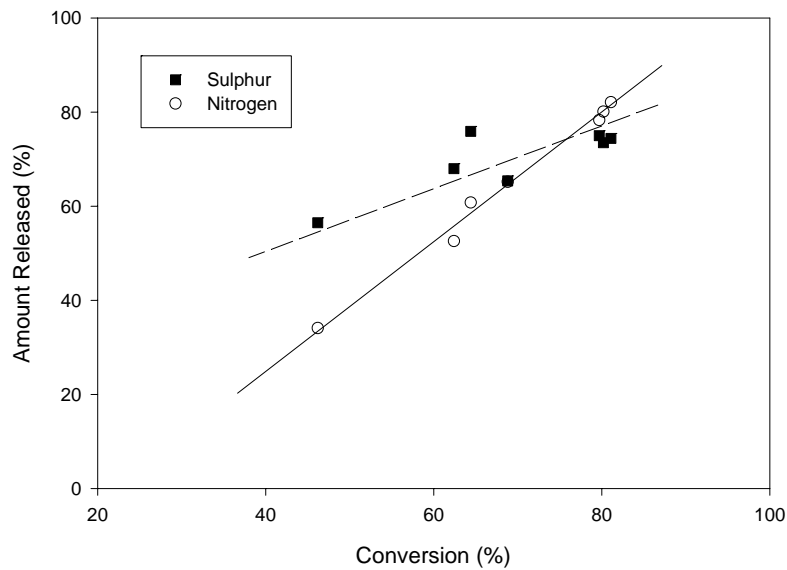


Figure 3.5 The amount of S and N released from the coal as a function of conversion

The results of the trace element analyses are shown in Table 3.2. This table also includes the degree of vaporisation (i.e. the relative amount of material in the gas phase to that in the feed) for sodium and potassium. It was not possible to determine the degree of vaporisation for mercury and cadmium because the concentrations of these elements in the feed coal were below the detection limits of the analytical technique.

Table 3.2 Concentration of trace elements in reactor off-gas

Pressure (MPa)	Residence Time (s)	Na (mg/Nm ³)	Na Deg of Vap (%)	K (mg/Nm ³)	K Deg of Vap (%)	Hg (µg/Nm ³)	Cd (µg/Nm ³)
0.15	0.1	0.13	11	0.11	11	0.076	0.50
0.15	0.5	0.15	13	0.17	17	0.073	0.38
0.15	1.71	0.20	5	0.20	5	0.10	0.60
0.5	0.5	0.10	9	0.12	13	0.15	0.22
1.2	0.1	0.12	21	0.12	25	0.30	0.30
1.2	0.5	0.08	15	0.08	17	0.08	0.32
1.2	2	0.13	11	0.16	17	0.10	0.65

In general, these results show that only a small proportion of the inorganic species sodium and potassium were released under these conditions. It would be beneficial from an emissions point of view if this was also the case for the toxic elements but at this stage this is not known and would be a useful area for further research.

4 Emissions from Coal and Char Gasification

The PhD student, Dongchan Park, was appointed in February 2000. He was enrolled at the University of Newcastle, although he was based mainly at the CSIRO Division of Energy Technology's North Ryde laboratories. The initial scope of the work was to comprise mainly experimental measurements on the PEFR at Pinjarra Hills, however, commissioning problems experienced with this facility delayed the project to such an extent that an alternative work program was developed. A few runs were made on the PEFR, but the bulk of the experimental

program involved measuring emissions from coal chars under gasification conditions using a bench-scale fixed bed reactor at the North Ryde laboratories.

Mr Park's thesis, which contains the details of the experimental program and the results obtained, was submitted to the University of Newcastle in February 2004, and he graduated in September 2004. The main findings of his research are summarised in the following sections.

4.1 PEFR Experiments

The reactor system operated by VTT, although similar in design to the Pinjarra Hills system, was originally designed to operate under isothermal combustion conditions. Consequently, the results obtained for the high volatile Hunter Valley bituminous coal were not strictly under the gasification conditions envisaged for a pressurised entrained flow system.

Despite some problems associated with commissioning the Pinjarra Hills facility, several runs were made at temperatures significantly higher than was possible in the Finnish system. The results of the experiments are described below.

4.1.1 Experimental

Gas Analysis System

A schematic layout of the gas analysis system used for both the PEFR and bench scale fixed-bed reactor experiments is shown in Figure 4.1. Off gas from the reactor was withdrawn via a heated stainless steel line and split into two streams. One stream was directed into a heated Fourier transform infrared (FTIR) cell. The other was directed into a manifold system which supplied several online analysers (NO_x , CO_2 and CO) and a micro GC.

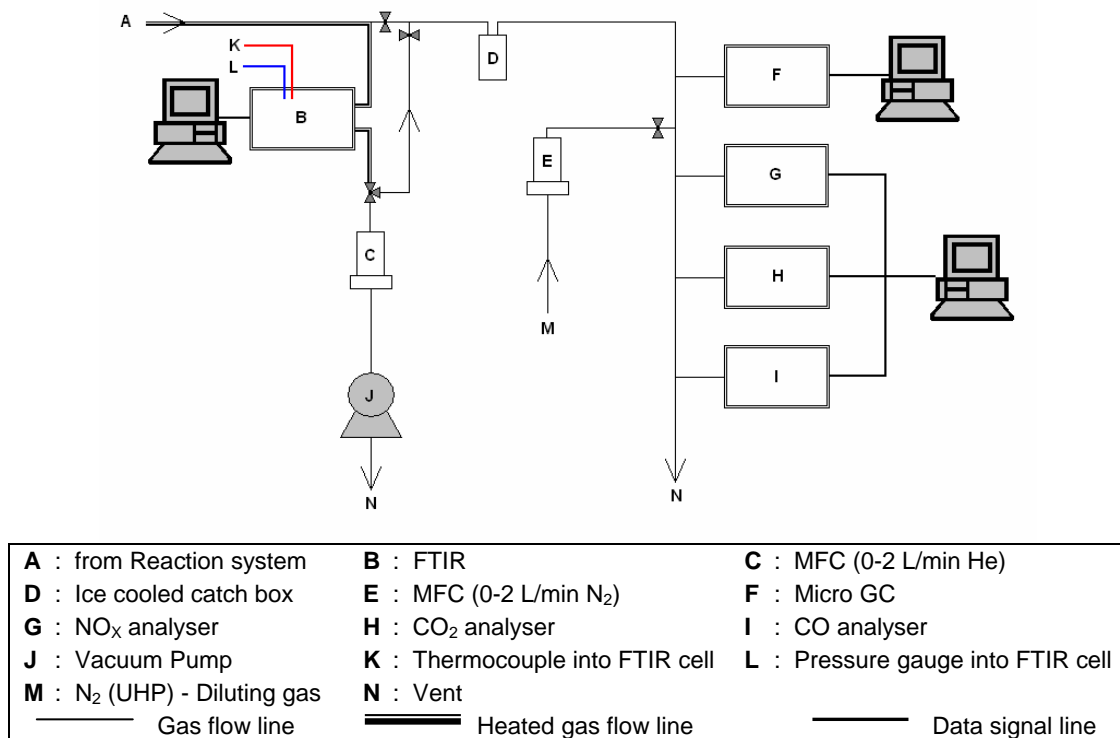


Figure 4.1 Schematic layout of the gas analysis system used for the experimental program of the project

Where necessary, the feed to the online analysers was diluted with high purity nitrogen to keep the target species within the dynamic range of the instruments. Data from the various instruments were continuously logged on a data acquisition system.

Quantitative FTIR analyses usually require the use of standards, however, due to the difficulty in obtaining standard gas mixtures for some of the compounds of interest and the number of compounds being targeted, the use of standards was considered to be impractical for this project. Instead, an alternative approach using a computational calibration method was adopted for this project. The system, known as MALT (Multiple Atmospheric Layer Transmission) was developed by Griffith, 1996, for the analysis of trace species in the atmosphere. In this system, synthetic calibration spectra are constructed from a database of spectroscopic parameters for each compound which are then compared to the analyte to provide a quantitative measurement.

During the initial stages of the project this technique was extensively validated by comparing the results obtained through MALT to those of various standard gas mixtures. In all cases the agreement was excellent thus confirming the robustness of the method. Use of this method greatly facilitated the processing of the large volumes of data generated during the course of the project.

Gasification Runs

High temperature and pressure coal gasification experiments were performed in the Pinjarra Hills PEFR with a Queensland high volatile thermal coal. Dry coal was pneumatically fed into the top of the reactor feeder at a rate of 1.6 kg hr^{-1} with a nitrogen carrier gas. In all experiments, the gasifying medium was five percent oxygen in nitrogen at a pressure of 2 MPa. The temperature of the system was either 1100 or 1400 °C. The position of the system's sampling probe was varied from 0 to 1805 mm, providing residence times within the reactor of about 1 to 5 seconds. A schematic diagram of the PEFR is shown in Figure 4.2.

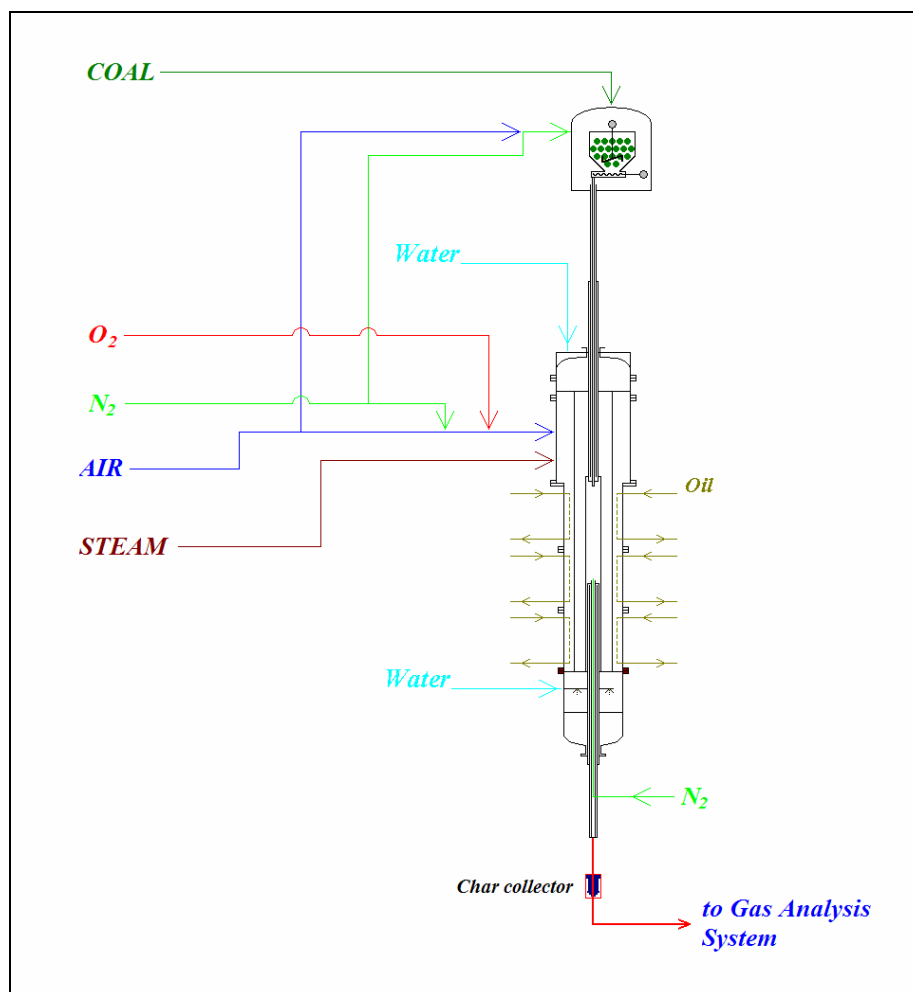


Figure 4.2 Schematic layout of the Pinjarra Hills PEFR system

Gas analyses were performed with the facility's continuous gas analysers (O₂, CO₂, CO) and the GC and FTIR system described in the previous section (N and S species).

4.1.2 Results

Nitrogen conversion

The species HCN and NH₃ were the only observed N-containing products from coal gasification in the PEFR. It is likely that N₂ was also present, however, since the system was operated with a large excess of nitrogen in the gas stream it was not possible to identify any N₂ originating from the coal. Other N-containing species such as NO, N₂O and HNCO were not detected under any of the experimental conditions examined in this study.

At 1100 °C, more NH₃ was produced than HCN throughout the reactor but at 1400 °C, HCN dominated the gas-phase N products. This is illustrated in Figures 4.3 and 4.4. This finding is consistent with the results of other studies (Duffy and Nelson, 1997) which also showed increasing HCN with increasing temperature.

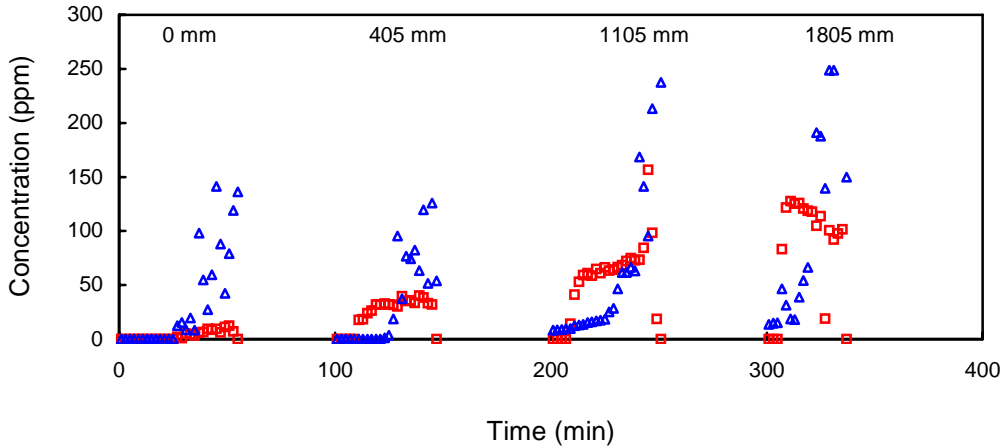


Figure 4.3 Concentration profiles of HCN (□) and NH₃ (△) measured during coal gasification at 2 MPa and 1100 °C at various locations within the PEFR.

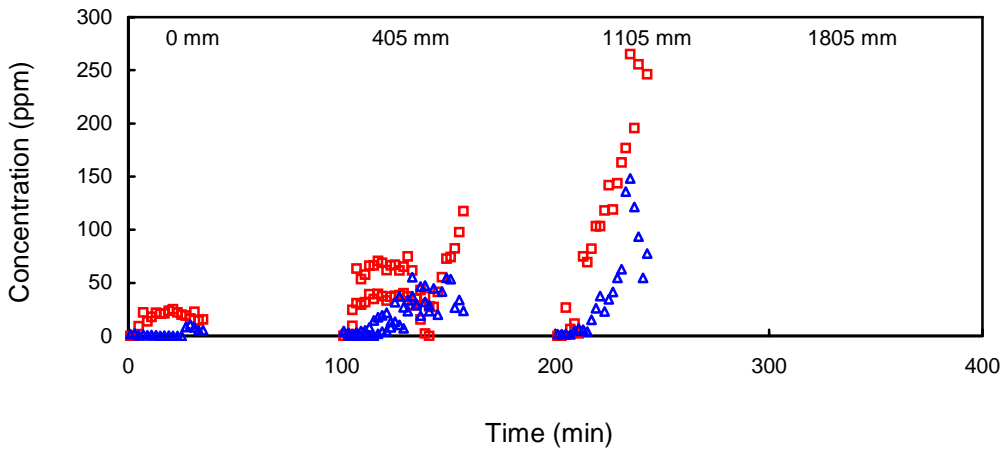


Figure 4.4 Concentration profiles of HCN (□) and NH₃ (△) measured during coal gasification at 2 MPa and 1400 °C at various locations within the PEFR.

It is apparent from Figures 4.3 and 4.4 that there was considerable scatter in the NH₃ data but significantly less for the HCN. The reason for higher level of scatter in the NH₃ data is probably a result of NH₃ absorption/adsorption onto the wall surface of the reactor and sampling line and hence it took some time for the true NH₃ concentration to be seen at the analyser. The physical size of the solid sample collection system of the PEFR meant that it was not usually practical to run individual experiments for more than about 50 minutes (and therefore allow steady state NH₃ concentrations to be achieved). Note that the times shown in Figures 4.3 and 4.4 are the total running time of the PEFR. The sample pot was emptied between each run.

Figures 4.3 and 4.4 also show that both HCN and NH₃ were present in higher concentrations during the early stages of gasification (i.e. in the upper part of the reactor which corresponds to the higher probe settings) than in the later stages (base of the reactor at 0 mm). This was the case for both temperatures examined.

The reason for the disappearance of HCN and NH₃ as gasification progresses is possibly due to secondary reactions of the gas phase species with solid char as the material passes through the reaction zone. These reactions transform the HCN and NH₃ into other N-containing

compounds, probably mainly N_2 , which as noted earlier could not be detected under the conditions of these experiments.

The extent of the reduction of HCN and NH_3 as a result of secondary reactions was greater at the higher temperature. More than 90 percent of the total nitrogen (i.e. HCN + NH_3) measured during the early stages of gasification had disappeared by the time the reactants had passed through the reactor at 1400 °C, but at 1100 °C, only half of the total nitrogen had been transformed over the same period indicating the significance of temperature on the secondary conversion of nitrogen intermediates in the gasification region.

Increasing temperature and decreasing residence time influenced the extent of secondary reactions of product gas on the surface of remaining solid char, resulting in formation of less NH_3 . At 1100 °C, the NH_3 /HCN ratio appeared to be governed by both the gasification temperature and residence time in the reaction zone. At the higher temperature, however, the rate of reaction appeared to be sufficiently high so that the influence of residence time became insignificant. The PEFRR runs showed that, under the conditions of these experiments, about 50 percent of the original coal-bound N was released as HCN and NH_3 during the gasification process.

The results obtained on the Pinjarra Hills reactor appear quite different to those obtained using the VTT system. In the Finnish reactor, significant amounts of NO were found which was not detected in the product gas of the Pinjarra Hills reactor under any of the conditions examined. It is interesting, however, that the amount of NO detected in the VTT reactor decreased with increasing contact time suggesting that NO is involved in secondary reactions yielding increased levels of NH_3 and HCN (and possibly other N-containing compounds). It is possible that had the Finnish experiments been performed at the higher temperatures of the Pinjarra Hills facility, the rate of disappearance of NO would have resulted in much lower NO levels to yield a product gas with a composition more consistent with that observed in the Pinjarra Hills results.

Sulphur conversion

The compounds H_2S and, to a lesser extent, COS were the only S-containing products observed in the gas phase during coal gasification in the PEFRR. The gasification temperature was found to affect both the total conversion of coal-S and its distribution in the gas phase products. Conversion of coal-S to gas phase products (H_2S and COS) increased significantly with increasing temperature. At 1100 °C, about 30 – 50 percent of the coal-S was converted to H_2S and COS, however, at 1400 °C, most of the sulphur in the coal had been converted to gas phase products.

Under all of the experimental conditions examined, H_2S was the dominant product, however, the proportion of H_2S in the gas phase increased with increasing temperature. At 1100 °C, H_2S represented about 85 percent of the total sulphur products but at 1400 °C, the proportion of H_2S had increased to around 95 percent.

The residence time of the product gas in the gasification region did not apparently affect the sulphur conversion or its distribution in the gas phase products under these conditions. This suggests that, unlike the nitrogen species produced, the S-containing products in the gas phase (H_2S and COS) do not undergo significant secondary reactions in the reactor.

4.2 Fixed Bed Experiments

The fixed bed experiments represented the bulk of the experimental program of the project. These were performed at the CSIRO Energy Technology's laboratories at North Ryde.

4.2.1 Experimental

The system used in these experiments was based around a small fixed-bed reactor capable of operating at temperatures up to 1000 °C and pressures of up to 1 MPa. A gas control system capable of providing a range of gasification media including O₂, CO₂ and steam, was incorporated while the effluent gases from the reactor were analysed using the setup developed for the PEFBR runs described in the preceding section. A schematic diagram of the fixed bed reactor and the associated gas control system is shown in Figure 4.5.

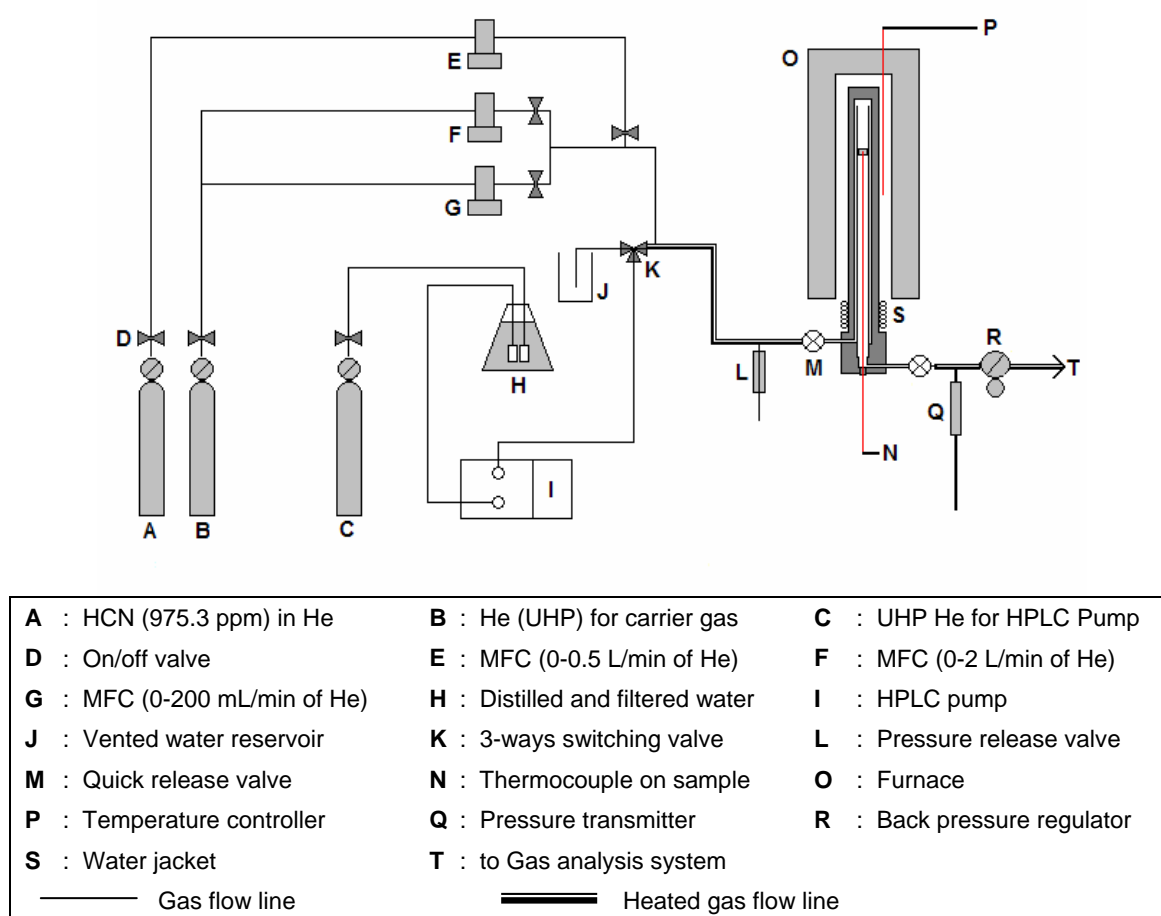


Figure 4.5 Schematic layout of the pressurised fixed-bed reactor and gas control system

Experiments were performed by weighing a small amount of char (~100 mg) into the quartz reaction tube then heating to 200 °C for half an hour to remove any impurities prior to starting each run. Small amounts of nitrogen-containing and other species were also released during this process. After conditioning the sample, the temperature of the reactor was increased to the required temperature (600 °C for O₂ experiments; 1000 °C for CO₂ and steam) in an atmosphere of flowing helium. Helium was chosen as the carrier for the gasifying medium to

enable any N₂ produced from the char to be quantified. The pressure of the system was adjusted between 0.1 to 1 MPa.

Once the system had stabilised at the set temperature, the required flow of O₂ or CO₂ was started and the composition of the product gases determined as a function of the time after the introduction of the reactive gases. In the cases where steam was the gasifying medium, distilled water was pumped with an HPLC pump into the system and preheated to about 350 °C to provide steam over the pressure and temperature range required by the experimental conditions.

A char prepared from a Queensland bituminous coal was used for the fixed bed experiments. For the steam gasification runs, a second char, made from a Queensland sub-bituminous coal, was also examined.

4.2.2 Results

O₂ Gasification

With two percent oxygen as the reactive gas, the dominant N species observed were N₂ and NO (Figure 4.6 a). At 0.1 MPa, approximately 60 percent of the total nitrogen released was in the form of N₂ while at 1 MPa, the proportion of N₂ increased slightly to about 70 percent of the total gas phase nitrogen. Small amounts of HCN (up to about 8 percent of the total gas phase nitrogen) were also found during O₂ gasification along with trace amounts of N₂O.

The results showed that even at very short contact times, NO was the main gas phase species produced. This suggests that this is the primary product formed from char-N release and that it is not produced as a result of secondary reactions. It seems that the other dominant species produced during O₂ gasification, N₂ is produced via secondary reaction, probably involving NO and surface N-containing species.

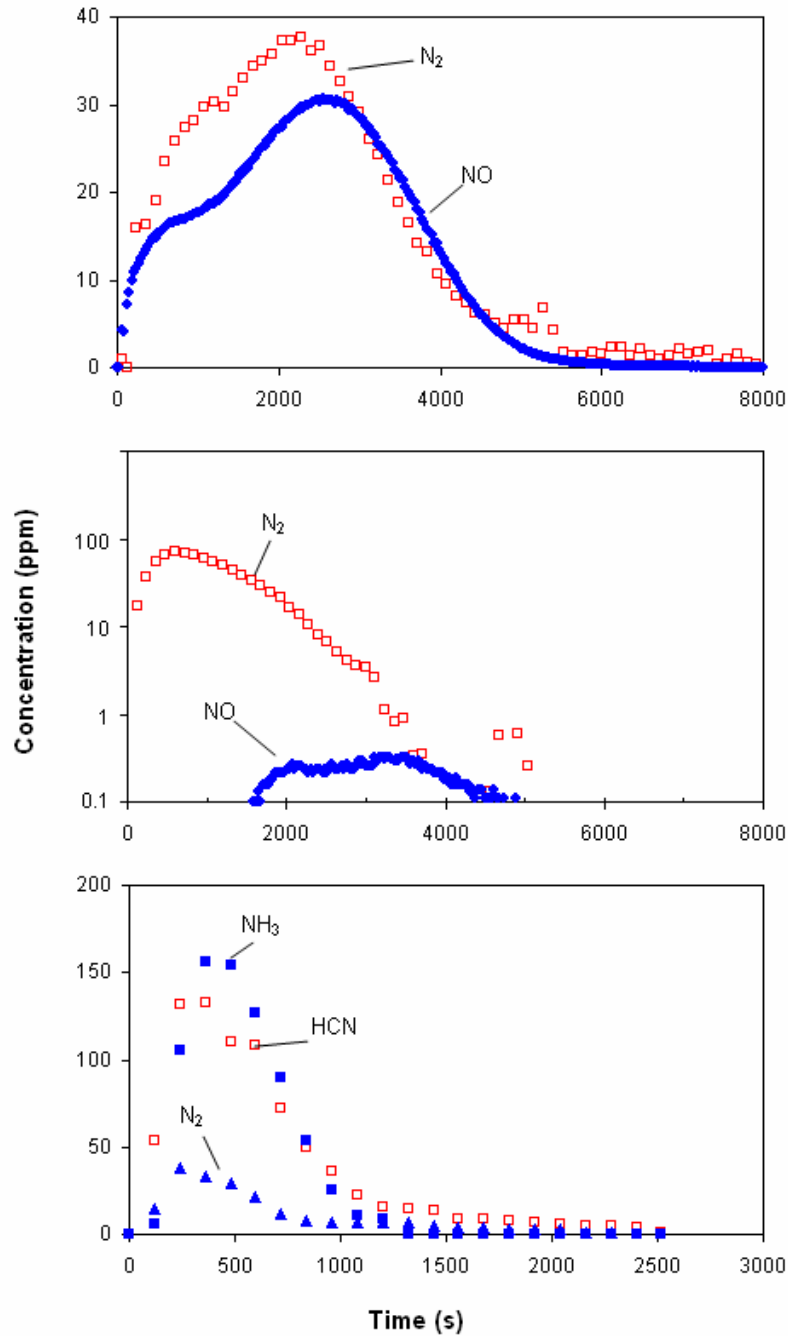


Figure 4.6 Concentration of the major N-containing products of the reactions of coal char with reactive gases (a) 2 % O₂ at 600 °C; (b) 100 % CO₂ at 1000 °C; (c) 38 % H₂O at 1000 °C. The pressure of each experiment was 0.1 MPa.

With regard to sulphur, the only species detected was SO₂. Analysis of the residual char showed that all of the sulphur had been released during the gasification process. Pressure was found to have a negligible effect on the conversion of sulphur to the gas phase, however, increased pressure appeared to delay the release of the sulphur relative to the conversion of carbon. At 0.1 MPa, most of the sulphur was released during the initial stage of gasification but at 1 MPa, most of the char-S was retained in the coal until the carbon conversion had reached about 40 percent.

CO₂ Gasification

Figure 4.6 (b) shows the profiles of the release of the major N-containing products during reaction with CO₂ at 1000 °C and 0.1 MPa. Like the O₂ results discussed above, the main species were N₂ and NO, however, the minor products observed with O₂ (i.e. HCN and N₂O) were not found with CO₂ as the reactant gas. In the case of CO₂, the vast bulk of the N-containing products were formed as N₂ with only about 1 percent of the total being present as NO (note the logarithmic scale in Figure 4.6 b). The results shown in Figure 4.6 (b) were from experiments performed at 1 atmosphere, however, increasing the pressure to 1 MPa had virtually no effect on the product distribution.

The effect of concentration was examined by varying the CO₂ concentration between 10 and 100 percent of the reactant gas. All of these experiments were performed at a pressure of 1 MPa. In all cases, the distribution of N-containing products was similar with N₂ being by far the most dominant species. NO was the next most abundant compound but it represented less than 1 percent of the total N released.

Although N₂ was the main nitrogen product of CO₂ gasification under most conditions, there was some evidence indicating that at very short contact times, significant quantities (up to about 20 percent of the total nitrogen products) of NO are produced. This is apparently rapidly reduced to N₂ by the presence of char C, or by reactions with product CO.

During CO₂ gasification, SO₂ was the only S-containing product found in the gas phase, however, the fractional conversion of the char-S was much lower than observed in the O₂ experiments. This suggests that other sulphur compounds were present but analytical difficulties associated with the presence of large excesses of CO₂ in the product gas meant that it was not possible to analyse for these compounds. It is possible that at least some of the unaccounted for material may have been present as H₂S and/or COS.

H₂O Gasification

Experiments were performed at 1000 °C and 1 MPa with steam concentrations ranging from 5.5 to 46 percent H₂O. Figure 4.6 (c) shows the main N-containing products formed with 38 percent H₂O at 0.1 MPa. Under these conditions, the main products were NH₃ and HCN with a smaller amount of N₂. As well, trace amounts of NO were detected under some conditions.

Unlike the CO₂ runs, pressure was seen to have some effect on the distribution of products. At 0.1 MPa, the fractional conversion of char-N to NH₃ was 44 percent, but this increased to around 52 percent at 1.0 MPa. This was accompanied by a decrease in the proportion of N₂ from about 17 percent at 0.1 MPa to 9 percent at 1 MPa. For HCN, the fractional conversion remained fairly constant at about 39 percent over this range of pressures.

Varying the concentration of H₂O in the reactant gas was found to affect the distribution of products in the off-gas. With an H₂O concentration of 5.5 percent, the fractional conversion to NH₃ was about 46 percent but this increased to about 57 percent with 46 percent H₂O in the reactant gas. There was a corresponding decrease in the N₂ conversion (23 % at 5.5 % H₂O to 17 % at 46 % H₂O). Indications were that there was also a reduction in the proportion of HCN formed with increasing H₂O concentrations, however, the measurements were close to the detection limits of the analytical system and it is therefore not clear if this was a real trend.

5 Conclusions

Sulphur and nitrogen release from Australian bituminous coal and char samples were studied under gasification conditions. Experiments were performed in both a pilot-scale pressurised entrained flow reactor using whole coal and a bench-scale fixed bed reactor with prepared coal char samples. The program encompassed a very wide range of conditions of temperature, pressure and gasification medium. The key findings of the program are summarised below:

- During O_2 gasification of a Queensland bituminous coal using the PEFR, HCN and NH_3 were the only nitrogen products observed (although N_2 was also likely to have been produced under some conditions). The distribution of products was dependent upon the temperature of the reaction. Hydrogen sulphide was the main sulphur species with lesser amounts of COS also produced. The PEFR runs showed that about 50 percent of coal N was released under these conditions. Approximately 50 percent of the S in the coal was released during the PEFR reaction at 1100 °C whereas at 1400 °C, essentially all of the S was released.
- The experimental program identified the main gaseous sulphur and nitrogen products from char gasification in a fixed bed reactor. In relation to nitrogen, the species produced were N_2 , NH_3 , NO and HCN depending on the reactant gas. With O_2 gasification, N_2 and NO were produced whereas in CO_2 , N_2 was the dominant product with very high selectivity over a wide range of pressures and CO_2 concentrations. Steam gasification produced mainly HCN, NH_3 and N_2 .
- Pressure was found to have little effect on the nitrogen compounds produced from char in either O_2 or CO_2 gasification, however, with H_2O as the reactive medium, increasing pressure resulted in a greater proportion of NH_3 at the expense of N_2 .
- In the fixed bed reactor, SO_2 was the only sulphur compound identified. With O_2 , the evidence suggested that this was the only compound produced, however, in CO_2 , mass balance deficiencies indicated that other compounds, possibly H_2S and or COS may also have been produced. Analytical difficulties prevented this from being confirmed.
- The large matrix of experiments performed enabled mechanistic pathways for the formation of the various nitrogen and sulphur compounds in the effluent gas to be postulated. The transformation routes proposed for nitrogen and sulphur are summarised in Figure 5.1 and 5.2 respectively. An important finding with respect to nitrogen emissions is that with appropriate control of the gasification conditions, most of the coal nitrogen which is initially released as NH_3 and HCN can be ultimately converted to N_2 within the reactor itself. This will benefit designers of gasification technology since it greatly simplifies the emission control system required to meet environment standards.

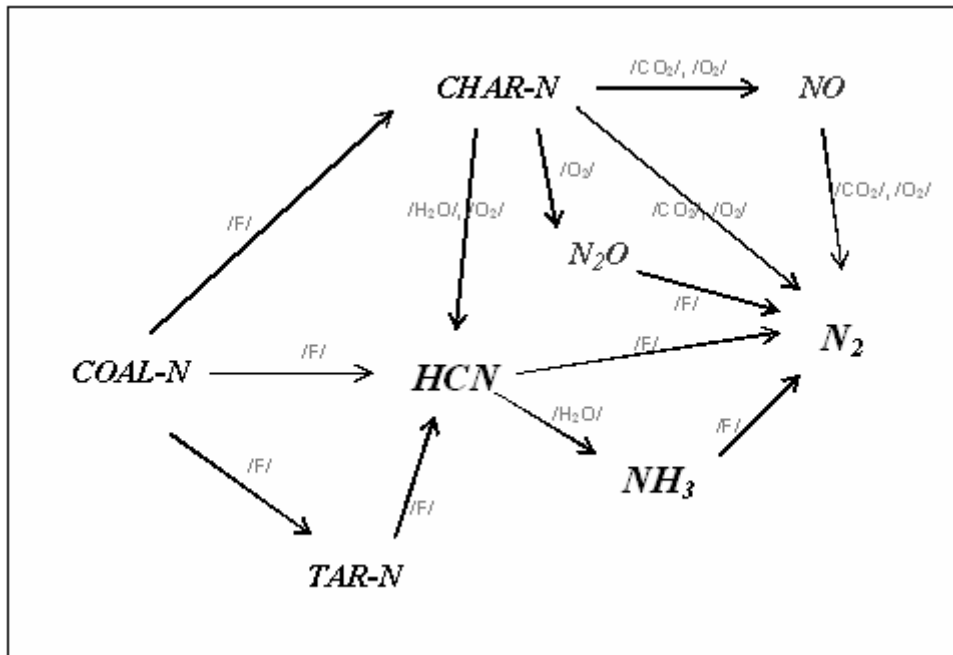


Figure 5.1 Possible nitrogen transformation routes during gasification. Note that /F/ indicates that the pathway is dependent on experimental conditions apart from the gasification atmosphere.

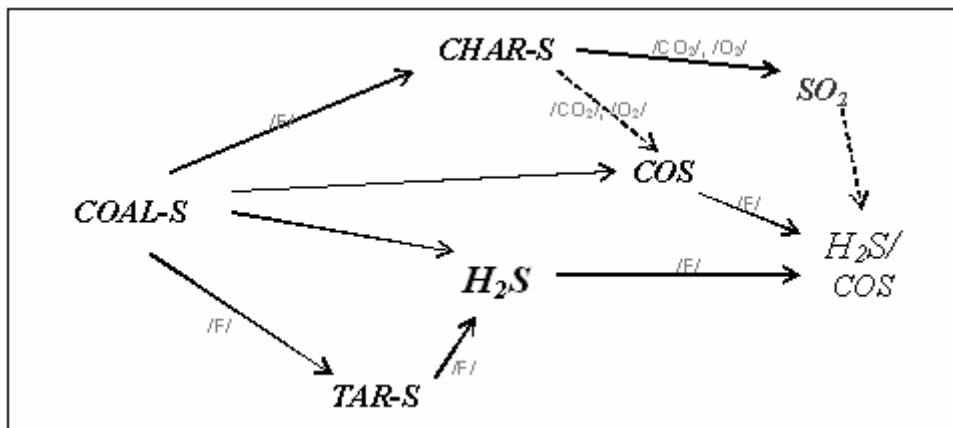


Figure 5.2 Possible sulphur transformation routes during gasification. Note that /F/ indicates that the pathway is dependent on experimental conditions apart from the gasification atmosphere.

6 Suggested Future Research

- The experiments performed on the VTT reactor confirmed that measurable quantities of the toxic elements cadmium and mercury were released. It is likely that other trace elements are also present in the product gases from coal gasification. At this stage, there are very few data relating to the fate of these species from gasification and is therefore an important area for further research.
- Due to early commissioning problems with the Pinjarra Hills reactor, the original work program designed for this facility was significantly curtailed. Hence there is still considerable scope to measure emissions from gasification in this system. In particular, further work is needed to investigate emissions at high temperatures (i.e. > 1400 °C). The effect of coal type on emissions needs to be examined.

- The experimental data gathered during this project has greatly increased our knowledge of the nature of the gaseous nitrogen and sulphur containing emissions from coal gasification. These data could now be used to begin development of appropriate emissions models.
- The release of sulphur appears to be a simpler process than that of nitrogen, however, difficulties in measuring some of the sulphur compounds, particularly in the presence of CO₂ and H₂O, meant that the mechanisms for sulphur transformations have not been fully elucidated. Further work on improved analytical methods is warranted to investigate this area more fully.

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