

# Coal as a Reburn Fuel for NO<sub>x</sub> Reduction

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The candidate confirms that the work submitted is his own and that appropriate credit has been given where reference has been made to the work of others.

# ABSTRACT

Experiments were conducted on a 200 kW downward-fired, pilot-scale furnace where residence times and temperatures are comparable to practical units. Nine bituminous coals were used as reburning fuels to investigate various aspects of the reburning process, including key process parameters (operating stoichiometries, reburn fuel fraction, primary zone NO concentration, reburn zone residence time, temperature and mixing effects) and to assess the effectiveness of pulverised coal, including microfine, as reburn fuel.

The results obtained showed that the extent of NO reduction was dependent on optimising the different process variables, and the maximum reduction achieved by doing so was 75%. The most influential variables were those coupled to the reburn zone, with the reburn zone stoichiometry being the dominant impact variable. For the range of reburn zone stoichiometries studied (0.85 - 1.03) no optimum value was obtained, however, higher reductions were generally achieved under fuel rich operations. The direct effect of varying primary zone stoichiometry on reburn performance was of minor significance, however, secondary effects such as variation in the reburn zone stoichiometry can be significant. The NO reduction process was mostly completed in the reburn zone where the optimum reburn zone residence time was around 450 ms, and only marginal gains were achieved beyond this point. The NO reduction efficiency increased with increasing primary NO concentration up to around 600 - 700 ppmv, after which the trend levels off, however, at low primary NO (<200 ppmv) it was difficult to obtain a positive NO reduction efficiency. The

amount of reburn fuel or  $R_{ff}$  required to generate the hydrocarbon radicals necessary for effective NO control was not conclusively quantified, however, from the results obtained the optimum amount of reburn fuel was in the region of 20-25% of the primary fuel input. Lower inlet gas temperature in the reburn zone generally enhanced NO reduction, however, this effect diminished under sufficiently fuel rich conditions. Furthermore, the effect of temperature in the reburn zone was dependent on residence time, with high temperature (1773 K) and long residence time (>500 ms) achieving higher reduction. Improved mixing conditions in the reburn zone enhanced reburning effectiveness, however, in fuel lean operations poorer mixing was found to improve NO reduction through local fuel rich pockets. Finer particle size distribution of the reburning coal gave rise to better NO reduction and higher burnout efficiency. The carbon burnout efficiency was around 85% - 95%, and higher gas temperature improved carbon burnout efficiency, however, under fuel rich conditions ( $SR_2=0.85$ ) burnout efficiency was hampered by the low oxygen concentration.

Finally, the results of the multi-variate analysis undertaken to determine the importance of some of the above operational parameters on NO reduction as well as the influence of reburn coal properties such as fuel nitrogen content and volatile matter, confirmed the importance of  $SR_2$  as the dominant variable in coal reburning. The proximate volatile matter content was the most influential characteristic of the reburn fuel affecting reburn performance, while fuel nitrogen content was not as influential a parameter for the range of operating conditions and coals studied.

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# CHAPTER ONE

## Introduction

### 1.1 Historical Background

Coal is the most abundant fuel in the world, accounting for about 70% of the worlds known fossil energy reserves (Siegel, 1992). Historically, coal has played a significant role in the energy picture for the United Kingdom as well as the world. During the early 1900s coal provided the major portion of the energy requirements for the industrial sector and was heavily utilised even for domestic heating applications. It remains the preferred method of combustion in utility boilers. However, in the last two decades, energy from coal has lost ground to oil, gas and nuclear energy as a result of strict regulations on stack flue gas emissions and increasing demand to burn coal in an environmentally acceptable manner. Its use is now limited primarily to electric power generation and large industrial energy sectors.

The oil crises in the early 1970s focused world attention on the fact that oil reserves were limited and depleting rapidly. Gas reserves, however, continue to increase due to abundant supplies. Also, the once promising nuclear industry came under pressure because of growing concerns over safety, long term storage of radioactive wastes and the high decommissioning costs. At present, growth in the nuclear industry has essentially been halted. These developments, coupled with the fact that coal is the



world's most abundant energy source, have led to a revived interest in expanding the use of coal.

Despite the fact that coal is relatively cheap and provides the certainty of long term supply, it is comparatively less convenient to use than oil and gas and contains varying amounts of sulphur and nitrogen. The nitrogen content of coal can be as high as 2% and the sulphur as high as 7%. When coal is burned, these elements are released into the atmosphere in the form of nitrogen oxides (NO<sub>x</sub>) and sulphur oxides (SO<sub>x</sub>) in combustion flue gases. Mineral matter is also trapped within the coal matrix and comprises of the combustion residue known as ash, which along with trace metal compounds contribute to particulate emissions.

Carbon dioxide (CO<sub>2</sub>) which is a major contributor to the 'greenhouse' effect is also emitted during coal combustion. The amount of CO<sub>2</sub> produced from coal-fired plants is generally more than either oil or gas plants (Table 1.1) (Green Energy Matters, 1994). This is due to the fact that the C/H ratio in coal is greater than either oil or gas.

**Table 1.1** Comparative Emissions from Different Fuels  
(taking the emissions per kWh as 100 for basic coal-fired stations)

	SO <sub>2</sub>	NO <sub>x</sub>	CO <sub>2</sub>
<b>Coal</b>	100	100	100
<b>Heavy fuel oil</b>	100	75	85
<b>Orimulsion</b>	138	<75	85
<b>CCGT<sup>1</sup></b>	0	21	50

<sup>1</sup>CCGT = combined-cycle gas turbine operating on natural gas.

These pollutants have an adverse effect on the environment, and in the last two decades greater emphasis have been placed on reducing atmospheric pollutants associated with fossil fuel combustion. Nitrogen oxides (NO<sub>x</sub>) for example have been implicated in a variety of environmental effects both from their direct emission to the atmosphere and their role in the formation of secondary compounds, such as ozone and nitric acid.

Most of the NO<sub>x</sub> produced during combustion by stationary sources exit the stack in the form of nitric oxide (NO), with small amounts of nitrogen dioxide (NO<sub>2</sub>). However, in the atmosphere, the NO is readily oxidised to NO<sub>2</sub>, a brown gas which may initiate the formation of ozone or undergo oxidation to form nitric acid which is a constituent of acid rain. The increase in ozone concentration can be translated globally as a contribution to the greenhouse effect. It is estimated that NO<sub>2</sub> will have a global warming potential 40 times greater than that of CO<sub>2</sub> (by weight) over a 100-year time horizon. While N<sub>2</sub>O which is also emitted during coal combustion has a global warming potential 290 times greater than that of CO<sub>2</sub> over the same period (Sloss *et al.* 1992).

Regional effects of NO<sub>x</sub> include contribution to 'photochemical smog' which leads to extreme loss in visibility and damage to both human health and vegetation, and the formation of nitric acid which is known to cause damage to both wildlife and buildings e.g. historical monuments which are costing the government millions of pounds in restoration work. It is also worth noting that both NO and NO<sub>2</sub> are listed as 'known substances' from the physiological-metabolic point of view. The EC

recommends that 100 ppbv should not be exceeded for more than one hour a month (Sloss *et al.*, 1992).

The impact these pollutants have on the environment present a serious limitation to the increased utilisation of coal as an economical and abundant energy source. Therefore, there is an urgent need for a better understanding of the processes that control the formation of combustion generated pollutants.

Historically, air pollution from coal is not a new issue. The burning of "Sea Coal" was protested in England even in the 13th century, and at one time under Edward II, the use of coal in London carried the death penalty (Sawyer, 1981). However, concerted efforts to reduce emissions are rather recent, and the major advances in emission control technologies for coal combustion have only come in the last 20 years.

The first international agreement to control NO<sub>x</sub> emissions from stationary combustion sources was made in June 1988 by the European Union (EU). The agreement was set out in a directive known as the Large Combustion Plant Directive (LCPD). The LCPD sets emission limits for SO<sub>2</sub>, NO<sub>x</sub> and particulate for new plant (i.e. plant commissioned after 1st July 1987), and progressive reductions in SO<sub>2</sub> and NO<sub>x</sub> emissions for existing plant (i.e. plant commissioned before 1st July 1987) compared with 1980 emission levels. The directive covers combustion plants having a thermal input of over 50 MWt and aims to achieve a community-wide NO<sub>x</sub> reduction of 30% by 1998, out of which the UK is required to reduce its emissions by 30% as shown in Table 1.2 (Hjalmarsson and Vernon, 1989; Council Directive 88/609/EEC).

The second agreement to limit NO<sub>x</sub> emissions came when a legally binding protocol was signed by twenty five countries on November 1st 1988 under the umbrella of the United Nations Economic Commission for Europe (UNECE) (Argen, 1989). The agreement constituted the second of two protocols supplementing the UN Convention on Long Range Transboundary Air Pollution. The first protocol to this convention was signed in 1985 which committed its signatories to reduce their SO<sub>2</sub> emissions by 30% (Hjalmarsson and Vernon, 1989).

Specifically, the NO<sub>x</sub> protocol aims at freezing emissions at 1987 levels by 1994. In other words, it does not prescribe any actual reductions. However, it does lay down measures to be taken to bring about reductions from both stationary and mobile sources.

Having signed both the LCPD and the NO<sub>x</sub> protocol, the UK was then required to implement both agreements into its national plan. As a result of this the Environmental Protection Act 1990 (EPA) was introduced and has been in force since 1991 (Table 1.3). However, nitrogen oxide emission regulations will undoubtedly become more stringent over the next century and will thus require a well planned environmental legislation coupled with advances in technology to meet future targets. The LCPD is currently under review and in the draft revision the emission limits are tightened and are closely in line with what is considered achievable by the Environment Agency (Slater, 1997).

## 1.2 Control of Emissions

Several control techniques have been developed for SO<sub>x</sub> control. These include : prewashing of the coal to reduce its sulphur content (pyritic and organic) prior to combustion, wet scrubbers to wash the sulphur oxides from the exhaust gases after combustion (Flue Gas Desulphurisation), and lime stone capture of sulphur during combustion. These techniques, although expensive, have been shown to be effective measures and are now commonly used in coal burning operations.

**Table 1.2** NO<sub>x</sub> emissions reduction targets for existing plants over 50 MWt in the EU (Sloss *et al.*, 1992)

Country	1980 baseline, kt NO <sub>x</sub>	1993 targets, % reductions	1998 targets, % reductions
Belgium	110	- 20	- 40
Denmark	124	- 3	- 35
FRG	870	- 20	- 40
Greece	36	+ 94	+ 94
Spain	366	+ 1	- 24
France	400	- 20	- 40
Ireland	28	+ 79	+ 79
Italy	580	- 2	- 26
Luxembourg	3	- 20	- 40
The Netherlands	122	- 20	- 40
Portugal	23	+ 157	+ 178
United Kingdom	1016	- 15	- 30
Total	3678	- 10	- 30



**Table 1.3** NO<sub>x</sub> emission limits for new combustion plants (>50 MWt) in the UK  
(Environmental Protection Act, 1990)

Fuel	Calendar monthly average should not exceed: mg/m <sup>3</sup>	Not more than 5% of all 48hr averages should exceed in a calendar year: mg/m <sup>3</sup>
Solid Fuel	650	715
Liquid Fuel	450	495
Gas Fuel	350	385

Reference conditions: waste gas volumes referred to 273K and 1 atmos; 3% O<sub>2</sub> for liquids and gaseous fuels, 6% O<sub>2</sub> for solid fuels

Particulate emissions from coal combustion have also been successfully controlled if not completely eliminated by the use of large fabric filters and electrostatic precipitators. Both technologies have an efficiency greater than 99.5% and improvements in the design of electrostatic precipitators and the increased availability of new materials for fabric filters are helping extend their range of operating temperatures. efficiencies. Investigations are also underway to develop dual systems using both electrostatic precipitators and fabric filters simultaneously (Energy World, 1997). Carbon dioxide emissions, on the other hand, are directly linked to the efficiency of the plant and could be reduced by increasing the efficiency of the coal-fired plant i.e. a 10% increase in efficiency would reduce CO<sub>2</sub> by over 25% while a 20 % increase in efficiency would reduce CO<sub>2</sub> emissions by 40% (European Commission, 1995).

The control technologies used for both sulphur oxides and ash have resulted in decreasing SO<sub>x</sub> and particulate emissions, whereas NO<sub>x</sub> emissions have been



increasing due to a global increase in the use of coal (Energy World, 1997). Also, unlike SO<sub>x</sub> emissions which are directly linked to the sulphur content of the fuel rather than the design of the combustion system, NO<sub>x</sub> emissions depend not only on the nitrogenous content of the fuel but also on the manner in which the combustion air is mixed with the fuel and the temperature reached during combustion. Thus NO<sub>x</sub> emissions are largely determined by furnace design and/or burner design. And although fuel nitrogen conversion efficiency is lower than that of sulphur, the acceptable limits for NO<sub>x</sub> emissions are much lower than for SO<sub>x</sub>.

Some measure of success has been achieved by using combustion modification techniques, but their effectiveness varies. These will be discussed in more detail in Chapter Two. On the other hand, post combustion NO<sub>x</sub> control techniques such as selective catalytic reduction (SCR) is considered as an expensive control option. This is mainly due the high cost of catalyst (although prices are falling) and the necessary engineering requirements and safety aspects of storage and transport of large quantities of ammonia.

The pressing demand for more stringent regulations to control nitrogen oxides emissions from coal combustion calls for a better understanding of existing and emerging pollution control technologies. A promising technique for the control of NO<sub>x</sub> is referred to as 'reburning'. Reburning is an in-furnace NO<sub>x</sub> reduction technique whereby a source of hydrocarbon radicals is introduced into a secondary combustion stage to react with NO generated in the primary combustion stage. In a reburning configuration, three combustion zones are established by diverting portions of both fuel and air to locations downstream of the main combustion zone

with the ultimate aim of maximising the destruction of NO through manipulation of the combustion environment. The primary combustion zone accounting for 80-90% of the fuel consumption is normally operated fuel lean and its where the bulk of the NO is formed. In the secondary combustion zone, the remaining fuel is added but usually no additional air. Thus, the second stage stoichiometry is fuel rich providing a reducing environment which favours the destruction of NO to form N<sub>2</sub> and other nitrogenous intermediates such as HCN and NH<sub>3</sub>. In the third stage, the combustion process is completed by the addition of excess air.

### **1.3 Objectives of this Research and Structure of the Thesis**

The principal aims of this research are :

- To investigate various aspects of the reburning process, including key reburning parameters (operating stoichiometries (SR<sub>1</sub> and SR<sub>2</sub>), reburn fuel fraction (R<sub>ff</sub>), primary NO concentration, residence time and carrier gas oxygen concentration) and their interaction in order to provide a better understanding of the fundamentals of the reburning process using a pilot-scale furnace.
- To assessing the effectiveness of pulverised coal (including microfine) as a reburn fuel.
- To identify the significant operating parameters in reburning, to carry out detailed examination of the individual parameter in order to determine their individual contributions, and to establish optimum or near optimum conditions under which reburning would be most effective.

- To investigating the influence of the more important and rank-related coal properties, namely, volatile matter content (VM, dry ash free basis) and elemental carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S) on reburn performance and to evaluate the extent of association between NO reduction efficiency and each of the above reburn coal properties.
- To examine the effect of mixing in the reburn zone by using different reburning configurations and to establish optimum or near optimum conditions that can be applied to a practical combustor.
- To examine the effect of temperature in the reburn zone since from the review of the literature in Chapter Two the temperature effects are not fully established.
- To generate empirical correlation relating reburning effectiveness to operating parameters which could be used quantitatively to predict the effect of each variable on NO reduction efficiency as well as the reburning performance of any non-tested reburning coals under the same experimental conditions.

Experiments were conducted on a 200 kW downward-fired, pilot-scale furnace where the configuration is representative of commercial units in terms of characteristic times and temperatures. It was fired using propane gas laden with ammonia as fuel-nitrogen. The reburning coal was injected into the furnace at a rate of 1-4 kg/hr depending on the reburn fuel fraction required, and in the final stage overfire or burnout air was introduced to complete the combustion process. This work was focused on establishing the effectiveness of coal as a reburn fuel as well as determining the effect of the different process parameters on reburn performance. The effect of each operational variable was examined separately over a range of

conditions and the optimum or near optimum conditions identified. The unit was designed to bridge the gap between the more fundamental drop tube experiments and full-scale coal combustion experiments. The facility is described in more detail in Chapter Three.

The thesis is arranged as follows; Chapter Two gives a brief description of the NO<sub>x</sub> formation mechanisms during fossil fuel combustion followed by a review of the different NO<sub>x</sub> reduction techniques, and then a detailed literature review on the reburning concept is presented along with a brief outline of current and future research activities on the subject. The argument for Coal as a reburn fuel is then presented and the limitations discussed. Chapter Three describes the details of the experimental setup, procedures and analytical techniques. In Chapter Four the different results of the pulverised coal reburning experiments undertaken in the 200 kW furnace are presented in graphical form and duly discussed. Finally, the conclusions and proposals for future work are given in Chapter Five.

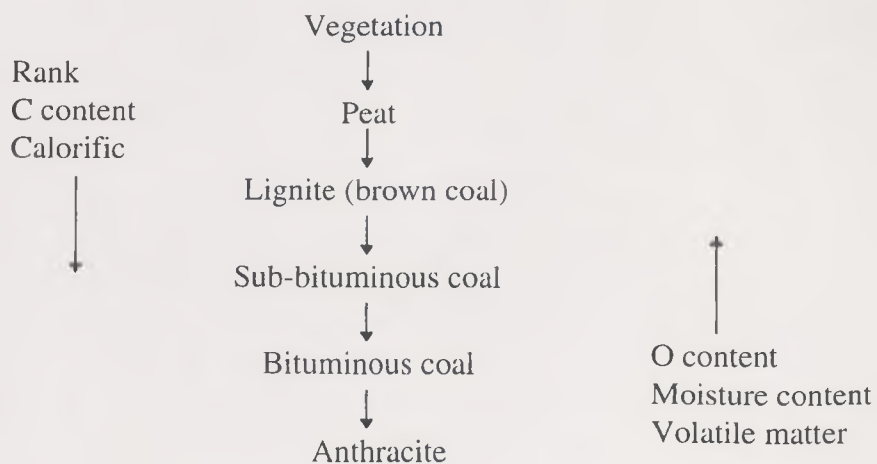
# CHAPTER TWO

## Literature Review

### 2.1 Origin, Structure and Classification of Coal

Coal is a brownish-black, heterogeneous, organic matter produced by a natural process involving slow pyrolysis of prehistoric plant materials. Differences in coal properties are the result of varying degrees of coalification as well as the type of plants included and even the type of soil they grew in. Thus, it is not surprising to find radical variations in coal composition and structure. Coal samples taken from the same mine or even different particles within a single sample can have significantly different characteristics (Jones, 1993).

Generally, coal coalification or formation sequence follows the Peat-Anthracite series and is as follows :





Hence lignite is the lowest rank or least mature coal with low heat value and carbon content while anthracite is a highly metamorphosed coal with high carbon content and little moisture. Peat is not coal, but it is the initial step of a progressive coalification process.

The organic part of the coal other than the volatile matter is called the fixed carbon. Pyrolysis or devolatilisation refers to the volatile loss on heating. The solid material left after devolatilisation consists mainly of the fixed carbon and ash and is normally referred to as char.

Classification of coals is normally done using the proximate and ultimate analysis techniques. The most common and widely used methods are the British standards (BS), the American Society for Testing Materials (ASTM) and the International Standards Organisation (ISO). The proximate analysis provides some qualitative information about how the coal behaves when heated. The results are reported as the weight percent of moisture, volatile matter, fixed carbon and ash. While the ultimate or elemental analysis provides the weight percent of carbon, hydrogen, sulphur, nitrogen, oxygen and other chemical elements such as chlorine and carbon dioxide. Details of how these test are carried out can be found in British standards BS 1016 part 3 (1973).

Such tests and classification methods provide useful information which can be used to design furnaces, heat transfer surfaces and fuel handling equipment, but they do not provide any insight into how the coal particle is bound together and how it decomposes during combustion.



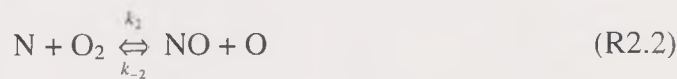
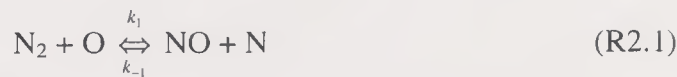
## 2.2 Pulverised Coal Combustion : Mechanisms of NO<sub>x</sub> Formation

The classic model of coal combustion refers to three processes that are not entirely independent and may overlap, namely, devolatilisation, volatile combustion, and char combustion. On entering a combustion chamber the coal particles are heated at rates of the order of  $10^4$  to  $10^6$  K/s. This causes the volatiles to be driven off the coal particles; a process known as devolatilisation. What remains of the coal, following the release of the volatiles, constitutes the char. The oxidation reactions that follow may involve both the volatile matter and the char. Oxidation of nitrogen and sulphur bound into the coal matrix and subsequent release as volatile matter, or during combustion of the remaining char results in the formation of nitrogen oxides and sulphur oxides which are emitted with the combustion flue gas. The processes that occur in the early stages of coal combustion have been reviewed by Wendt (1980) and Morrison (1986). Only the chemical processes that lead to the formation of NO<sub>x</sub> will be discussed.

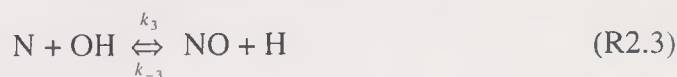
The term NO<sub>x</sub> refers to the total amount of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), with NO as the dominant species, normally representing 90-95% of the total NO<sub>x</sub> in combustion flue gases. NO<sub>2</sub>, a reddish brown, highly toxic and irritating gas with a pungent odour, generally constitutes most of the remainder (Hjalmarsson, 1990). Combustion generated NO<sub>x</sub> is known to be produced by three distinct mechanisms: thermal NO<sub>x</sub>, prompt NO<sub>x</sub> and fuel NO<sub>x</sub>. Depending on the fuel and/or combustion environment, any combination of these mechanisms may be at work.

### 2.2.1 Thermal NOx

This is a temperature related phenomenon, whereby O<sub>2</sub> and N<sub>2</sub> molecules in the combustion air are dissociated at high temperature into their respective atomic states. The dissociation products (N and O) then produce NO<sub>x</sub> by the well known Zeldovich mechanism which is a two-step sequence.



The mechanism was postulated by Yakov B. Zeldovich in 1946. The first step is rate limiting and, due to its high activation (314 kJ per mol), requires high temperatures to be effective. As flame conditions move closer to stoichiometric i.e. depleting the oxygen pool (OH >> H > O), a further reaction is included (Lavoie *et al.*, 1973).



Where  $k_1$ ,  $k_2$  and  $k_3$  are rate constants for the forward reactions of R2.1 to R2.3 respectively, and  $k_{-1}$ ,  $k_{-2}$  and  $k_{-3}$  are the corresponding reverse rates.

All three steps are usually referred to as the 'extended Zeldovich' mechanism. The mechanism is most pronounced in lean, high temperature (above 1800 K) flames with long residence times (Morrison, 1986).

$$\frac{dNO}{dt} \propto O_2, t_r, \exp^{Temp} \quad (2.1)$$

Generally, in pulverised coal combustion, there is a substantial amount of excess oxygen present thus creating a situation whereby the rate of consumption of nitrogen atoms equals its rate of formation and under this 'quasi steady state' assumption the following equation for the rate of formation of thermal-NO becomes valid.

$$\frac{d[NO]_r}{dt} = 2k_1[O][N_2] \left\{ \frac{1 - [NO]^2 / K[O_2][N_2]}{1 + k_{-1}[NO] / k_2[O_2] + k_3[OH]} \right\} \quad (2.2)$$

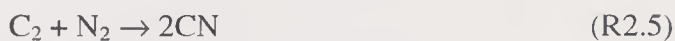
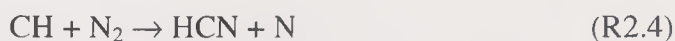
where  $K = (k_1/k_{-1})(k_2/k_{-2})$  is the equilibrium constant for the reaction between  $N_2$  and  $O_2$ . This is the mechanism that is inhibited by low-NOx burners, since staged combustion is first too fuel-rich, then too cool to allow significant conversion of atmospheric nitrogen to NOx.

It must be noted that the thermal mechanism is the major source of NOx formation during the combustion of clean fuels i.e. fuels which contain no inherent nitrogenous compounds such as natural gas.

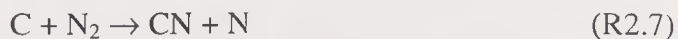
### 2.2.2 Prompt NOx

Prompt NO formation was first identified by Fenimore (1971) who showed that under fuel rich conditions, additional NO can be formed in the presence of  $N_2$  in hydrocarbon, but not  $H_2$  or CO flames. The additional NO could not be attributed to the Zeldovich mechanism in fuel rich flames. This path of NO formation increases in

significance as the hydrocarbon concentration increases. Fenimore concluded that this phenomenon occurred very rapidly in the early stages of the combustion process and was the result of an attack of hydrocarbon fragments on molecular nitrogen. He proposed the following reactions



Alternative reactions were suggested by Hayhurst and Vince (1983)



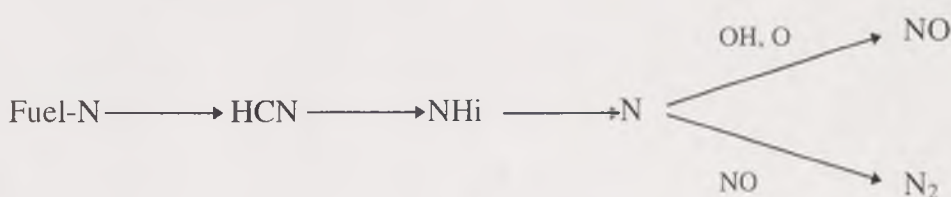
NO is later formed by the oxidation of the cyanide species. At short residence times and fuel rich conditions (stoichiometric ratios less than 0.85), the Fenimore mechanism accounts for virtually all the fixed nitrogen (the sum of all nitrogenous species except  $\text{N}_2$ ) (Miller *et al.*, 1987).

### 2.2.3 Fuel NO<sub>x</sub>

The third principal source of NO<sub>x</sub> in combustion systems is nitrogen that is chemically bound in the fuel. Fuel NO<sub>x</sub> formation is particularly dominant in the combustion of coal which typically contains 0.5 to 2% nitrogen by weight (Sloss *et al.*, 1992). Although the total quantity of nitrogen present in the coal is small compared to molecular nitrogen in the combustion air, the high conversion

efficiency of fuel nitrogen to NO<sub>x</sub>, typically around 15-40%, can result in more than 80% of the total NO<sub>x</sub> produced being attributed to the fuel NO<sub>x</sub> mechanism (Pershing and Wendt, 1977). This is mainly due to local combustion environment i.e. stoichiometry and to a lesser extent temperature, and the fact that N-H and N-C bonds common in fuel-bound nitrogen are weaker than the triple bonds in molecular nitrogen which must be dissociated to produce thermal NO<sub>x</sub> (Palmer and Seery, 1973).

NO<sub>x</sub> formation mechanism via fuel nitrogen is complex and involves several nitrogenous radical species, namely, hydrogen cyanide (HCN), ammonia (NH<sub>3</sub>), nitric oxide (NO) and molecular nitrogen (N<sub>2</sub>). The generally accepted sequence of nitrogenous species during the early stages of coal combustion is that HCN and NH<sub>3</sub> are formed as the products of coal devolatilisation, with HCN being the dominant intermediate species. The conversion of fuel nitrogen to HCN is very rapid and is not rate limiting (Miller *et al.*, 1984). HCN is then slowly converted to amine species (NH<sub>i</sub>; i=0,1,2,3) which then has two competing routes to form NO or N<sub>2</sub> (Haynes, 1977a, 1977b; Fenimore, 1971, 1976).



The relative yields of NO and N<sub>2</sub> are strongly dependent on local stoichiometry with the N<sub>2</sub> formation path being favoured under fuel rich conditions.



During coal combustion, the chemically bound nitrogen in the coal is split between that in the volatile fraction and that in the char. Reactions involving the volatile fraction, as well as those involving the char, result in the formation of NO. However, the volatile nitrogen contribution is higher than that of the char, and account for about three-quarters of the fuel-NO (Pershing and Wendt, 1977). During pyrolysis the volatile nitrogen components are thought to fragment and rapidly form cyanic and amine species which are precursors to NO<sub>x</sub> (Fenimore, 1971). Oxidation of char nitrogen is then presumed to take place heterogeneously with a somewhat lower conversion efficiency. The low char nitrogen contribution was suggested by Pohl and Sarofim (1977) to be due to low local oxygen levels surrounding the burning char particle and that some of the NO formed was subsequently reduced by the char. Generally, char nitrogen contribution to NO depends on temperature, with lower conversions at higher temperatures and lower stoichiometries (Song *et al.*, 1982a, 1982b).

The volatile nitrogen conversion to NO decreases with decreasing stoichiometry and with increasing temperature (Pohl and Sarofim, 1977). The stoichiometry effect is due to delayed contact between the volatile nitrogen and oxygen which reduces NO formation. The weak dependence of fuel-NO formation on temperature was discussed by Song *et al.* (1982b). At higher temperatures, more nitrogen is evolved from the volatile fraction, however, the conversion of volatile nitrogen to NO decreases with temperature and both effects cancel out.

Generally, the most obvious variable to explore in determining fuel-NO emissions is the nitrogen content of the coal. However, the efficiency of conversion of coal



nitrogen to NO decrease with increasing nitrogen content (Pershing and Wendt, 1977; Clarke and Williams, 1991). Pershing and Wendt (1977) showed in their investigations of four coals and one coal char that fuel NO could not be correlated with nitrogen content alone, even though flow conditions were kept constant.

There is also evidence that the form of the nitrogen-bearing volatiles can vary and thus affect the conversion of volatile nitrogen to NO. Chen *et al.* (1982) conducted a parametric study of 50 different coals under air staged conditions and found that the total fixed nitrogen (TFN is the sum of all nitrogen-bearing compounds except N<sub>2</sub> i.e. NO + NH<sub>3</sub> + HCN) leaving the first stage generally increased with coal nitrogen content, but the TFN distribution was dependent on coal rank with low volatile coals forming essentially no NH<sub>3</sub> or HCN. In their study, HCN was greater than NH<sub>3</sub> with bituminous coals, but less than NH<sub>3</sub> with sub-bituminous and lignite coals. Also, first stage NO was found to generally decrease with decreasing coal rank. The TFN speciation leaving the first stage was found to be important in determining the ultimate NO yield. When NO was the dominant TFN species the second stage conversion of TFN to NO was very high, however, as the balance shifted in favour of HCN and NH<sub>3</sub> the conversion to exhaust NO decreased.

### **2.3 NO<sub>x</sub> Control Options for Coal Combustion**

NO<sub>x</sub> control technologies can be divided into two categories; those that involve modification of the combustion process to control the formation of NO<sub>x</sub> and those that remove NO from the product of combustion once NO<sub>x</sub> is formed. The latter category is widely referred to as post-combustion control methods. The level of uncontrolled NO<sub>x</sub> emission depends on the type of combustion, operating conditions

i.e. combustion intensity, local stoichiometry and fuel composition (Thompson, 1974). Different control measures are required based on the level of uncontrolled NO<sub>x</sub> emission as well as the specific regulations on NO<sub>x</sub> emissions.

Combustion modification measures are normally the initial steps to be taken when controlling NO<sub>x</sub> emissions since they are relatively more economical. If, however, emission limits are not met by combustion modification alone then post-combustion methods can be employed. These are normally very expensive due to catalyst costs, and require more frequent maintenance procedures. The two control options are considered as follows.

### **2.3.1 Combustion Modification Techniques**

The control of NO<sub>x</sub> emissions using combustion modification is dictated by the mechanisms by which NO<sub>x</sub> is formed during combustion processes. The two major mechanisms of NO<sub>x</sub> formation in combustion processes are thermal-NO<sub>x</sub> and fuel-NO<sub>x</sub>.

The thermal mechanism is dominant when the fuel used contains no inherent nitrogen such as natural gas and gasoil. Here the NO formation mechanism is entirely temperature dependent, thus the combustion modification techniques employed to reduce NO formed in this way are based on the dependence of the NO formation rate on temperature and oxygen concentration as presented in equation 2.1 (Bowman, 1992) . Some of these measures include :

- i) decreasing the combustion temperature in all reaction areas to below 1300 °C  
and decreasing the furnace heat release rate

- ii) decreasing the residence time in all high temperature zones
- iii) decreasing the excess air and hence lowering the concentration of atomic oxygen in high temperature zones.

On the other hand, fuels which contain inherent nitrogen such as coal and heavy fuel oils tend to have the fuel-NO mechanism as the dominant NO formation process. The level of fuel-NO emission is a function of fuel type and varies with amount of fuel nitrogen present in the parent fuel (Bartok and Sarofim, 1991).

The rate of conversion of fuel-N to NO is dependent on local combustion conditions during volatilisation of the nitrogen compounds. Control methods involve suppressing the volatilisation process by controlling the amount of oxygen in the combustion zone such that volatilisation occurs in a fuel rich environment prior to massive entrainment of oxygen (Mason, 1979). This approach can also reduce thermal-NO<sub>x</sub>. Another option to reduce fuel-NO<sub>x</sub> is to use a fuel with lower nitrogen content.

Thus combustion modification techniques aim to limit NO<sub>x</sub> formation in the early stages of the combustion process and some of the techniques used to achieve this are considered below. Some or all apply equally to oil, coal and gas fired systems.

### **A. Air Staging**

The general principle of air staging is to control the level of available oxygen in zones where it is critical for NO<sub>x</sub> formation (Hjalmarsson, 1990). This is done by staging the combustion air so that the primary combustion zone operates with an overall fuel rich stoichiometry and the remaining combustion air is injected

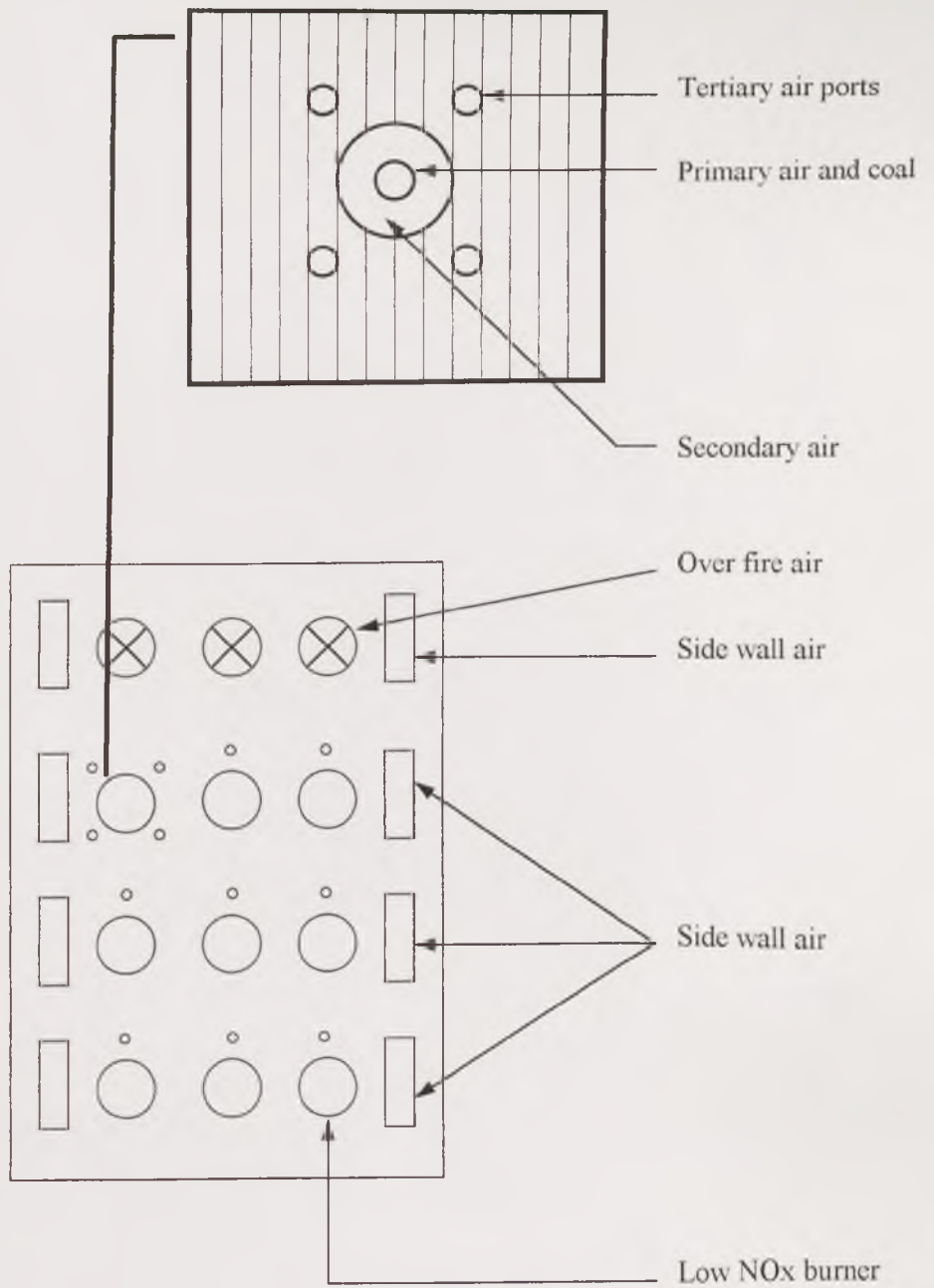
downstream. Air staging in combustion systems can be achieved by either staging the furnace or staging the burner, or both.

Furnace air staging normally referred to as Two Stage Combustion (TSC) involves reducing the amount of air to the primary combustion zone so as to create a sub-stoichiometric region where NO<sub>x</sub> can be reduced to nitrogen. The additional air required for complete combustion is then supplied downstream of the main combustion zone. This additional air can be introduced into the furnace in a number of ways. It can be added directly above the burners through ports called Over Burner Air (OBA), through openings located high up in the furnace called Over Fire Air (OFA), or through side ports located between the burners or OFA ports and the side walls to protect the walls from corrosive gases (Fig 2.1). Other arrangement involve operating selected burners fuel-rich while the remaining burners operate with air-rich or air alone to achieve the same overall effect of air staging. This type of staging is known as biased firing, off-stoichiometric or burners-out-of-service (BOOS).

Two stage combustion results in the reduction of both thermal and fuel NO<sub>x</sub>; as the flame region is fuel rich, fuel-N is encouraged to form nitrogen due to lack of oxygen. Also thermal-NO<sub>x</sub> is reduced as the peak temperatures occur at a point where oxygen concentration is at its lowest (Siegmond and Turner, 1974).

## **B. Low NO<sub>x</sub> Burners**

Low NO<sub>x</sub> burners are designed to achieve the staging effect through partitioning the air and fuel flow fields inside the burner in such a manner so as to delay combustion, reduce the availability of oxygen and reduce peak flame temperature; all of which



**Figure 2.1** Example of different locations of staged air on a furnace wall and in a burner (wall-fired boiler) Hjalmarsson, 1990.



help reduce NO<sub>x</sub>. They are currently a variety of low NO<sub>x</sub> burners being used on both retrofit and new installations to meet emission control limits. However, although they might differ in design they all have the ability to considerably reduce NO<sub>x</sub>. Some of the burner types include staged-air burners, stage-fuel burners, low excess air burners, and ultra low NO<sub>x</sub> burners which are capable of integrating two NO<sub>x</sub> reduction measures into a single burner thus increasing their NO<sub>x</sub> reduction potential. The nitrogen oxide reduction potential of these burners is given in Table 2.1.

In staged air burners the combustion air is separated into primary and secondary flow regimes. The primary air is mixed with the total quantity of fuel producing a fuel rich flame which is both relatively cool and deficient of oxygen, conditions which inhibit fuel-NO<sub>x</sub> formation. Secondary air is introduced downstream of the primary flame zone at which point combustion is completed in an environment which is sufficiently cool to limit thermal NO<sub>x</sub> formation (Wilcox, 1995).

Another type of low NO<sub>x</sub> burner makes use of fuel staging (reburning) principle to control nitrogen oxides produced in flames. Fuel staging in burners was first introduced by Foster Wheeler in the mid 1970s as a means of controlling NO<sub>x</sub> formation in flames (Vatsky, 1983) . Functionally, fuel staging is a means of internally staging a burner to produce a very substoichiometric flame, along the burner's axis, which is surrounded by another flame (from the main burner). The internal flame produces partially burned products in the form of hydrocarbon radicals which then pass through the main flame. These radicals then react with

nitric oxide in the NO<sub>x</sub> reduction zone and complete burnout occurs in the oxidising zone through staged air in the burner.

Advances in fuel staged burners have led to the development of ultra low NO<sub>x</sub> burners which make use of secondary fuel injectors to create a fuel rich zone within the flame. Figure 2.2 shows a schematic representation of such a system.

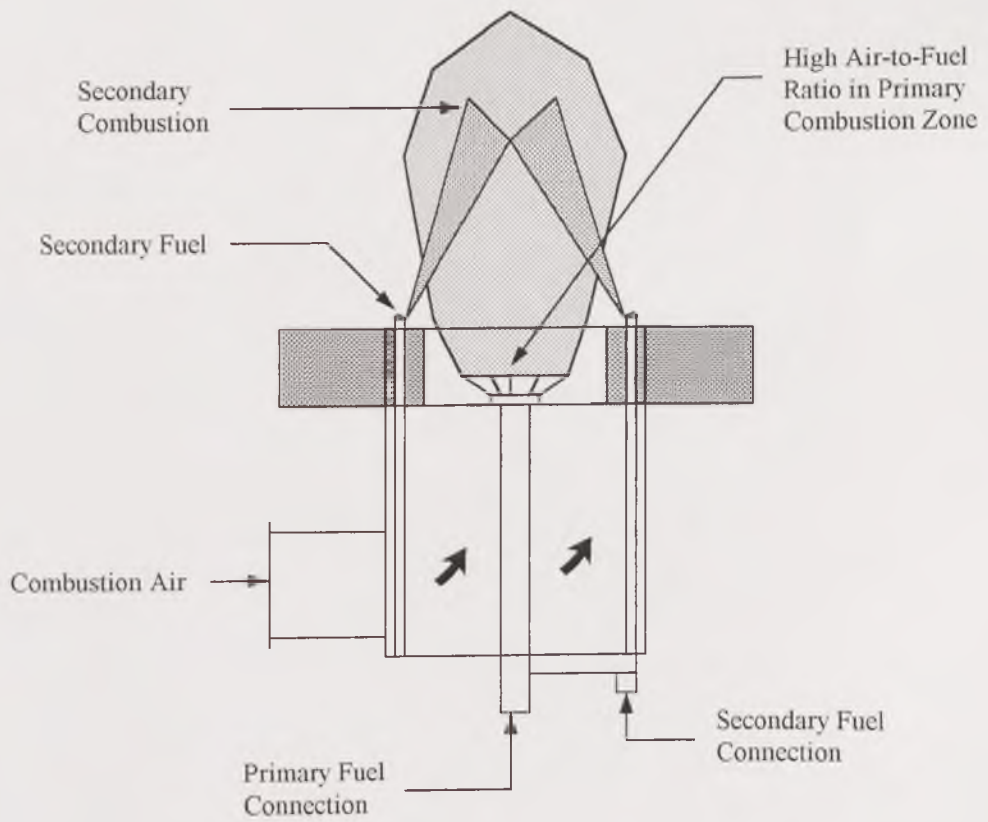
Low excess air burners are capable of reducing NO<sub>x</sub> emissions by up to 25% at 1.10 stoichiometric air by completing combustion with the lowest amount of excess air possible (Collette, 1985). Any further reduction in excess air levels could lead to increases in soot and CO emissions and cause problems with flame stability (Garg, 1994). Increases in excess air result in increases in NO<sub>x</sub> formation.

**Table 2.1** NO<sub>x</sub> Reduction Capabilities of Different Burners

<b>Burner Type</b>	<b>NO<sub>x</sub> Reduction</b>
Staged-Air Burner	25-35%
Staged-Fuel Burner	40-50%
Low-excess-Air Burner	20-25%
Burner with External FGR	50-60%
Burner with Internal FGR	40-50%
Air or Fuel-Gas-Staging with Internal FGR	55-75%
Air or Fuel-Gas-Staging with External FGR	60-80%

### **C. Flue gas recirculation**

Flue gas recirculation (FGR) is a technique which introduces a diluent into the combustion chamber. This is normally done by separating part of the flue gas flow from the main flow, normally after the particulate control system, and then re-routing it to be mixed with the incoming combustion air or staging air either in the



**Figure 2.2** Schematic of a Staged Fuel Gas Burner (Garg, 1994)

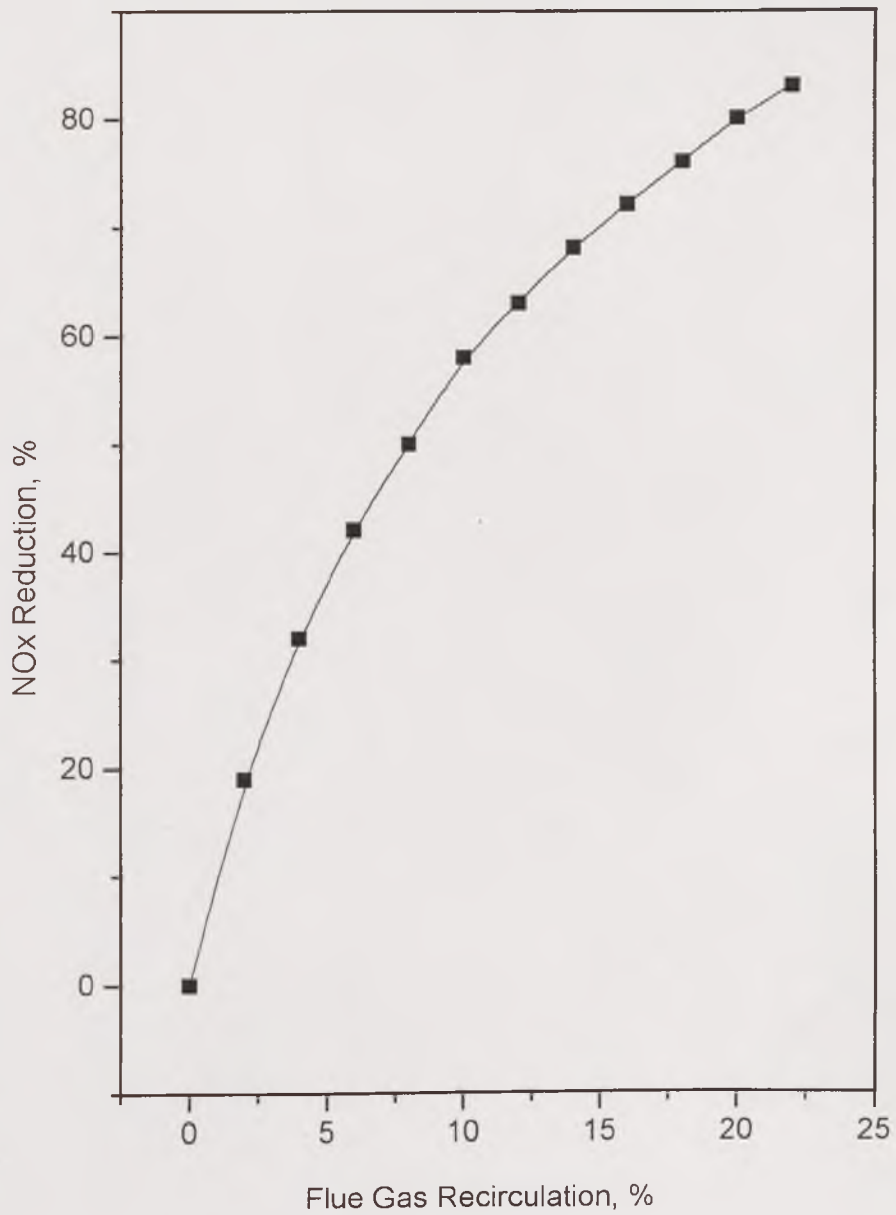
burner or in the furnace itself. Burner FGR being more efficient than furnace FGR (Clarke and Williams, 1991).

The recirculated flue gas, normally in the order of 10-20% of the combustion air (Fig. 2.3), has a two-fold effect of reducing the temperature and diluting the oxygen in the air; both of which are key factors in the control of thermal NO<sub>x</sub>. However, this technique does very little for the control of fuel NO<sub>x</sub> (Sarofim and Flagan, 1976). Moreover, it is known to cause about 1% reduction in the thermal efficiency of the furnace due to the extra load required to drive the recirculation fan and in the long run added precaution is required so as to prevent corrosion and erosion of boiler walls and tubes by fine particulate. This tends to increase maintenance costs (Thompson, 1979). Also increasing the amount of FGR beyond the optimum value of 20% could lead to flame instabilities and increased combustion and hydrocarbon emissions (Clarke and Williams, 1991).

The high capital cost of FGR coupled with the practical problems involved in installing extra ducting and high temperature blowers renders this technique economically unattractive (Sarofim and Flagan, 1976). However, because FGR acts as an inert diluent it can be used as a transport medium for solid reburning fuels in staged fuel combustion (Sloss *et al.*, 1992).

#### **D. Excess Air**

Lowering the overall excess air level is one of the simplest NO<sub>x</sub> control technologies. Normally, as the amount of excess air is increased in the furnace NO<sub>x</sub> levels also increase (Nsakala and Patel, 1985). This is because an increase in excess



**Figure 2.3** NOx reduction as a function of the amount of flue gas recirculated (Wood, 1994)



air level causes the oxygen concentration in the flame zone to increase, and although the temperature is reduced, thermal NO<sub>x</sub> emissions pass through a maximum value which depends on the mixing pattern in the combustion zone (Armento and Sage, 1975). On the other hand, as fuel NO<sub>x</sub> is insensitive to the changes in temperature it tends to increase unaffected with increased excess air (Martin and Berka, 1972; Sarofim and Flagan, 1976). The combined effect of both fuel and thermal NO<sub>x</sub> leads to unacceptable levels of NO<sub>x</sub> emissions as the excess air is increased.

Lowering excess air levels to a point which is consistent with complete combustion will limit both fuel and thermal NO<sub>x</sub> formation. Further reductions in the excess air level will reduce NO<sub>x</sub> emissions even more, but this may be at the expense of unwanted problems such as unstable combustion, reduced burnout, slagging, fouling and corrosion.

An added advantage of using low excess air levels is the higher thermal efficiency that can be achieved without major modification to a boiler and the fuel saving which results from such an operation. (Sarofim and Flagan, 1976; Morrison, 1980; Mason, 1979).

## **E. Operating Conditions**

Before considering any NO<sub>x</sub> control measures it is necessary to optimise operational conditions so as to achieve the lowest possible emissions without any loss in combustion efficiency. Achieving this balance is not always easy and requires tight control and fine tuning to achieve the best air to fuel ratio at each burner. This necessitates the installation of control equipment and reliable continuous

instrumentation to monitor emissions in order to ascertain which operational conditions affect NO<sub>x</sub> emissions and adjust them accordingly.

Normally a band of operation exists for NO<sub>x</sub> emission, and although different for different combustion systems, it does provide the operator with a means of controlling combustion without the loss in optimum efficiency. The band also takes into account other factors that might affect performance and, more importantly, operating cost (Williams and Hampartsoumian, 1993).

### **2.3.2 Post-Combustion NO<sub>x</sub> Control**

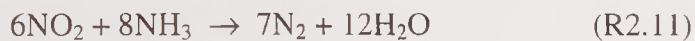
Post-combustion NO<sub>x</sub> control is normally installed to a combustion system when limits on NO<sub>x</sub> emissions cannot be met by combustion modification alone. Such control options help remove NO<sub>x</sub> after it has formed in the combustion process and are thus referred to as flue gas treatments. They are applied downstream of the combustion zone and are categorised as 'dry processes' i.e. NO<sub>x</sub> is not absorbed into an aqueous solution (Bosch and Janssen, 1988). Dry processes are generally more economical and much simpler than wet processes, and unlike wet processes which are normally used to remove both NO<sub>x</sub> and SO<sub>2</sub> together, dry processes are designed to remove only NO<sub>x</sub>. Their relative simplicity and lower cost makes them the more attractive option for the control NO<sub>x</sub> in coal-fired power stations. Dry NO<sub>x</sub> removal processes can be subdivided into 3 categories:

- A. Selective Catalytic Reduction (SCR)
- B. Selective Noncatalytic Reduction (SNCR)
- C. Nonselective Catalytic Reduction (NSCR)

## A. Selective Catalytic Reduction (SCR)

Selective catalytic reduction (SCR) is one of the most dominant NO<sub>x</sub> abatement methods currently used in both Germany and Japan on stationary sources of nitrogen oxides. It can offer a NO<sub>x</sub> reduction of over 70-90% compared to the 40-50% removal efficiency of other NO<sub>x</sub> control technologies (Hardison *et al.*, 1991; Cobb *et al.*, 1991; Hjalmarsson, 1990).

In this technique ammonia (NH<sub>3</sub>) is injected through a grid system into the flue gas and the resulting mixture passes through layers of base-metal catalyst which is normally located between the economiser and the air preheater. On the catalyst surface NH<sub>3</sub> reacts with NO<sub>x</sub> to form molecular nitrogen and water vapour and because this is a catalytic gas phase reaction there is no by-product to dispose of. The presence of oxygen in the flue gas is essential for denitrification and thus SCR favors air rich conditions. However, since the process is selective ammonia only reacts with NO<sub>x</sub> at the correct operating temperature rather than being oxidised by oxygen. The reactions which are assumed to take place on the surface of the catalyst are :



For the above reactions to take place the catalyst bed should be maintained at a specific operating temperature at which NO<sub>x</sub> removal efficiency is at its highest. The choice of catalyst will depend on the range of operating temperatures in the plant. Each catalyst type has its own optimum temperature range e.g. 300 °C - 400 °C for vanadium or titanium-based catalyst and 240 °C - 265 °C for platinum catalyst. Thus the process is only workable over a very narrow range of operating temperatures known as 'Operating Temperature Window', and operating beyond either limits renders the catalyst useless. On lower temperature end operability is restricted by the inability of the catalyst to carry out the NO<sub>x</sub> reduction reactions, and on the upper end by the generation of NO<sub>x</sub> from ammonia in the presence of platinum according to the following reaction (Cobb *et al.*, 1991) :



An SCR system consists primarily of an ammonia injection grid, and a SCR reactor containing an assembly of catalyst modules. Each module consists of square elements made of a rigid, honeycomb catalyst cells. These cells contain the active materials (base metal oxides) which are either impregnated on a metallic or ceramic substrate, or are integral with homogenous type substrate. Various compounds are also added to the catalyst which are used to promote high activity, increase selectivity, enhance durability, decrease oxidation characteristics, and provide resistance to contamination (Cobb *et al.*, 1991).

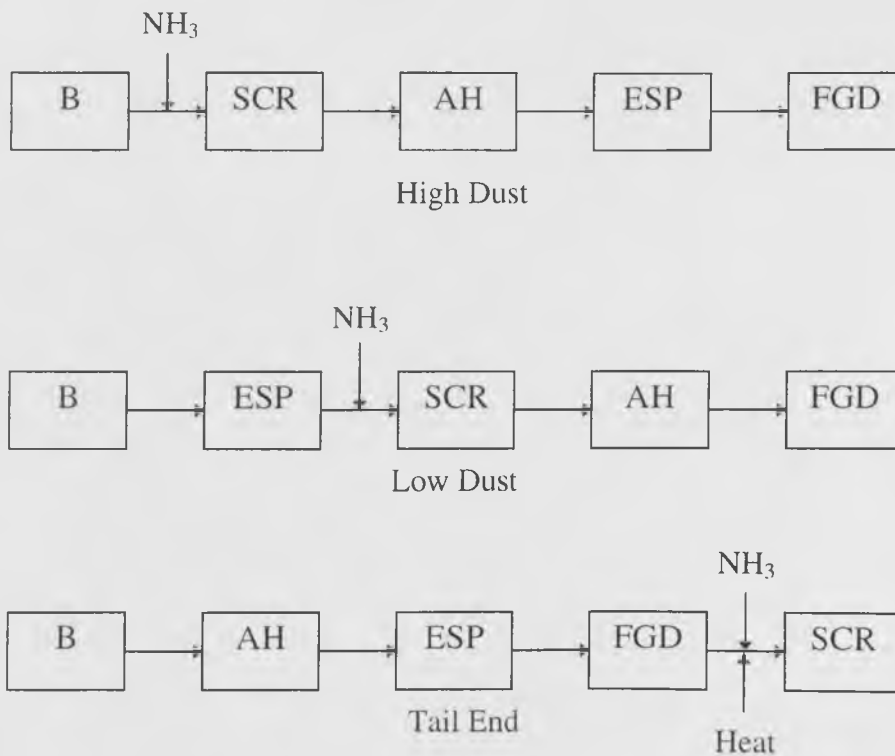
Base metal like titanium and vanadium oxides are the predominant SCR catalysts in use on coal at present, however, new types are emerging. One known as zeolite has a molecular sieve ceramic body inside which NO<sub>x</sub> reduction reaction takes place. It can operate at higher temperatures than conventional catalysts; typically in the range of 300 °C - 430 °C, and due to its molecular sieve structure poisoning and fouling effects are greatly reduced (Sloss *et al.*, 1992; Cobb *et al.*, 1991). Other catalysts which are also in use include noble metals, iron, and activated carbon. The working temperatures of the different catalysts are given in Table 2.2. The main deciding factors which determine the type of catalyst are gas temperature, sulphur content, and dust loading (Cho, 1994).

The location of the catalyst is governed by the operating temperature range of the catalyst. The three positions commonly used for catalyst location are: high dust, low dust and tail end as shown in Fig. 2.4.

**Table 2.2** Types of Catalyst in Operation on Coal and their Working Temperatures

Titanium oxide based	270-400 °C
Zeolite	300-430 °C
Iron oxide based	380-430 °C
Activated coal/coke	100-150 °C





- B = boiler
- AH = air preheater
- ESP = electronic precipitator
- SCR = selective catalytic reduction
- FGD = flue gas desulphurisation

**Figure 2.4** Position of Catalyst (Hjalmarsson, 1990)

High dust location (between the economiser and air preheater) is the preferred position for most SCR applications since at that point the flue gas temperature is ideal for most types of catalyst. However, since the flue gases passing through the catalyst contain all the fly ash and sulphur oxides from combustion catalyst degradation will be eminent. Low dust location, on the other hand, offers dust free flue gases but still containing sulphur dioxide. Finally, the tail end systems have the catalyst located at the end of the chain of flue gas cleaning equipment thus providing

a relatively clean flue gas which contains small amount of SO<sub>2</sub>. The only draw-back, however, is that the flue gas temperature is too low for most types of catalyst and thus reheating of the flue gas is essential. Out of all three system the tail end location is probably the most suitable for coal-fired boilers, however, high dust location has been used on coal-fired systems (Cho, 1994).

The NH<sub>3</sub>/NO<sub>x</sub> ratio is another important parameter in the effective performance of the SCR process. According to the most dominant reaction process (R2.10) ammonia injection rates must be controlled to give a 1:1 NH<sub>3</sub>/NO<sub>x</sub> mole ratio. However, due to the uneven and incomplete mixing of both reactants excess ammonia is normally injected. The unreacted ammonia slips through the catalyst bed and into the stack. This is referred to as ammonia slip and should be minimised to avoid forming ammonium sulphate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and ammonium bisulphate NH<sub>4</sub>HSO<sub>4</sub> both of which cause flow blockage, corrosion and fouling of downstream equipment. This effect can be minimised by limiting the amount of ammonia slip and SO<sub>3</sub> concentration to less than 10 ppm and 5 ppm respectively. For coal fired plants, ammonia slip should be kept to below 5 ppm (Cho, 1994).

The life time of a catalyst is limited to 2 - 4 years after which the activity declines and the catalyst will need to be replaced.

Operating experience with SCR on coal-fired plants is rapidly growing especially in Japan and Germany where most of the existing SCR plants are located. Nevertheless, SCR systems are spreading in other parts of Europe like Austria and The Netherlands where a full-scale demonstration plant has been operating since 1987. Sweden and Denmark also have a number of SCR pilot plants in operation.

Due to this increasing experience coupled with improved technical innovations and increased competition among SCR manufacturers the costs of SCR systems are declining. This is nowhere more apparent than in Germany where the price per m<sup>3</sup> of catalyst has more than halved since 1985 (Amann, 1989).

## **B. Selective Non-Catalytic Reduction (SNCR)**

This method of NO<sub>x</sub> control makes use of different reducing chemicals to selectively reduce nitrogen oxides through controlled thermal reactions. This is achieved by injecting ammonia or other reducing agents into the air rich flue gas; the NO<sub>x</sub> reduction takes place without use of a catalyst. It is very cheap compared to the selective catalytic method. The SNCR process is very temperature sensitive and, therefore, the effectiveness of NO<sub>x</sub> removal depends on successful temperature control. The NO<sub>x</sub> removal efficiency is lower than SCR, and the chemical consumption is higher.

The first application of SNCR started in Japan in 1974 where its potential was realised when 65% NO<sub>x</sub> reduction was achieved. It was a developmental process in which the catalytic systems were first applied to natural gas fired units, then to oil-fired units and finally in 1985, after greater understanding of the chemical kinetics of the process, to coal fired boilers (Hurst, 1986).

There are two major SNCR systems available commercially: the Exxon Thermal DeNO<sub>x</sub> ammonia injection system and the Fuel Tech NO<sub>x</sub>OUT urea injection system.

## I) Thermal DeNOx

Thermal DeNOx is a homogenous gas phase reduction process which selectively reduces NOx by reaction with NH<sub>3</sub> without the use of a catalyst. A specific temperature range is required to allow the desired reactions to occur (850 °C - 1200 °C) (Sloss *et al.*, 1992). This is achieved by injecting gaseous ammonia directly into the upper part of the boiler where two competing reactions take place.



Reaction (R2.14) is dominant in the temperature range of 850 to 1200 °C, resulting in a reduction of NOx. If the temperature rises above 1200 °C a competing reaction (R2.15) starts to prevail, causing increased NOx production. Below 850 °C, ammonia fails to react thus being unable to either produce or destroy NOx. For higher efficiency of NOx reduction, the reaction temperature must be tightly controlled in a narrow temperature range of 850 to 1040 °C, with an optimum temperature of about 950 °C. This 'temperature window' can be lowered to about 740-760 °C by also injecting H<sub>2</sub> which is readily oxidised (Sloss *et al.*, 1992; Faucet *et al.*, 1978).

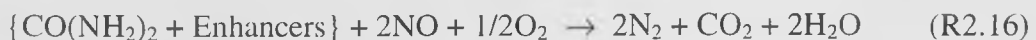
Thermal DeNOx has demonstrated its effectiveness when used on gas-fired boilers giving a NOx removal efficiency of 70% to 80% provided it is operated within the limits of its temperature window. A 40% to 60 % removal was also achieved on oil and coal-fired systems (Kunz *et al.*, 1992; Mittlebach, 1989). However, several

potential problems still exist with this technique: the high NH<sub>3</sub>/NO<sub>x</sub> (3:1) ratio required causes some slip of ammonia thus producing ammonium bisulphate which causes clogging in the air preheaters and leads to ammonia in the fly ash. Another disadvantage is the safety problems encountered in the storage and handling of anhydrous ammonia.

## II) NO<sub>x</sub>OUT

This process was originally discovered and patented in the late 1970s by the Electrical Power Research Institute (EPRI) where urea was found to be effective at reducing NO<sub>x</sub> to molecular nitrogen, but only within a narrow temperature range, 950-1000 °C. The process was then further developed by Fuel Tech Ltd (UK) to use urea in combination with a number of 'proprietary enhancers' (additives) which considerably widen the temperature window (to 1000-2100 °C) over which NO<sub>x</sub> removal is effective. It is currently being marketed by Fuel Tech as the NO<sub>x</sub>OUT process and is now available for full scale commercial use (Rhoads *et al.*, 1990).

In the NO<sub>x</sub>OUT process an aqueous solution containing urea and chemical enhancers is injected into the air rich upper part of the furnace through multiple injection point. Essentially, the reaction that takes place is :



Good mixing of urea with the flue gas is essential to maintain the relatively fast reaction times needed for effective NO<sub>x</sub> reduction, but is difficult to achieve because of the variations in flue gas velocity profiles. The temperature window and the urea



to NO<sub>x</sub> ratio affects the efficiency of the process in the same way as for Thermal DeNO<sub>x</sub>. Multiple level injection are effective in reducing NO<sub>x</sub> specially during temperature/load variations (Epperly *et al.*, 1988).

Although urea is more expensive than ammonia, capital cost associated with this process are normally lower than the Thermal DeNO<sub>x</sub> process. NO<sub>x</sub> reduction efficiency of 35% to 70% have been achieved on gas and coal-fired boilers

### **C. Non-Selective Catalytic Reduction (NSCR)**

In this process an oxygen deficient flue gas is required and this can be achieved by either introducing a reducing gas such as methane into the radiant zone of the boiler so as to chemically bind any excess oxygen or by employing low excess air firing, or both (Faucet *et al.*, 1978). Normally both measures are used together for effective oxygen control and to cut down on operating cost by using less of the reducing fuel. The oxygen starved flue gas is then passed over a non-noble metal catalyst which reduces SO<sub>2</sub> and NO<sub>x</sub> to H<sub>2</sub>S and N<sub>2</sub> (Bosch and Janssen, 1988).

The main disadvantages of this process are the high operating cost due to the large quantities of reducing gas required and increased corrosion in the boiler due to the high temperature reducing atmosphere.

### **2.3.3 Simultaneous NO<sub>x</sub> / SO<sub>x</sub> Removal Processes**

These processes combine two separate control measures of desulphurisation and denitrification, and although each can be operated separately, have an increased synergistic effect when operated together. Most of these techniques are still in their

early stages of development and are considered to be complex and expensive but show great potential especially if more stringent regulations are imposed on sulphur and nitrogen dioxide emissions. An added advantage of the combined approach is the yield of a refined saleable product (e.g. sulphur and sulphuric acid) that several of the processes produce.

The processes are again divided into wet and dry methods with only a few of the former proceeding for further development. These include complex ion and oxidation/absorption processes. Dry processes using adsorption, irradiation, and catalytic absorption have reached operational stages.

#### **A. Adsorption**

This process uses activated carbon to adsorb both SO<sub>2</sub> and NO<sub>x</sub> (Faucet *et al.*, 1978). In the first stage the flue gas is passed over an activated carbon bed maintained at a temperature of 90-150 °C. Sulphur dioxide is catalytically oxidised with the moisture in the flue gases and forms sulphuric acid which is adsorbed on the activated carbon. The carbon adsorbent then undergoes high temperature regeneration ready for the second stage. The SO<sub>2</sub> gas thus obtained is processed to elemental sulphur, sulphuric acid, or liquid SO<sub>2</sub> (Neumann, 1987). Ammonia is also injected into the flue gas before it enters the second stage. In the second stage NO<sub>x</sub> reacts catalytically with the ammonia to form N<sub>2</sub> and H<sub>2</sub>O. The operational problems encountered include high carbon losses, handling of the hot activated carbon, and uneven adsorption distribution. Despite the above, this process has achieved removal efficiencies of 98% and 80% for SO<sub>2</sub> and NO<sub>x</sub> respectively on both pilot scale and commercially (Marnet *et al.*, 1987; Richter *et al.*, 1989).

## B. Irradiation

This process uses electron beams as an energy source to provide the activation energy necessary to start the reactions that would remove NO<sub>x</sub> and SO<sub>2</sub> simultaneously from the flue gas (Rosenberg *et al.*, 1978). It was developed in Japan by Japan Atomic Energy Research Institute (JAERI) and Ebara Manufacturing and work is currently going on in Germany, Italy and Denmark to further develop this technique (Sloss *et al.*, 1992; Kuhr *et al.*, 1988; ENEL, 1988 and Dinelli *et al.*, 1988).

The reduction process is carried out in a reactor where a dust-free flue gas (< 5 mg/m<sup>3</sup>) is first cooled using water injection or heat exchanger to 70-120 °C and is then reacted with ammonia or lime in the presence of an electron beam (1-3 Mrad). The resultant product is a complex, powdery mixture which is removed using an electrostatic precipitator. The major disadvantages of this technique include high capital and energy costs, a secondary waste disposal problem and low (<80%) SO<sub>2</sub> removal.

**Table 2.3** NO<sub>x</sub> Reduction Potential for Different Technologies

Technique	Applicability	NO <sub>x</sub> Reduction
Excess Air	All fuels	1-15%
Air Staging	All fuels; multiple-burner devices	30-60%
Low NO <sub>x</sub> Burners	All fuels	30-50%
Flue Gas Recirculation	Gas fuels and low-nitrogen fuels	40-80%
Reburning	All fuels	50-70%
Selective Catalytic Reduction	Gas fuels and low-sulphur fuels	70-90%
Selective Noncatalytic Reduction	All Fuels	25-50%
Nonselective Catalytic Reduction	All Fuels	25-50%

It should be noted that in processes where a combination of NOx control technologies are adopted the stage wise efficiencies of these technologies are multiplicative rather than additive. For example, assuming a baseline NOx emission level of 100 ppmv and by applying the following control technologies with their respective efficiencies in the progressive order: low-excess-air, low-NOx burners, and flue gas recirculation, the stage wise emission reductions are as given in Table 2.4.

**Table 2.4** Emission Reductions of Multiple Control Technologies

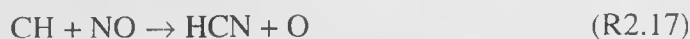
Control Technology	Efficiency	Final NOx Level, ppm
Low-Excess-Air	10%	$100(1-0.10) = 90$
Low-NOx Burners	40%	$90(1-0.40) = 54$
Flue Gas Recirculation	60%	$54(1-0.6) = 21.6$

## 2.4 The Reburning Process

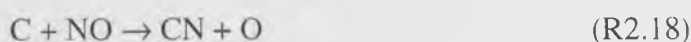
Having discussed the two main options traditionally used for controlling NOx emissions (combustion modification and flue gas treatment), attention will now be turned to a promising technique which utilises the reduction properties of hydrocarbons. Different terms such as reburning, fuel staging, distributed fuel addition, staged fuel injection, and in furnace NOx reduction have been used by many researchers to refer to the process. However, in this thesis it will be referred to as reburning.

Reburning falls under the combustion modification category and involves diverting parts of both the fuel and air to locations down stream of the main combustion zone. This leads to the creation of three combustion zones which can be manipulated to reduce NO<sub>x</sub> emissions (Fig. 2.5). In the primary combustion zone about 80-90 % of the fuel is burned in an oxidising atmosphere thus accounting for the majority of thermal input to the system and is where the bulk of NO species are formed. The second stage or reburn zone is where the rest of the fuel is introduced to the system to give an overall fuel rich stoichiometry which favours the destruction of NO to form N<sub>2</sub> (and other nitrogenous species, namely, HCN and NH<sub>3</sub>).

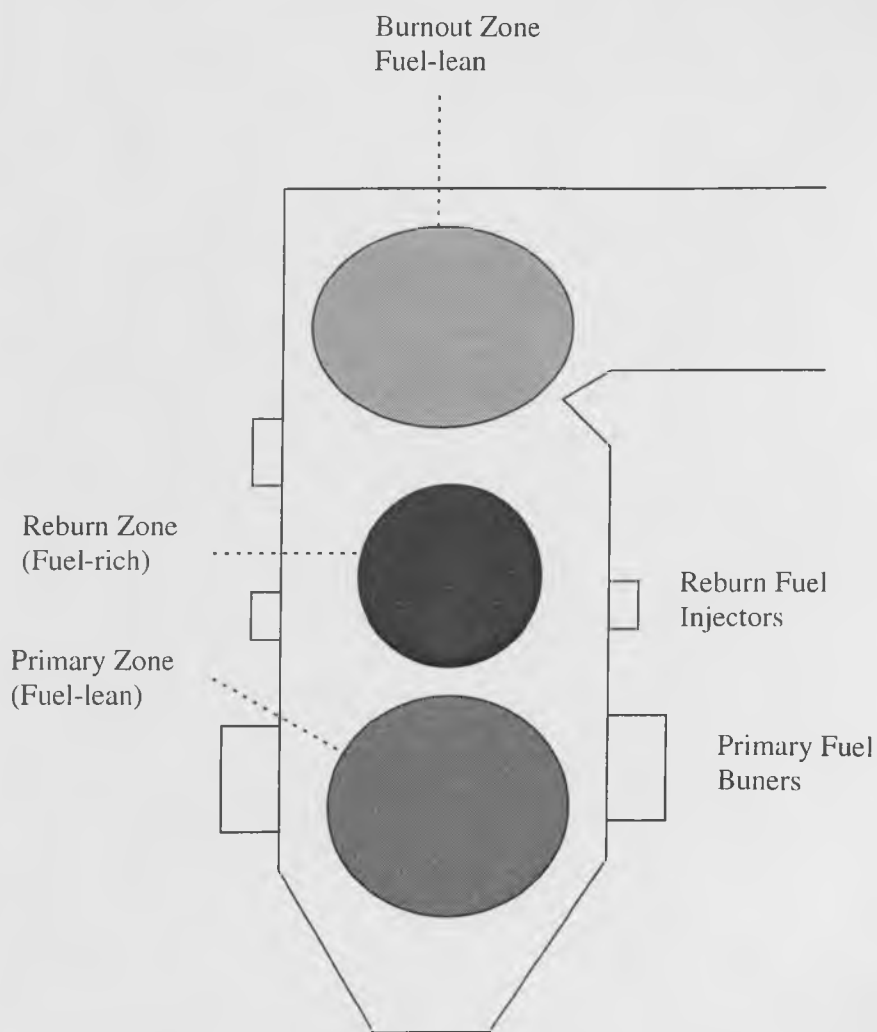
The first major kinetic barrier is the conversion of NO to HCN by reaction with various hydrocarbon fragments. Reactive nitrogen enters this zone from the primary stage and, if the reburn fuel contains nitrogen e.g. coal, from the reburning fuel. These reactive nitrogen species then react with the hydrocarbon fragments (CH and CH<sub>2</sub> radicals) produced by the break up of the reburning fuel due to the excess oxygen from the first stage to produce intermediate species such as HCN and NH<sub>3</sub>. One key example of such a reaction is given by Chen *et al.* (1986).



other reactions which also contribute to the destruction of NO include :

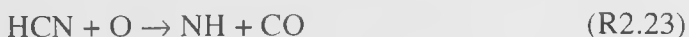
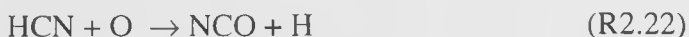






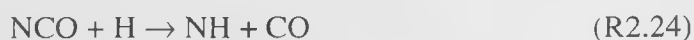
**Figure 2.5** Reburning configuration on a wall-fired boiler

Since the rate constants for all three reactions are roughly within one order of magnitude (Miller and Bowman, 1989), the dominant mechanism in the conversion of NO to HCN is strongly dependent on the relative concentrations of the reducing species produced. The end product, however, is always HCN regardless whether it was formed directly or by rapid conversion of intermediate species such as CN. (Burch *et al.*, 1990). The second major reaction step is the conversion of HCN to other nitrogenous species via the following reactions: (Miller and Bowman, 1989)



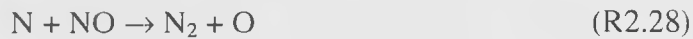
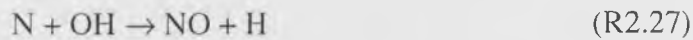
These and other similar reactions combine to give an effective NO<sub>x</sub> reduction in the second stage. Although these initial hydrocarbon attacks result in a reduction of NO, the total fixed nitrogen (TFN is the sum of all nitrogen-bearing compounds except N<sub>2</sub> i.e. NH<sub>3</sub>, HCN, NO and char nitrogen) is not reduced and other reactions must follow if NO is ultimately to be converted to N<sub>2</sub>.

After the second major reaction step the subsequent conversion to N atoms is very fast and occurs through the rapid decay of NCO → NH → N (Chen *et al.*, 1986)





The N atoms are then either recycled to form NO or are converted to N<sub>2</sub> via the reverse Zeldovich reaction :



In the third or burnout stage additional air is introduced to complete the combustion by eliminating any residual hydrocarbons from the furnace exhaust and to produce an overall lean environment (Greene *et al.*, 1986; Bartok *et al.*, 1990). The TFN species are converted to either NO or N<sub>2</sub>. When coal is used as reburn fuel the fuel-bound nitrogen in the coal is thought to produce too much HCN and NH<sub>3</sub>, which would be partly converted to NO in the lean stoichiometry of the burnout stage (Burch *et al.*, 1994).

In a typical coal reburning application, the first stage coal flame would be operated fuel lean thus promoting a high conversion of fuel-N to NO. Since coal contains a relatively high percentage of inherent nitrogen, the NO<sub>x</sub> concentration at the exit of the first stage could exceed 1000 ppm. However, other fixed-nitrogen compounds such as HCN and NH<sub>3</sub> are minimal due to the lean stoichiometry.

Each of the three zones created by the introduction of secondary fuel and air streams are governed by a number of operational variables such as type of reburn fuel, stoichiometry, temperature and residence time in the reburn zone; all of which affect

the outcome of reburning i.e. the degree of NO<sub>x</sub> reduction or reburning effectiveness. These variables play an important role in determining the outcome of the reburning process and because some are interdependent, the effect of one variable will surely influence other variables. Thus it is important to identify all the process variables and examine their effects separately. A review of the effects of different variables on the effectiveness of reburning in reducing NO concentrations is presented in the following section.

## **2.5 Parameters Affecting Reburning**

Each of the three combustion zones in the reburning process has a number of parameters influencing it. These parameter will be reviewed separately according to the zone they are associated with. The full range of parameters in each zone are considered in the following sections. This review applies to all fuel types i.e. gas, oil and coal.

### **2.5.1 Primary Zone Parameters**

In this first stage of reburning the primary fuel is burned under fuel lean conditions and NO<sub>x</sub> is produced along with other combustion products. The key process variables affecting this zone are:

**Stoichiometry:** Variation in primary zone stoichiometry has been shown by many researchers (Greene *et al.*, 1986; Kelly *et al.*, 1983) to have very little effect on reburning effectiveness. However, it is desirable to maintain a low primary zone stoichiometry in order to reduce the amount of fuel which would be required to produce the desired reburn zone stoichiometry, and therefore reducing the possibility

of having fuel pockets around the reburn fuel jet that would cause variations in local stoichiometry (Baldacci *et al.*, 1989; McCarthy *et al.*, 1988). Other advantages of having low primary zone stoichiometries include increased peak flame temperatures, increased reburn zone residence times and reduced primary NO<sub>x</sub> formation (Overmoe *et al.*, 1986). Nevertheless, a certain amount of oxidant is required in the reburn zone to initiate the generation of hydrocarbon radicals from the reburning fuel (Merson, 1975). Also oxygen containing radicals promote the conversion of HCN to NH<sub>3</sub>. However, if the oxygen level is too high, formation of CO will be favoured compared to hydrocarbon radical formation, and the reduction of NO will be diminished (Glarborg, 1990).

Various studies have shown that as long as the primary zone is operated fuel lean, changes in the primary zone stoichiometry causes no real detrimental effect on reburning effectiveness. Kelly *et al.* (1983) obtained slightly better reductions of NO<sub>x</sub> at lower stoichiometries, whereas, Yang *et al.* (1986) showed that higher stoichiometries might improve reburning effectiveness. Greene *et al.* (1985) studied the effect of varying the primary zone stoichiometry at constant residence time and constant primary NO levels where he found no significant changes in reburning effectiveness at two primary NO levels of 170 and 570 ppm. However, the effect of the primary zone stoichiometry cannot be examined separately since any change in the stoichiometric ratio would introduce changes to other reburning parameters, such as temperature and residence time.



Generally researchers (Kipinen *et al.*, 1990; Greene *et al.*, 1986) have concluded that provided the primary zone is operated fuel lean ( $SR_1 = 1.05-1.10$ ) there is little effect of varying the primary zone stoichiometry on reburning effectiveness.

**Fuel Type:** Different types of primary fuels have generally been used on reburn applications but have not had a direct effect on reburning effectiveness. Primary fuels used range from the nitrogen free gas fuels to liquid fuels with moderate amounts fuel nitrogen and solid fuels containing substantial amounts of fuel nitrogen. There will be a greater potential for a fuel containing more fuel nitrogen to form  $NO_x$  than the N free fuels. On the other hand, fuels containing more fuel nitrogen would be able to produce HCN by virtue of their high nitrogen content and thus capable of reducing NO to  $N_2$  (Smart and Morgan, 1994). Also reaction times for the three types of fuels are different with the reactive gaseous fuels requiring shorter times to fully burn than both the liquid and solid fuels; the solid fuels having the longest reaction times. Reaction time in reburning is translated into residence time which along with primary NO are known to influence reburning effectiveness.

**NO Concentration:** The NO concentration formed in the oxidising conditions of the primary zone determines the amount of NO entering the reburn zone (assuming the reburn fuel is N-free), and as such acts as an important parameter that affects the overall effectiveness of the reburning process. The primary fuel determines to some extent the primary zone NO level together with temperature and stoichiometric ratio in that zone.

Early large scale investigations carried out by Takahashi *et al.* (1983) on the application reburning to boilers indicated that NO destruction was independent of primary NO levels. This was shown later to be incorrect by several researchers (Lanier, 1984; Mulholland and Hall, 1986; Greene *et al.*, 1985; Chen *et al.*, 1986; Lanier *et al.*, 1986; McCarthy *et al.*, 1988; Miyamae *et al.*, 1986). They found a direct relationship between the primary NO concentration and the amount of NO reduced, especially at low levels of primary NO.

Lanier (1984) was the first to point out that NO reduction is not first order with respect to initial NO and his results showed that NO reduction decreased with lower primary NO. Lanier *et al.* (1986) later showed that the overall NO destruction rate has a partial order with respect to primary NO between 1.5 and 1.6. The strong dependence of NO destruction mechanism on primary NO was also reported by Mullholland and Hall (1986, 1987) who found that at low levels of primary NO, 50% reduction was limited by the nitrogen content of the reburn fuel i.e. for initial NO level of 200 ppm and less, reburning fuel nitrogen should not exceeding 1 percent for a 50% reduction to be plausible. Reburning fuels containing more than 1 percent nitrogen resulted in an increase in NO emissions for an initial NO level of 200 ppm. And for high initial NO levels, greater than 500 ppm, he found that the presence of fuel nitrogen enhances NO reduction to N<sub>2</sub>. Chen *et al.* (1986) also reported a decrease in NO reduction at low primary NO which he also attributed to the oxidation of the fuel nitrogen in the reburning fuel, however, at normal primary NO level and 20% reburning a 50% reduction in NO emissions was observed.

The dependence of reburning effectiveness on the primary NO level is expected since the destruction of NO by hydrocarbon radicals to form HCN depends on the initial NO concentration. Furthermore, HCN and NH<sub>3</sub> are partially oxidised to form NO in the final stage of reburning. At primary NO levels below 200 ppm, an added complication might be the formation of additional HCN as a result of N<sub>2</sub> fixation by hydrocarbon radicals (Fenimore, 1971), mainly due to CH + N<sub>2</sub> reaction. Thus, NO and N<sub>2</sub> may compete for the consumption of hydrocarbon radicals as the primary NO concentration decreases.

**Residence Time:** Primary zone residence time is an important parameter since it establishes the primary zone burnout, the reburn zone location and hence reburn fuel injection temperature, and reburn zone residence time. All three parameters affect reburning effectiveness.

Reducing the primary zone residence time should in principle enhance NO reduction since the reburn fuel would be injected into a high temperature zone where higher chemical reaction rates are favoured. However, experiments by Chen *et al.* (1986) on different coals indicated that decreasing the primary zone residence time from 330 ms to 70 ms had a significant detrimental impact on reburning effectiveness. This was basically due to the significant increase in the effective reburn zone stoichiometry (SR<sub>2</sub>) which was caused by the incomplete burnout in the primary zone and the carryover of excess oxygen into the reburn zone. Thus, although it is essential to have the reburning fuel injectors placed as close to the main burner as possible, a large enough primary zone residence time is important to ensure that NO<sub>x</sub> formation is completed and available reactive oxygen is consumed.

## 2.5.2 Reburn Zone Parameters

The reburn zone is the second stage of the reburning process, created by injecting a secondary fuel downstream of the main combustion zone. The reburn zone stoichiometry is normally fuel rich thus providing a reducing environment which encourages the destruction of NO by hydrocarbon fragments such as CH and CH<sub>2</sub>. The operating parameters which influence the balance between NO forming and releasing reactions are of critical importance to the entire reburning process.

**Stoichiometry:** The reburn zone stoichiometry is the controlling parameter in NO<sub>x</sub> reduction in the reburning zone since it dictates the amount of hydrocarbon radicals present in that zone and thus the extent of NO<sub>x</sub> reduction. It also controls the oxygen concentration in the reburning zone which is required to convert HCN (formed during hydrocarbon radical reaction with NO) to NCO.

The reburn zone stoichiometry is affected by factors such as mixing and temperature, however, the overriding effect comes from the primary stoichiometry, the carrier-gas stoichiometry, and the reburn fuel fraction. All three parameters combine to give a single parameter, the secondary stoichiometry. An optimum value for the reburn zone stoichiometry is one which corresponds to a maximum reduction in NO<sub>x</sub> emissions. Researchers have given contrasting values for the optimum reburn zone stoichiometry, however, almost all agreed on the need to have an overall fuel rich environment in this stage of the reburning process.

Typical values of optimum reburn zone stoichiometries range from 0.8 to 0.9 (Chen *et al.*, 1986; Green *et al.*, 1985; Kolb *et al.*, 1988; Knill and Morgan, 1990; Chen *et*

*al.*, 1983). However, the results of Mulholland and Lanier (1985) and Mulholland and Hall (1986) in a package boiler simulator indicate that an optimum reburning effectiveness might be attained at reburn zone stoichiometries below 0.7. On the other hand, bench scale reburning tests by Miyamae *et al.* (1986) and Myerson (1975) indicated that reburn zone stoichiometries above 0.94 were most effective. This difference in optimum reburn zone stoichiometry could be attributed to the size of the combustor which in effect influences the mixing behaviour. Large scale experiments normally exhibit poor mixing which can create large variations in local stoichiometries. Lafond and Chen (1987) hypothesized that reburning effectiveness would be greatly influenced by stoichiometry and higher reductions would be possible, as the size of the system decreased. Miyamae *et al.* (1986) also reported that NO<sub>x</sub> reduction in pilot furnaces is better than that in full size furnaces. Thus the location of the optimum reburn zone stoichiometry is clearly dependent on furnace dimensions as well as other factors such as residence time and temperature.

**Reburning Fuel Type and Nitrogen Content:** The introduction of the reburn fuel to the second stage of the reburning process has a twofold effect; it creates a fuel rich environment which promotes the destruction of NO through a path which favours N<sub>2</sub> formation, and it provides a source of hydrocarbon radicals which initiates the destruction of NO. This makes the secondary fuel an important element in the reburning process with both the nature and chemical properties of the fuel having a significant effect on reburning effectiveness.

Greene *et al.* (1986) showed that from a variety of reburning fuels, ranging from hydrocarbon (propane) and nonhydrocarbon (CO and H<sub>2</sub>) gaseous fuels to different



rank and nitrogen content coals, propane was the most effective at reducing NO. This was attributed to the rapid formation of CH fragments which convert primary NO to HCN and NH<sub>3</sub>. Both CO and H<sub>2</sub> failed to produce enough HCN and NH<sub>3</sub> in the reburn zone. Similar results were reported by Chen *et al.* (1986). With regards to solid fuel reburning, the Yallourn coal was the most effective due to its low fuel nitrogen content and high volatility. However, reburning effectiveness decreased with increasing fuel nitrogen indicating that reactive nitrogen present in the coal was contributing to exhaust NO<sub>x</sub> emissions. This effect was confirmed by Mulholland and Hall (1986) who doped natural gas with ammonia and found that exhaust NO<sub>x</sub> emissions increased in proportion to ammonia doping. Chen *et al.* (1986) also reported that introducing fuel nitrogen into the system with the reburning fuel would effectively be similar to proportional increase in primary NO; thus indicating that total nitrogen (from both primary and reburn fuels) conversion to NO<sub>x</sub> was independent on fuel type. A similar observation was made by Smart and Morgan (1994).

The volatility of the reburning fuel which is a measure of reactivity was also shown to have an effect on reburning effectiveness. Greene *et al.* (1986) compared reburning with coal to reburning with propane doped with ammonia to the same nitrogen content as the coal. The gaseous reburning fuel gave better results. Recently, Liu *et al.* (1995a) investigated the effect of reburning with a char of a gasified coal and compared it to reburning, under the same conditions, with its parent coal. The results indicated that the volatile fraction of a particular coal is more effective than the remaining char in destroying NO<sub>x</sub>.

**Reburn Fuel Fraction:** The amount of reburn fuel is an important parameter for both the reburning effectiveness and the process economy. This is because it has a direct effect on the optimum stoichiometry in the reburn zone and also controls the amount of hydrocarbon radicals present in that zone. The quantity of fuel required to produce the radicals is not yet known conclusively, however, results from different researchers (Greene *et al.*, 1986; McCarthy *et al.*, 1988; Kilpinen *et al.*, 1990; Chen *et al.*, 1986) indicate that under most practical conditions the optimum amount of reburn fuel is 10-20% of the total fuel input, corresponding to an optimum reburn zone stoichiometry of approximately 0.9.

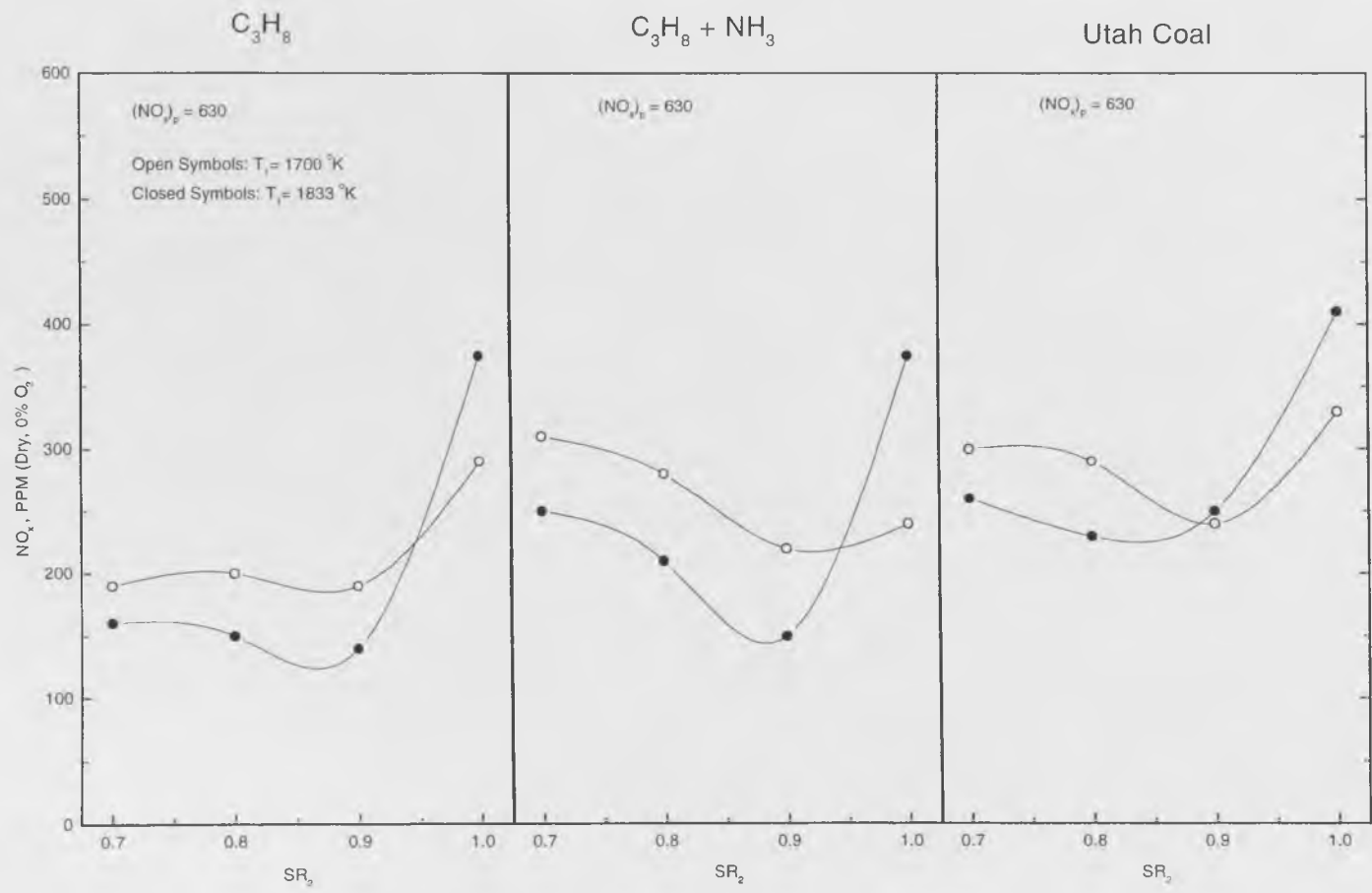
**Temperature:** Although the direct effect temperature in the reburn zone requires further investigation, it does not appear to influence reburning effectiveness to the extent that was once thought. Initially there was a general agreement (Myerson, 1975; Lanier, 1984; Greene *et al.*, 1986) that higher temperatures in the reburn zone can enhance reburning effectiveness under most conditions. The results of Mulholland and Hall (1987), however, indicated that as the reburning temperature increased from 1300-1600 K the reduction of NO to N<sub>2</sub> in the burnout zone was accelerated. The conversion of N<sub>2</sub> to NO was also accelerated, but the net effect was a shift in equilibrium favouring N<sub>2</sub> formation. This apparent advantage was offset by higher conversion of the remaining TFN to NO at elevated temperature in the burnout zone. The result is typically no net effect on NO concentrations at the burnout zone exit.

Although the direct effect of temperature is small, secondary effect related to temperature can be significant. NO destruction in the reburn zone is mostly due to

both  $\text{NO} + \text{CH}_i$  and  $\text{NO} + \text{NH}_i$  reactions. The temperature dependence of the kinetic rate coefficients of these reactions (Glarborg *et al.*, 1986; Miller and Bowman, 1989) show that NO destruction by  $\text{CH}_i$  species is favoured at higher temperatures, whereas, NO destruction by  $\text{NH}_i$  species is favoured at lower temperatures. Furthermore, higher temperatures promote the decay of HCN due to reactions with O and OH radicals. The effect of temperature on HCN is possibly the dominant factor in the reburn zone, since HCN is an intermediate in the path that favours  $\text{N}_2$  formation under fuel rich conditions.

Another secondary temperature effect investigated by Greene *et al.* (1986) is the apparent shift in optimal stoichiometry with reburning temperature changes. His results (Fig. 2.6) show that as the reburn zone stoichiometry approached the fuel lean side (greater than 0.95), lower temperatures produced higher NO reductions and thus higher reburning effectiveness. This is partly due to the low concentrations of HCN and hydrocarbons (radicals) normally present when the reburn zone stoichiometry is close to the fuel lean side.

In the case of coal reburning Chen *et al.* (1986) found that with pulverised coal, significant heat removal from the fuel rich reburn zone was beneficial with respect to overall  $\text{NO}_x$  emissions and postulated that selective reduction of NO by  $\text{NH}_3$  in the burnout zone was responsible. However, if the reburn coal is injected into a notably cool reburn zone (below  $930^\circ\text{C}$ ) significant quantities of fuel nitrogen will be retained in the char and subsequently converted to NO in the burnout zone.



**Figure 2.6** Influence of reburning zone temperature and stoichiometry (Greene et al., 1986)

**Mixing Rate and Injection Momentum:** The mixing of the reburn fuel with the primary effluent is an important parameter in the reburning process since it has a significant impact on NO<sub>x</sub> emissions. Mixing can limit the destruction of NO by hydrocarbon radicals generated from the reburning fuel, since mixing affects the contact of primary zone NO with the secondary fuel radicals. It also affects the contact of the reburning fuel with oxygen from the primary zone and consequently, the decomposition of the reburning fuel to reducing radicals. And it controls the overall conversion of any reburning fuel nitrogen to NO<sub>x</sub> as well as the oxidation of any gas or solid phase nitrogen species leaving the reburn zone. Thus, effective mixing and greater dispersion of the reburning fuel in the fuel rich secondary zone is a prerequisite for better NO<sub>x</sub> reduction efficiency and therefore improved reburning effectiveness (Chen *et al.*, 1986; Miyamae *et al.*, 1986; Overmore *et al.*, 1986; Kolb *et al.*, 1988; Mereb and Wendt, 1990; Knill and Morgan, 1990; Kicherer *et al.*, 1994).

Overmore *et al.* (1986) investigated the effect of different fuel jet velocities, penetration depths, and entrainment rates on reburning effectiveness. They concluded that increasing jet penetration and mixing would result in reduced NO<sub>x</sub> emissions, however, the effect of primary NO<sub>x</sub> levels were found to increase. Using natural gas as a reburn fuel in a 3 MW down-fired furnace, Chen *et al.* (1986) demonstrated that improved and rapid mixing conditions in the reburn zone had a clear and positive influence on reburning effectiveness. However, they argued that for nitrogen containing reburning fuels such as coal, there exists a trade-off between high dispersion rates to achieve effective incineration of primary NO<sub>x</sub> and low

reburning jet mixing rates to minimise the conversion of reburning fuel nitrogen. The use of an inert gas carrier, such as  $N_2$  or FGR, was recommended to reduce the oxidation of the reburning fuel and thus decrease the conversion of fuel nitrogen to NO, while maintaining rapid dispersion of the reburning fuel.

In another study, Kolb *et al.* (1988) suggested that insufficient mixing would result in slow entrainment of primary NO<sub>x</sub> thus creating local fuel lean regions where NO reduction would not be favourable, and fuel rich pockets where hydrocarbon radicals reacted with NH<sub>3</sub> to produce HCN rather than reacting with primary NO to give N<sub>2</sub>. This resulted in high concentrations of HCN in the reburn zone which was eventually transformed to NO in the burnout zone. Greene *et al.* (1986) concluded that improved mixing would be beneficial to the reburning process because it allowed for more hydrocarbon and primary NO interaction before the consumption of the reburn fuel. Consequently, less fuel rich pockets would be formed in the reburn zone, less nitrogenous species and less NO in exhaust. Furthermore, improved fuel and oxygen contact produced higher temperatures in the reburn zone. However, when the reburn zone was operated under fuel lean condition, local fuel rich regions around the fuel jet arising from the diffusion nature of the reburn fuel flame resulted in up to 20% reduction in NO emissions.

The impact of mixing is more severe as the scale of the system increases, because of the large distances across which mixing must occur and it is harder to achieve adequate mixing. The results of Myerson (1975) and Miyamae *et al.* (1986) suggest that reburning in small, well mixed bench scale systems can create sharp dependencies on stoichiometry in the reburn zone. Also NO reduction, higher than



80%, would be possible. Results on large scale systems typically result in lower reburning effectiveness and a broader dependence on reburn zone stoichiometry (Lanier *et al.*, 1986; Lanier and Mulholland, 1988; Knill and Morgan, 1990). Indeed, Knill and Morgan (1990) results show that for a full scale system turbulent mixing in the reburn zone would need to be very fast in order to obtain the same NO<sub>x</sub> emissions measured on bench scale systems. Chen *et al.* (1986) also demonstrated that successful scale up of reburning is possible, only if adequate mixing conditions can be maintained in the reburn zone.

Basically, poor mixing in the reburn zone can create local variations in stoichiometry which would prevent complete optimisation of the reburning process. That can produce lower reductions in overall NO emissions and a broader dependence on reburn zone stoichiometry in a practical combustor, as compared to a bench scale system, where better mixing conditions can be achieved. However, poor mixing may enhance reburning effectiveness if the reburn zone is operated fuel lean or close to the fuel lean side, where the presence of fuel rich pockets can be beneficial in destroying NO (Greene *et al.*, 1986).

**Residence Time:** Residence time requirement in the second stage is a crucial factor in the overall reduction of NO. The reburn zone residence time must be sufficiently long to allow for the TFN species to decay in the reducing environment. A short residence time, specially for solid fuels where longer reaction times are required, normally leads to a decrease in the NO<sub>x</sub> reduction efficiency, since residual nitrogen species such as HCN and NH<sub>3</sub> are easily oxidised to NO<sub>x</sub> by additional O<sub>2</sub> in the burnout zone (Miyamae *et al.*, 1986). Gaseous fuels such as propane, however, tend

to react immediately after injection and hence require shorter residence times (Kicherer *et al.*, 1994).

The necessary residence time in the reburn zone is determined by the mixing time and the required reaction time (Glarborg, 1990). Primary NO level and temperature in the reburn zone can also affect residence time requirement. If the temperature in the reburn zone is increased, HCN and NH<sub>3</sub> decay is enhanced and additional residence time will be required to allow these nitrogenous species to decay (Miyamae *et al.*, 1986). The results of Chen *et al.* (1986) and Greene *et al.* (1986) indicate that longer residence times are required at higher levels of primary NO.

Opinions on the minimum residence time required in the reburn zone were varied, with some studies suggesting that rapid NO reduction is possible within a short time scale of less than 0.1 seconds (Myerson *et al.*, 1975; Lanier *et al.*, 1986). However, a number of bench and pilot scale studies indicated that the reaction time for conditions typical of a pulverised coal boiler is between 0.4-0.5 seconds (Miyamae *et al.*, 1986; Chen *et al.* 1986; Boltz and Offen, 1988).

### **2.5.3 Burnout Zone Parameters**

In the burnout zone, final air is added which serves to complete the combustion process and oxidise any remaining fuel fragments. The reactive nitrogenous species (HCN, NH<sub>3</sub> and NO) enter this zone from the reburn zone. When the burnout air is added, most of this nitrogen is oxidised to NO<sub>x</sub>, however, a significant part is reduced (by reaction with NO) to N<sub>2</sub> (Lanier *et al.*, 1986).

The parameters associated with this stage are of minor significance since the overall reduction in NO is dependent on the levels and distribution of the nitrogenous species exiting the reburn zone. Nevertheless, this stage forms part of the reburn process and some effort should be made to improve and optimise its performance so as to have a positive effect on the overall reburning process.

**Temperature:** The burnout zone temperature has an important role to play in the reduction of NO if it falls within the range (850-1200 °C) (Sloss *et al.*, 1992) characteristic of the Thermal DeNO<sub>x</sub> process, and if relatively high levels of NH<sub>3</sub> exit the reburn zone. Under these conditions, additional destruction of NO is possible by selective reduction of NO at the hand of N<sub>2</sub>H<sub>2</sub> species (Chen *et al.*, 1986). However, the low temperatures associated with this process are too low for any practical application in reburning, and such low temperatures could also prevent complete burnout of the uncombusted fuel leaving the reburn zone.

**Excess Air and Mixing Rate:** The dual objectives of the burnout zone are to minimise NO<sub>x</sub> reformation and to complete burnout. Rapid and thorough mixing in this zone is therefore necessary to achieve the latter objective, and minimise pockets of unburned hydrocarbons.

The amount of air entering the burnout zone should be just enough to achieve the desired fuel burnout; an overabundance of excess air will contribute to the dry gas losses and will increase the potential for NO<sub>x</sub> reformation.

**Table 2.6** Summary of the Influence of Process Variables on Reburning Effectiveness

Parameter	Impact
<b>Primary Zone</b>	
Stoichiometry	Provided it is operated fuel lean, no effect
Fuel Type	No direct effect; can influence through temperature and NO <sub>x</sub> concentration entering the reburn zone
NO Concentration	Strong effect; more difficult to reduce lower levels of primary NO <sub>x</sub>
<b>Reburn Zone</b>	
Stoichiometry	Major influence; optimum level dependent on size of combustor
Mixing Rate	Faster mixing preferred
Fuel Type	Hydrocarbon fuels more effective; fuel-N content detrimental at lower primary NO level
Temperature	conflicting results; needs further investigation
Residence Time	Varied depending on type reburn fuel; for coal reburning optimum range between 0.4-0.5 seconds
Carrier Gas	Inert transport (O <sub>2</sub> free) desirable since less reburning fuel is required to attain optimum stoichiometry
<b>Burnout Zone</b>	
Excess Air	Not important , except to achieve the desired fuel burnout
Mixing Rate	Not important; good mixing desirable
Temperature	Not important unless is dropped to 850-1200 °C where selective NH <sub>i</sub> -NO reaction can take place to enhance reduction

## 2.6 Cost of Various Abatement Strategies and Reburning Economics

The costs of various NO<sub>x</sub> control technologies vary a great deal which make cross referencing difficult, if not impossible. This variation is mainly due to differences in design, plant size, fuel properties, baseline NO<sub>x</sub> emissions, new or retrofit, operating hours, etc. Accountancy procedures such as interest rates and exchange rates variation also play a part in the variability of costs estimates. However, the Electrical Power Research Institute (EPRI) in the United States and other bodies are developing comparative costing procedures for emission abatement systems (Hjalmarsson, 1990).

Table 2.3 shows reburning to be second only to SCR in NO<sub>x</sub> reduction effectiveness. However, Fig. 2.7 illustrates the high capital cost of SCR even at large boiler capacities where the cost per MW is reduced. The reburning technology shows a decline in the rating to cost ratio to a point where the large utility scale unit becomes more cost effective than if using advanced air staging. The high reduction to cost ratio of reburning is also illustrated in Table 2.5 which is based on studies undertaken by the Gas Research Institute (USA) and the Energy and Environmental Research Corporation (USA), thus confirming the potential of such a technology both on an economic and environmental point of view (Williams *et al.*, 1992). The combination of reburn and SNCR is termed Advance Reburn. The operational costs for coal reburning on a coal-fired plant are also expected to be lower than SCR systems which currently stand between 5 and 10 mills/kWh (mainly due to the high cost of NH<sub>3</sub>) for the 2-3 years guaranteed lifetimes of these systems (Offen *et al.*, 1987).

SCR: Selective catalytic reduction  
OFA: Over fire air  
PM: Pollution minimum burners

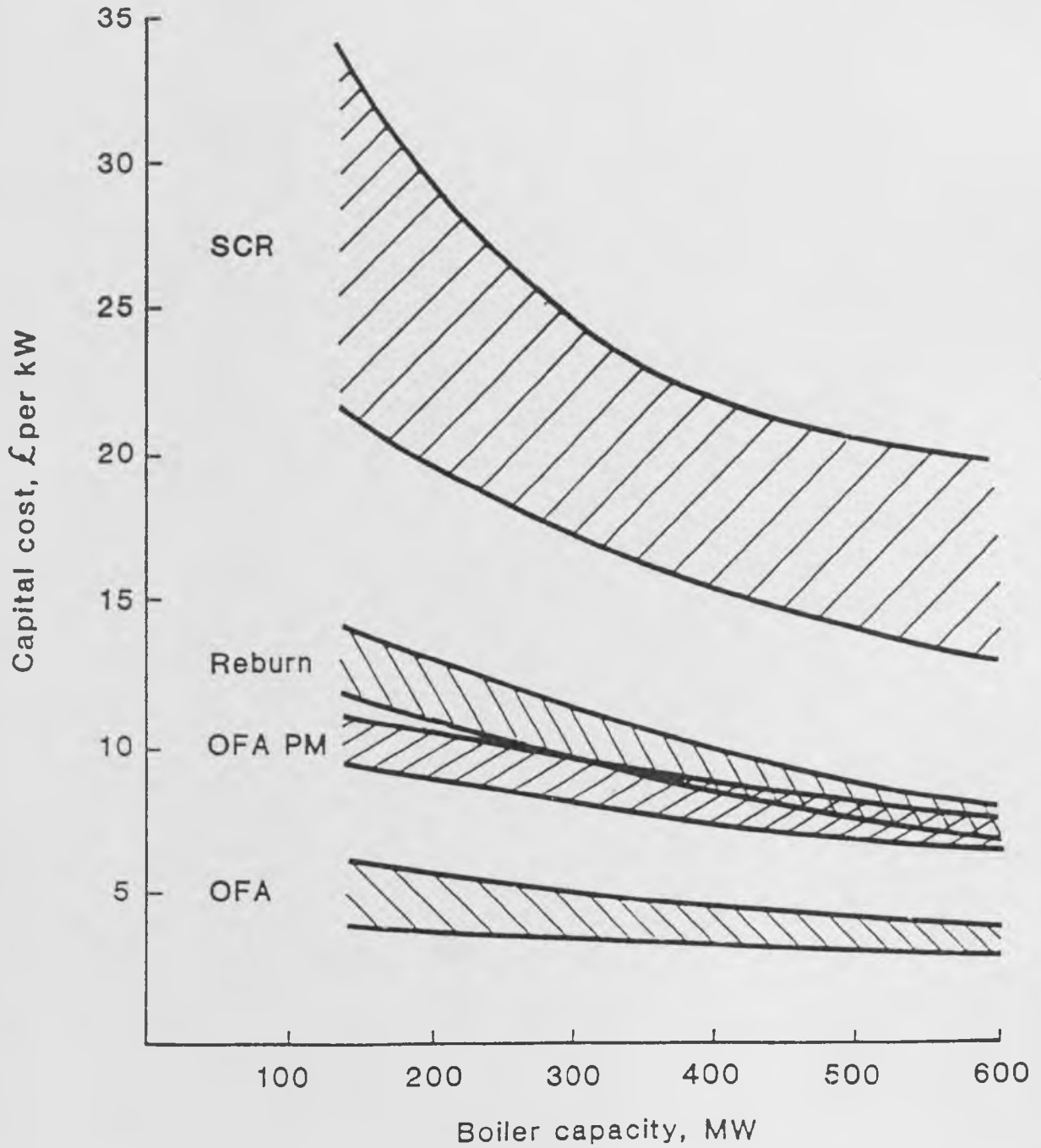


Figure 2.7 Capital Cost Comparisons for various In-Furnace NO<sub>x</sub> Reduction Techniques Applied to Wall Fired Boilers (Lisauskas *et al.*, 1987)

**Table 2.5** Capital Costs of Installing NOx Reduction Techniques on a 500MWe Boiler

Technique	NOx Reduction %	Capital Cost £'10 <sup>6</sup>
Low NOx burners	40	5
SNCR	50	3
SCR	80	20
DOFA	50	5
Gas Reburn	60	5
Advanced Reburn	85	10

The economic viability of reburning technology is also highly dependent on the relative cost of the reburning fuels (oil, gas and coal), the quantity of reburn fuel required, the on-site availability of the reburning fuel and the NOx reduction target. Applying coal reburning to a 200 MW cyclone unit to achieve a 50% NOx reduction was found to have a total capital cost and a 10-year busbar power cost of \$41.4/kW and 1.7 mills/kWh respectively (this includes costs for coal handling and pulverising/coal piping) compared to \$44/kW and 3.1 mills/kWh when using natural gas as reburn fuel (Farzan *et al.*, 1989).

## 2.7 Current Status of Reburning Research and Commercial Applications

It has been more than three decades since Myerson *et al.* (1957) discovered the reduction powers of hydrocarbons in the conversion of NOx to N<sub>2</sub>. The first commercial utilisation of this process happened in the late 1960s when the John Zink Corporation developed and patented a NOx control process for nitric acid



plants which involved the injection of natural gas in a staged manner (Reed, 1969). The process involved introducing  $\text{NO}_2$  and  $\text{NO}$  into an incinerator where they were destroyed by hydrocarbons to form  $\text{N}_2$  in a reducing environment. The first application of secondary fuel injection to reduce  $\text{NO}_x$  emissions inside furnaces was performed by Wendt *et al.* (1973) who also introduced the name “reburning” to describe the process. Myerson *et al.*, (1975) used a ceramic flow reactor to investigate  $\text{NO}$  reduction by reburning with gas. However, reburning was only established as a practical  $\text{NO}_x$  reducing method when Takahashi *et al.* (1983) reported more than 50% reduction of  $\text{NO}$ , with no negative impact on boiler efficiency, in tests at Mitsubishi Heavy Industries. The tests reported were based on extensive laboratory-, pilot-, and full-scale evaluation of a process they called Mitsubishi Advanced Control Technology, or MACT, and it was the first time reburning was applied to a large boiler. The encouraging results of MACT revived the interest in reburning as a technically and economically feasible technique for  $\text{NO}_x$  control in coal fired utility boilers.

Research was then directed towards understanding the fundamentals of reburning and its potential for large scale application. Bench and pilot scale tests were used to identify a number of operational variables, the effects of these variables on reburning, and how each variable interacts with other reburning parameters to give a more precise understanding of the process.

### **2.7.1 United States**

In the United States a number of energy related organisation tried to quicken the pace of introduction of the reburn technology on a commercial scale by sponsoring

studies aimed at developing a scaling methodology for reburning which would be suitable for boilers operating on gas, oil, or coal. Some of these organisations include the Department of Energy (DOE), the Environmental Protection Agency (EPA), the Electrical Power Research Institute (EPRI), and the Gas Research Institute.

The Energy and Environmental Research Corporation, under contracts with Environmental Protection Agency (EPA), the Gas Research Institute, and the Department of Energy (DOE), started a research program aimed at characterising the fundamental processes involved in reburning and thus provide the scaling information required for commercial application of reburning; especially for U.S. designed boilers. Chen *et al.* (1983) first conducted bench-scale studies on coal and gas as reburning fuels to investigate the effectiveness of the reburning process. Overmoe *et al.* (1986) then studied the impact of process variables on NO<sub>x</sub> reduction using a pilot scale furnace where realistic mixing phenomenon were involved. Chen *et al.* (1986) and MacCarthy *et al.* (1988) both used a 25 kW bench-scale furnace and a 3 MW pilot-scale furnaces to investigate reburning for a range of fuels. Greene *et al.* (1986) carried out full range parametric investigation of key process variables in a 24 kW bench-scale Control Temperature Tower. Bartok and Folsom (1988) combined gas reburning with sorbent injection for a cost effective reduction of both NO<sub>x</sub> and SO<sub>x</sub>. Heap *et al.* (1988) and Chen *et al.* (1989, 1991) combined reburning with ammonium sulphate injection to achieve over 80% NO<sub>x</sub> reduction and named the process 'advanced reburning'. Field evaluation involving

gas reburning and sorbent injection was undertaken by EER (Folsom *et al.*, 1991) on three coal fired utility boilers achieving 70% NO<sub>x</sub> reduction.

At the Acurex Cooperation Kelly *et al.* (1983) used a 16.1 kW bench-scale combustor to study the benefits of fuel staging using coal as reburn fuel. Mulholland and Lanier (1985) experimented on a 730 kW firetube package boiler where dominant process variables were identified. While Srivanstage and Mulholland (1988) applied fuel staging to both burner and boiler achieving an overall NO<sub>x</sub> reduction of 84%.

At the Environmental Protection Agency (EPA) Mulholland and Hall (1986) investigated the effect of volatile fuel-bound nitrogen in reburning application to a 0.73 MW pilot-scale firetube package boiler. Later Mulholland and Hall (1987) used two pilot-scale firetube package boilers to investigate key parameters and their impact on the reburning process.

The contribution to this field of study also came from organisations such as universities, companies manufacturing power plant units, power generation authorities, and so on. All of which added to the clear understanding of the reburning process and the reaction mechanisms involved. Burch *et al.* (1990, 1991) investigated the reduction and formation mechanisms of NO in the second stage of the reburning process, with emphasis on the distribution of nitrogenous species, using a bench-scale ceramic flow reactor. Burch *et al.* (1994) later simulated a reburning environment using the same flow reactor to study the interaction of fuel nitrogen from coal with NO. Mereb and Wendt (1990) investigated the formation, inter-conversion and destruction of all nitrogenous species in the fuel rich reburning

zone of a pulverised coal combustor with natural gas as reburn fuel. Using the same coal combustor Mereb and Wendt (1991, 1994) used both air staging and reburning tests to predict time resolved profiles of all nitrogenous species and incorporated their results into more complicated furnace models to predict NO emissions. Wendt and Lin (1994) studied the destruction of NO in a laminar counter flow diffusion flame under overall fuel lean conditions. They concluded that since there exists local fuel rich regions, significant NO destruction was achieved by reburning without the need to operate under reducing condition which on the long run could have adverse effect on the boiler.

At Riley stoker Corporation a 0.88 MW pilot-scale combustion facility along with a full-scale 29.3 MW burner test facility were used to investigate the effectiveness of natural gas and coal as reburning fuels (McHale *et al.*, 1988). At the same company a gas reburn process was developed for application to Municipal Solid Waste (MSW) combustion system (Penterson *et al.*, 1989). At Babcock and Wilcox Company (B&W), Farzan *et al.* (1989) demonstrated successfully the effectiveness of reburning on a pilot-scale cyclone boiler by achieving 67% NO<sub>x</sub> reduction for gas and oil reburning, and 57% for coal reburning. Cyclone boilers are prime candidates for fuel staging since they produce the highest NO<sub>x</sub> emissions than other boiler design and any modifications to the cyclone chambers are counter productive (Cioffi, 1989). Typical delayed combustion techniques are not applicable to cyclones because they rely on developing an oxygen deficient or reducing atmosphere to hamper NO<sub>x</sub> formation. A reducing condition in the confines of a cyclone barrel is unacceptable due to the potential for tube corrosion and severe maintenance

problems. Cyclone operation must occur under excess oxygen conditions and because reburning occurs while the cyclone operates in a normal oxidising condition, its effect on cyclone performance can be minimised. Efforts were then focused at establishing a scaling methodology for reburning on a 100 MWe power station boiler (Farzan *et al.*, 1991). By end of 1991 the reburn system startup was initiated at Wisconsin Power Generating Station Unit 2 which is the world's only application of the Cyclone reburn technology using pulverised coal as a reburn fuel (Maringo *et al.*, 1994). It is currently fully integrated into the routine operation of the unit achieving up to 62% reduction in nitrogen oxide emissions without adverse effect on the other operating parameters of the unit. While at Combustion Engineering, Borio *et al.* (1989) reported initial studies on a 108 MW cyclone boiler which will be modified for natural gas reburning.

### **2.7.2 Japan**

The Japanese experience started by developing the MACT process and applying it to full-scale practical power station units. The initial stages of development included bench-, pilot-, and large-scale testing. The bench-scale work focused on the fundamental reactions involved during reburning, mainly the decomposition of NO and various process parameters which influences it. Tests on this scale were performed using two electrically heated porcelain tubes and the results obtained were encouraging enough to prompt pilot-scale testing. These tests were carried out on a 1.37 MW vertical furnace with tangential firing using coal, oil and gas. The pilot-scale study was aimed at investigating the influence of fuel nitrogen content on NO<sub>x</sub> reduction as well as determining the combustion efficiency and the effect of the

reducing environment, imposed by this process, on boiler performance. Large-scale testing then followed on a 11.6 MWt furnace which was fired tangentially using three low NO<sub>x</sub> burners at each corner and at three firing elevations .

The MACT concept was finally applied to an existing 120 MW power plant and the demonstration was so successful that the technology is being applied to almost all new and to-be-modified boiler units of medium steam rate. Currently, 23 plants use MACT and several large units of over 500 MW as well as other smaller units are under preparation and design (Fujima *et al.*, 1990; Takahashi *et al.*, 1983).

### **2.7.3 Europe**

The European scenario has seen increasing interest in research and development on reburning technology in recent years, with Italy and Germany leading the way. The Italian Power Authority (ENEL) in collaboration with ABB Combustion Engineering of the United States initiated a comprehensive program in the late 1980s to evaluate the effectiveness of reburning with the aim of applying it to both new and existing tangentially-fired boilers (Baldacci *et al.*, 1989; Laflesh *et al.*, 1991; Ligasacchi, 1990). Research was carried out on three scales: a 50 kWt bench-scale furnace, a 15 MWe pilot-scale boiler simulator and a 35 MWe tangentially-fired power plant unit. Following the successful demonstration on the 35 MWe unit, ENEL has initiated full commercial operation of reburning on a number of tangentially-fired boilers and it is reported to be going very well.

In Germany, a great deal of interest has been shown in the application of reburning and a lot of the ground work as already been done. Kolb *et al.* (1988) used a 300 kW

furnace to demonstrate the effectiveness of natural gas as a reburn fuel and studied the effect of mixing and jet momentum on NO<sub>x</sub> reduction. With coal reburning in mind, Sybon *et al.* (1990) used the same combustor to investigate the effect of reburn fuel nitrogen content on NO<sub>x</sub> reduction by doping the reburn fuel (natural gas) with ammonia. Kremer *et al.* (1990) used an electrically heated cylindrical chamber with coal as primary fuel and natural gas as reburn fuel to find the optimum mixing conditions in the reburn zone. The use of coal as a reburn fuel was also demonstrated by Kircherer *et al.* (1994) on a 0.5 MWt pulverised fuel rig. Other studies include the use of coal pyrolysis gas as reburn fuel (Greul *et al.*, 1995), and more recently studies geared at reducing NO<sub>x</sub> emissions from both dry-bottom and slag-tap firing systems using reburning (Spliethoff *et al.*, 1995 & 1996). However, commercial application of reburning on coal fired units has been limited. This is mainly due to the severe emission limits applicable to coal fired plants over 300 MWt which are the most stringent in the world, and the inability of coal reburning to meet these limits (200 mg/m<sup>3</sup> ~ 100 ppm). Combining low-NO<sub>x</sub> burners with reburning could be the answer, however, 100 ppm is a very low limit and difficult to achieve in coal fired power plants without the use of flue gas treatment e.g. SCR.

Research work on reburning has also been done in the Spain, the Netherlands (as part of the combustion program under the International Flame Research Foundation, IFRF) and Scandinavian countries such as Denmark, Sweden and Finland (Bilbao *et al.*, 1994; Kilpinen *et al.*, 1990 & 1992; Collin and Goransson, 1990 & 1991; Knill and Morgan, 1989 & 1990; Smart and Morgan, 1994).

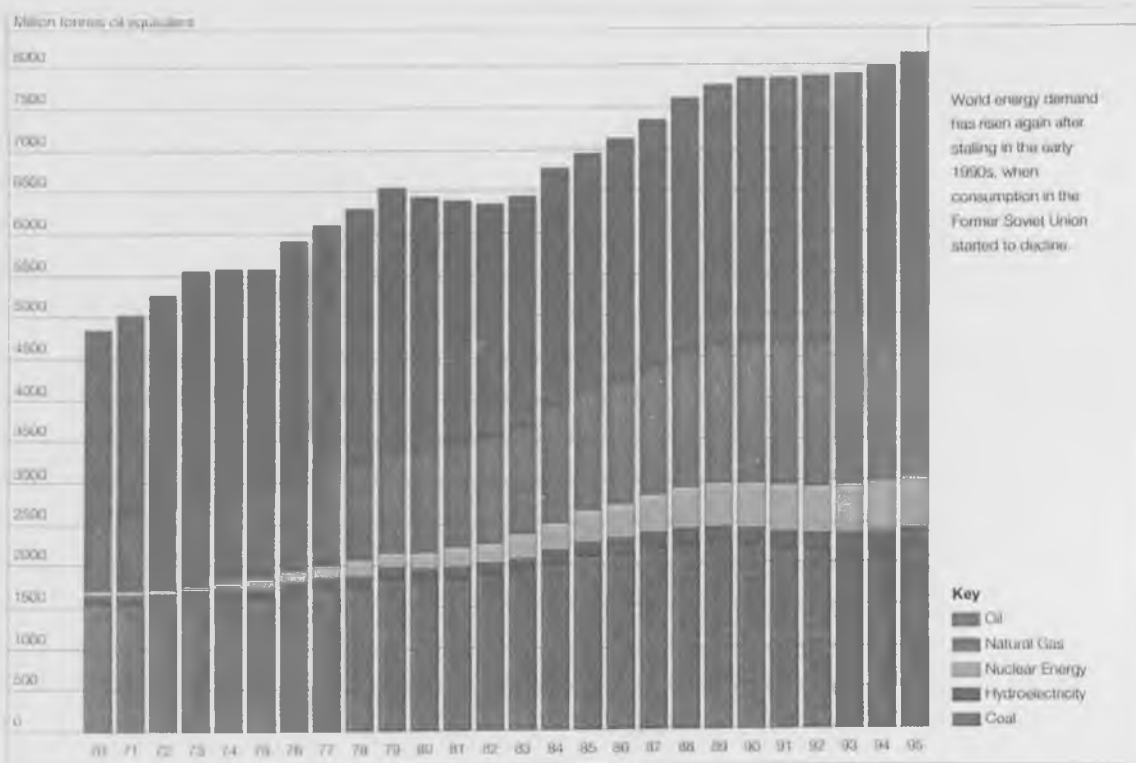


In the UK, reburning has attracted comparatively very little attention, however, the situation is changing with many of the big generating companies showing some interest in this technology. Powergen (UK) is currently involved in a Thermie supported project at Vado Ligure in Italy which involves applying the reburning technique to a 320 MWe coal-fired boiler. Initial design and modeling work has been completed and building is said to have started in December 1996. Powergen have also experimented with orimulsion as a reburn fuel on a pilot-scale pulverised fuel furnace (1 MW) where a 40% reduction was achieved with increased combustion efficiency (Irons and Jones, 1996). British Gas in conjunction with Scottish Power have applied gas reburning to one of the four 600 MWe boilers in Longnnet power station where a 70% reduction has been achieved (Clean Coal Technologies, 1996) . Also, Babcock Energy Limited have been experimenting with natural gas reburning on a 160 kW combustor and their preliminary results look promising (Hesselmann, 1994).

## **2.8 Coal as a Reburn Fuel**

### **2.8.1 Overview of World Energy Scene**

Both oil and gas are well proven in their effectiveness to reduce nitrogen oxides when used as reburning fuels. However, even though coal is not a very clean fuel (because it contains relatively more sulphur and nitrogen than both oil and gas) it has some major advantages over other fuels in that it is more abundant and also more easily available at existing utility boiler sites. However, the increased use of natural gas is having an impact on its present position (Fig. 2.8). The 1996 BP Statistical Review of World Energy puts coal reserves right on top at over one thousand billion

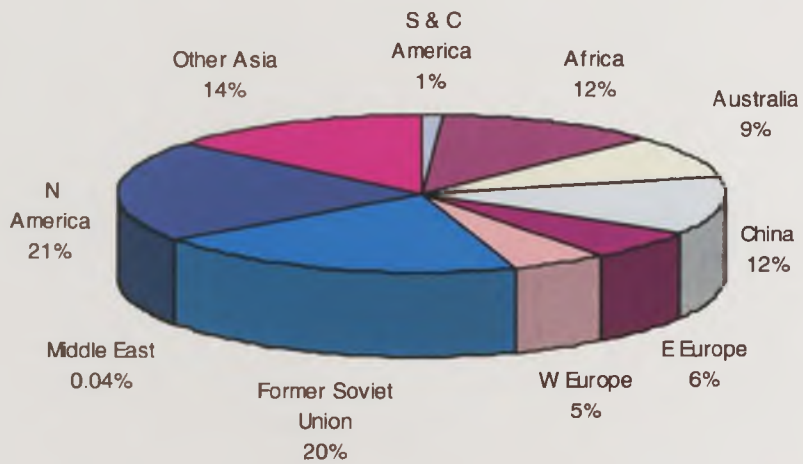


**Figure 2.8** World Energy Consumption (BP, 1996)

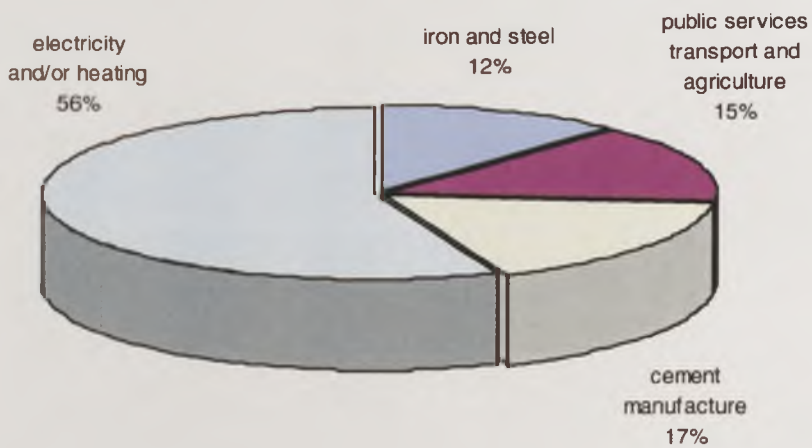
( $1 \times 10^{12}$ ) tonnes; five times larger than those of either oil or gas (BP, 1996). These reserves are evenly distributed around the world as shown in Fig. 2.9 and are sufficient to last an estimated 200-250 years at present production rates (Energy World, 1997). This excludes reserves yet to be found, and reserves that may become more accessible with improved mining techniques. This together with the fact that 40% of the EU's and 45% of the world's electricity are generated by coal-fired plants gives coal a high share of the world's energy market; around 30%. This share is likely to increase in the foreseeable future, since for many countries coal is the major, if not the only, indigenous energy source.

The greatest increases in world energy usage is expected in developing nation like China where 10-12 GW of coal-fired power are being added to the grid every year. By the year 2010 China's coal-fired generation is expected to reach a total of 450 GW, an increase of 270%. In Indonesia, electricity generation from coal is expected to increase by 1300% over the same period, with an associated 50% increase in power supplied to the rest of East Asia.

The European Union forecasts that electricity generation will rise by around 2% a year due to population growth and the rise in standard of living until the year 2005. The global energy requirement will therefore increase by between 50% and 100% over the same period. With known oil and gas reserves able to last in the region of 50 years at current rate of production, coal will surely play a major part in meeting future energy needs (Table 2.7). The quantity of coal required will probably rise in spite of the estimated 150% increase in the use of natural gas between 1990 and the turn of the century (European Commission, 1995).



**Figure 2.9** Coal reserves



**Figure 2.10** Uses of coal produced in 1994

World coal production is already on the increase rising by 55% between 1973 and 1992 and is expected to increase a further 40% by the year 2010. Of the coal produced, 56% is currently used for electricity generation and heating, 12% in the iron and steel production, 17% in cement manufacture and other industries and the remaining 15% in public services, transport and agriculture (Fig. 2.10) (Energy World, 1997).

Since over half of the world's coal production provides 45% of the world electricity demand, and the fact that developing countries are likely to increase this demand substantially before the year 2010, makes coal-based plant the preferred option for the future. This increases the requirement for more efficient coal-fired plants with lower environmental impact. An example of such plant is the Integrated Gasification Combined Cycle (IGCC) combustion system which is widely regarded as the most promising development in clean coal technology, capable of operating efficiencies of 45% or more, which would cut CO<sub>2</sub> emissions by 20-25% compared with conventional plant. Demonstration of this technology is currently underway at the Puetollano plant in Spain where a European Union's supported Thermie project will enable 335 MW of electricity to be generated (European Commission, 1995).

Research into such new technologies is very expensive owing to their sheer size and technical complexity, and as such, require the collaboration of several generating companies. However, the Organisation for Economic Cooperation and Development (OECD) estimates that by the year 2010 such technologies will become economically viable, but until then conventional coal-fired plant will continue to

produce 45% of the world's electricity. Also advances in engineering techniques are expected to increase the use of currently uneconomic lower grade coal.

**Table 2.7** World Proved Reserves at End 1995 (BP, 1996)

	<b>Reserves</b>	<b>Reserves/Production Ratio</b>
<b>Oil</b> (thousand million tonnes)	138.3	42.8
<b>Gas</b> (trillion cubic metres)	139.7	64.7
<b>Coal</b> (thousand million tonnes)	1031.6	228

In the UK the largest users of coal are power stations whose average weighted age is around 23.5 years (weighted by the size of each unit), but the need to meet current and future NOx emission regulations could mean the phasing out of such plants before the end of their working life (Furfari, 1992). A more viable economic option, especially for coal-fired power plant, is to apply a technology which is relatively cheap and capable of meeting stringent emission legislation. Coal reburning can offer both; out of all possible reburning fuels, coal is the most economical owing to its low energy cost, and because it is readily available for use on site where the necessary coal handling and processing equipment already exist, operational costs are also low. Coal's cost differential and dependability of supply give it the long term advantage. Another advantage of coal reburning is the ability to utilise different coals.

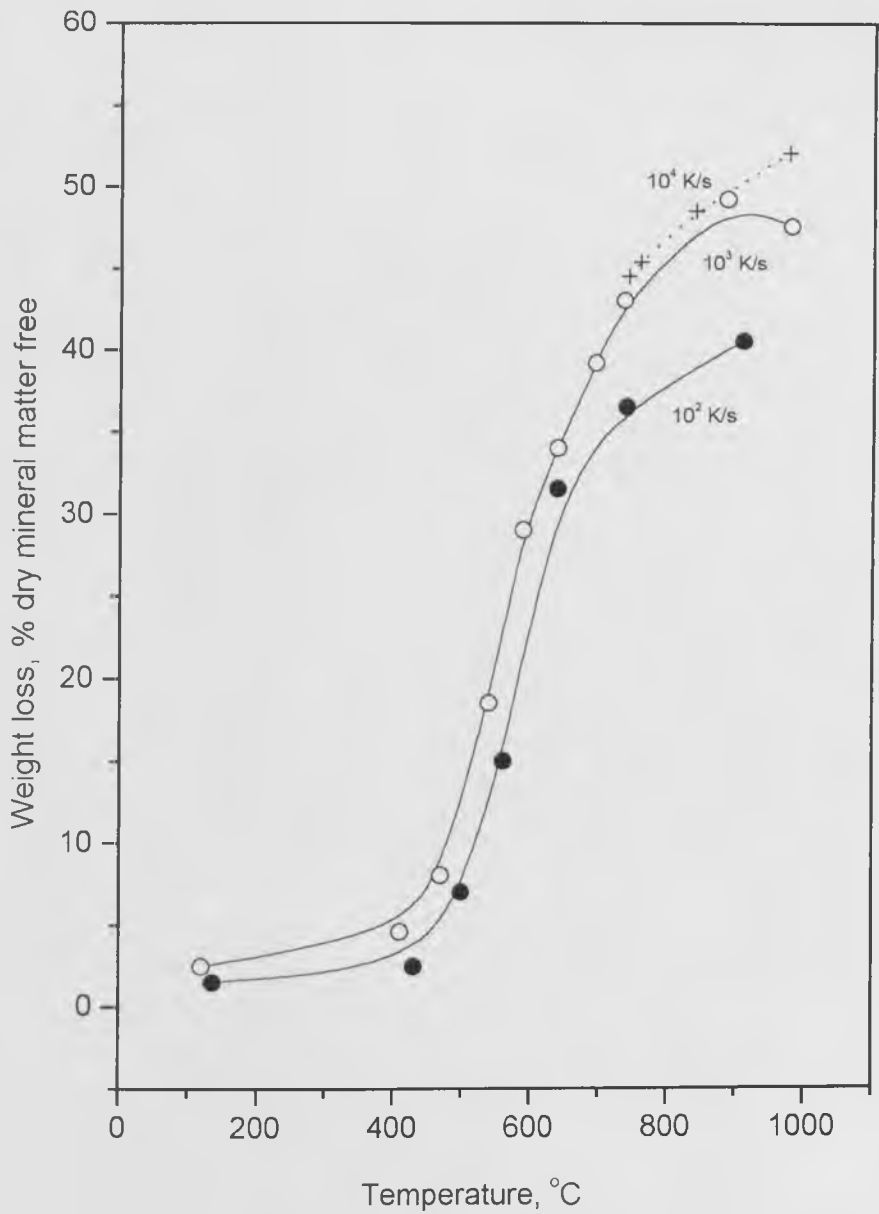
However, due to the complex and heterogeneous nature of coal a lot of questions regarding the performance of coal as a reburn fuel remain unanswered. In practice,

coal properties, both physical and chemical (rank, volatile matter, fuel-N and particle size), can affect reburning effectiveness. The following is a review of the various properties that could influence the outcome of reburning. It should be noted that this review is not exhaustive due to the limited number of publications on the subject, however, it will represent the current understanding and views of researchers studying these topics.

### **2.8.2 Effect of Coal Rank**

Coal rank normally refers to the extent of geological maturation the coal has undergone and this will vary with age, depth of burial and the temperature the coal has experienced. The proximate volatile matter and fixed carbon contents are generally used as indicators of coal rank, with higher rank coals having higher percentage of fixed carbon and less volatile matter, and visa versa. However, volatile matter is also a direct measure of coal devolatilisation behaviour during rapid heating conditions and in reburning terms it is a measure of hydrocarbon radicals release which are necessary to reduce NO<sub>x</sub>. It should be noted, however, that proximate tests are carried out at a temperature of 900 °C (BS 1016 part 3, 1973) which is much lower than furnace temperatures and heating rates and therefore it is expected that volatile yield will be higher and thus higher volatile-N (Howard, 1981; Saxena, 1990; Gibbins *et al.*, 1993). Figure 2.11 demonstrates the effect of temperature and heating rates on volatile yield. Thus, the mass of volatile evolved decreases with increasing coal rank and increases with increasing final temperature and heating rates (Morrison, 1986). In addition, char-N also increases with





Key to isothermal contact time:

	times, s	heating rate, K/s
—●—	0.5	10 <sup>2</sup>
—+—	30	10 <sup>4</sup>
—○—	30	10 <sup>3</sup>

**Figure 2.11** Volatile yield versus temperature for different heating rates (Morrison, 1986)

temperature owing to forced devolatilisation of other elements during pyrolysis (Rudiger *et al.*, 1997).

Generally, different researchers (Greene *et al.*, 1986; Kircherer *et al.*, 1994; Liu *et al.*, 1995a) have concluded that low rank coals are better at reducing NO<sub>x</sub> than high rank coals and attributed that to the relatively high proximate volatile matter content of the lower ranking coals. Greene *et al.* (1986) and Kircherer *et al.* (1994) both pointed out that high rank coals featuring high fixed carbon content required an extensive and sometimes impractical reburning residence time to achieve the desired burnout efficiency.

However, since proximate volatile content is not representative of the actual volatile yields under typical furnace conditions, it can not be used to fully account for the total volatile yield. Thus, in order to account for the total mass volatile release, there is a need to review the factors which affect volatile yields and some of the methods used to predict coal devolatilisation behaviour under pulverised furnace conditions where very high heating rates, short residence times, and high reactor temperatures exist.

All coals devolatilise on heating, however, the quantity and composition of the evolved volatiles is a strong function of temperature, heating rate, coal rank, reactor pressure and particle size (Bengtsson, 1986). Volatile yields tend to increase with increases in final temperature and although it is difficult to separate the effect of peak temperature and heating rates, recent experiments by Hindmarch *et al.* (1995) show that an increase in heating rate from 5 to 5000 K/s resulted in a 10% increase in volatile yield and a 12% increase in tar yield. Coal rank would influence the

volatile yield by affecting the plastic behaviour exhibited by the coal in the early stages of devolatilisation and the extent of secondary reactions (which involves heavier and higher hydrocarbons and tars) as decomposition takes place; both of which determine the rate of devolatilisation (Wendt, 1980).

The reactor pressure affects the volatile yield by influencing residence time of volatiles within the coal particles. As the pressure is increased the volatiles residence time is also increased resulting in extensive secondary reactions (such as cracking and carbon deposition) which decrease volatile yields (Howard, 1981; Saxena, 1990).

The thermal response and the extent of secondary reactions are both affected by coal particle size. Increases in particle size reduces the thermal response of the particle, thus for a given level of devolatilisation more time is required for larger particles. Also, as particle size increases, the volatiles residence time is increased resulting in the extensive secondary reactions mentioned above. Thus an increase in particle size reduces volatile yield (Niksa *et al.*, 1982; Suuberg *et al.*, 1979).

The kinetics of volatile release can be expressed by the following equation (Anthony and Howard, 1976):

$$\frac{dV}{dt} = k(V_m - V) \quad (2.3)$$

where  $V$  is the volatile yield at time  $t$  (kg/kg coal),  $V_m$  is the ultimate volatile yield at infinite time (kg/kg coal) and  $k$  is the reaction rate constant with an Arrhenius temperature dependence ( $s^{-1}$ ) i.e.  $k = A \exp(-E/RT)$  where  $A$  is the pre-exponential

factor,  $E$  is the activation energy (J/kmole),  $R$  is the universal gas constant (J/kmol K) and  $T$  is the temperature of the coal particle (K).

Integration of equation 4.20 gives:

$$V = V_m \{ 1 - \exp(kt) \} \quad (2.4)$$

The ultimate volatile yield can be found by relating it to that volatile matter obtained from the proximate analysis using the following correlation;

$$V_m = Q(1 - V_c)V_p \quad (2.5)$$

where  $Q$  and  $V_c$  are parameters empirically determined and  $V_p$  is the volatile matter obtained from proximate analysis.

Experimental values for  $Q$  obtained by Anthony and Howard (1976) varied from 1.3 to 1.8 depending on coal type, thus leading to values of  $V_m/V_p$  being greater than 1.

Another factor commonly used is the  $R$  factor which relates the actual volatile yield directly to the proximate volatile matter of the original coal (Gibbins *et al.*, 1993):

$$R = \frac{V_m}{V_p} \quad (2.6)$$

Typical values for the  $R$  factor vary from about 1.1 for high rank coals to around 1.5 for low rank coals.

In recent years, several coal devolatilisation models have been developed (Solomon *et al.*, 1990, 1993; Niksa *et al.*, 1991) with various capabilities for predicting coal

thermal decomposition under practical conditions. A common limitation of these models is that they require a large set of input data (kinetic parameters, gas precursor compositions, and parameters describing coal polymer structure) which must be generated based on a series of experimental measurements for each coal of interest. Predictions are thus limited to coals that have already been studied, since they originates from the complicated nature of the coal structure. On the other hand, some investigators have tried to correlate devolatilisation properties to coal types. For example, Ko *et al.* (1988) and Neavel *et al.* (1981) have developed methods of predicting the upper bound of tar yields from the coal elemental composition. The predicted tar yields can be used as an input parameter for general tar kinetic models such as those developed by Serio *et al.* (1987) and Suuberg *et al.* (1979). Niksa *et al.* (1991, 1993) have also proposed a correlation method for the FLASHCHAIN coal devolatilisation model that predicts the tar and the total volatile yields in pyrolysis based on ultimate analysis. More recently, Zhao *et al.* (1994) provided a direct correlation between coal elemental compositions and the input parameters of the FG-DVC (Functional Group - Depolymerisation, Vapourisation, Crosslinking) coal devolatilisation model, which can predict, in addition to the tar and total volatile yields, the yields of individual gas species, the tar molecular weight distribution, and the char fluidity.

The FG-DVC devolatilisation model was developed by Advanced Fuel Research Connecticut (AFR, 1992) and is based on experimental data compiled by Solomon *et al.* (1990 & 1991). The model uses as its basis the eight Argonne Premium Coals Samples Bank (Verres, 1989). For each coal the program has three files; the coal

data file describes the elemental and functional composition of the coal, the kinetic file describes the functional group evolution kinetics and the polymer file contains data on the coal's macromolecular network. Predictions of volatile yields are made by inputting coal type and temperature history into an instruction file.

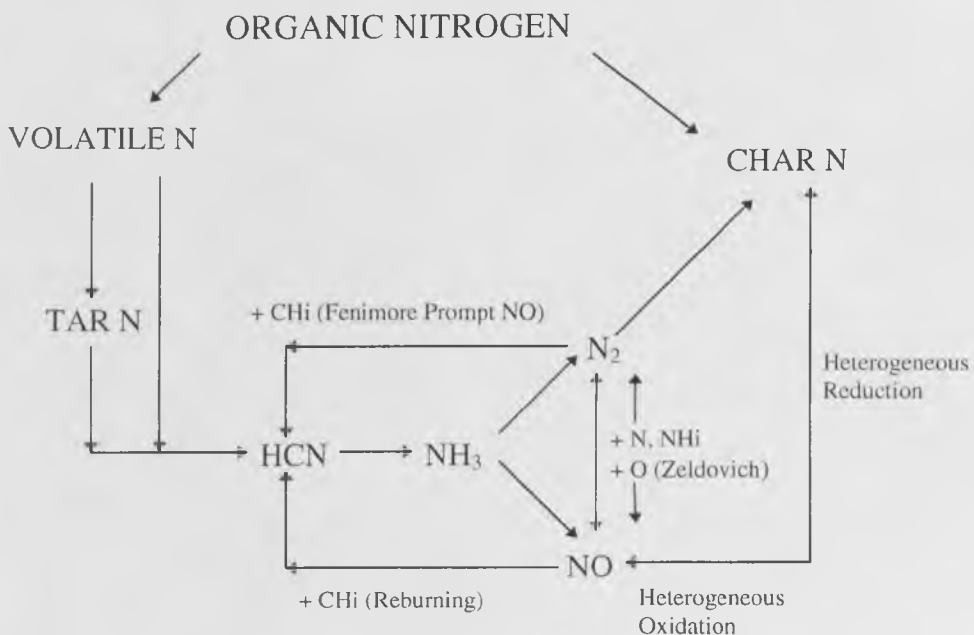
Thus, although the correlation analysis of Liu (1995c) highlighted the proximate volatile matter content as the most important coal property affecting NO reduction, it does not reflect the true relationship between NO reduction efficiency and the volatility of the reburning coals. Ideally, the true volatile yield should be experimentally determined under temperature, pressure and heating rate conditions similar to the reburning zone in that study, or by using the coal devolatilisation models mentioned above. Nevertheless, the proximate volatile matter can still serve as a rough indication of actual volatile yield.

### **2.8.3 Effect of Coal-N Content**

Increasing reburning coal-N content has been reported to have a negative effect on reburning effectiveness by essentially increasing the TFN species at the reburning exit which will then be converted to NO in the burnout stage (Chen *et al.*, 1986; Greene *et al.*, 1986). This is even more apparent at lower levels of primary NO where coal nitrogen can actually lead to an increase in exhaust NO, and Chen *et al.* (1986) likened it to a proportional increase in primary NO level.

However, the focus of the above studies was on the overall outcome of reburning, and the effect of coal-N content on nitrogenous species formation and destruction in the reburn zone was not fully examined. Nevertheless, Smart and Morgan (1994)

gave a detailed explanation to the effect and fate of coal-N during reburning. By considering the basic reburning mechanism shown in Fig. 2.12, they were able to account for the effect of coal-N on the TFN speciation in the reburn zone. They concluded that since reburning effectiveness depended on two major kinetic barriers i.e. the conversion of NO to HCN by reaction with  $\text{CH}_i$  ( $i = 0, 1, 2$ ) radicals, and the subsequent conversion of HCN to other nitrogenous species such as  $\text{NH}_3$  and finally  $\text{N}_2$ , coals which are not effective at producing HCN via the first kinetic route were quite effective at producing HCN directly from the fuel by virtue of their high nitrogen content and thus able to reduce NO to  $\text{N}_2$  via the second kinetic route. This explains the marginal effect of fuel-N on  $\text{NO}_x$  reduction at high primary NO. However, at low primary NO levels fuel-N has an adverse effect on  $\text{NO}_x$  reduction owing to the oxidation of residual fuel nitrogen in the burnout stage.



**Figure 2.12** Fate of Fuel-N in Coal Combustion (Smart and Morgan, 1994)



#### 2.8.4 Effect of Particle Size Distribution

The significance of particle size distribution on reburning effectiveness was investigated by a number of researchers (Knill and Morgan, 1989; Kircherer *et al.*, 1994; Liu, 1995c). Knill and Morgan (1989) found the difference between micronised and normal grind coal to be within experimental error and concluded that the only practical benefit of reducing coal particle size was to improve burnout efficiency. However, Kircherer *et al.* (1994) found that not only did finer grind particles improve burnout but also reduced NO<sub>x</sub> emission by a further 17%. This was mainly due to the fact that with finer particles the rate of coal devolatilisation increases leading to a an increase in hydrocarbon radicals release which in turn help reduce NO<sub>x</sub> (Hutny *et al.*, 1991). The higher burnout rate was attributed to the larger surface areas of fine particles which increases their reactivity. A similar observation was made by Liu *et al.* (1995c).

# CHAPTER THREE

## Experimental Facility, System and Procedure

This chapter describes the experimental facility that was employed in this investigation. A description of the sampling and analysis techniques is also presented.

### 3.1 Experimental Furnace

Experiments were conducted on a 200 kW (maximum thermal rating) downward-fired furnace shown schematically in Fig. 3.1. The furnace was rigidly secured by a steel frame and positioned in the center of the two platform construction where it was mounted on springs to allow for any axial movement caused by thermal expansion. It was of modular construction and comprised of 6 bolted sections each with an inside dimension of  $0.5 \times 0.35$  m. Each section was constructed using 3 mm thick stainless steel sheets made into a square box with flanges welded on both ends. To ensure that the sections did not buckle during high temperature operations they were re-inforced with steel bars; two bars placed vertically across each panel. The sections were then bolted together with high temperature gaskets and refractory sealant placed between each section to ensure that the arrangement is air tight. This modular construction allows for easy replacement of individual sections should maintenance or improvement be required.

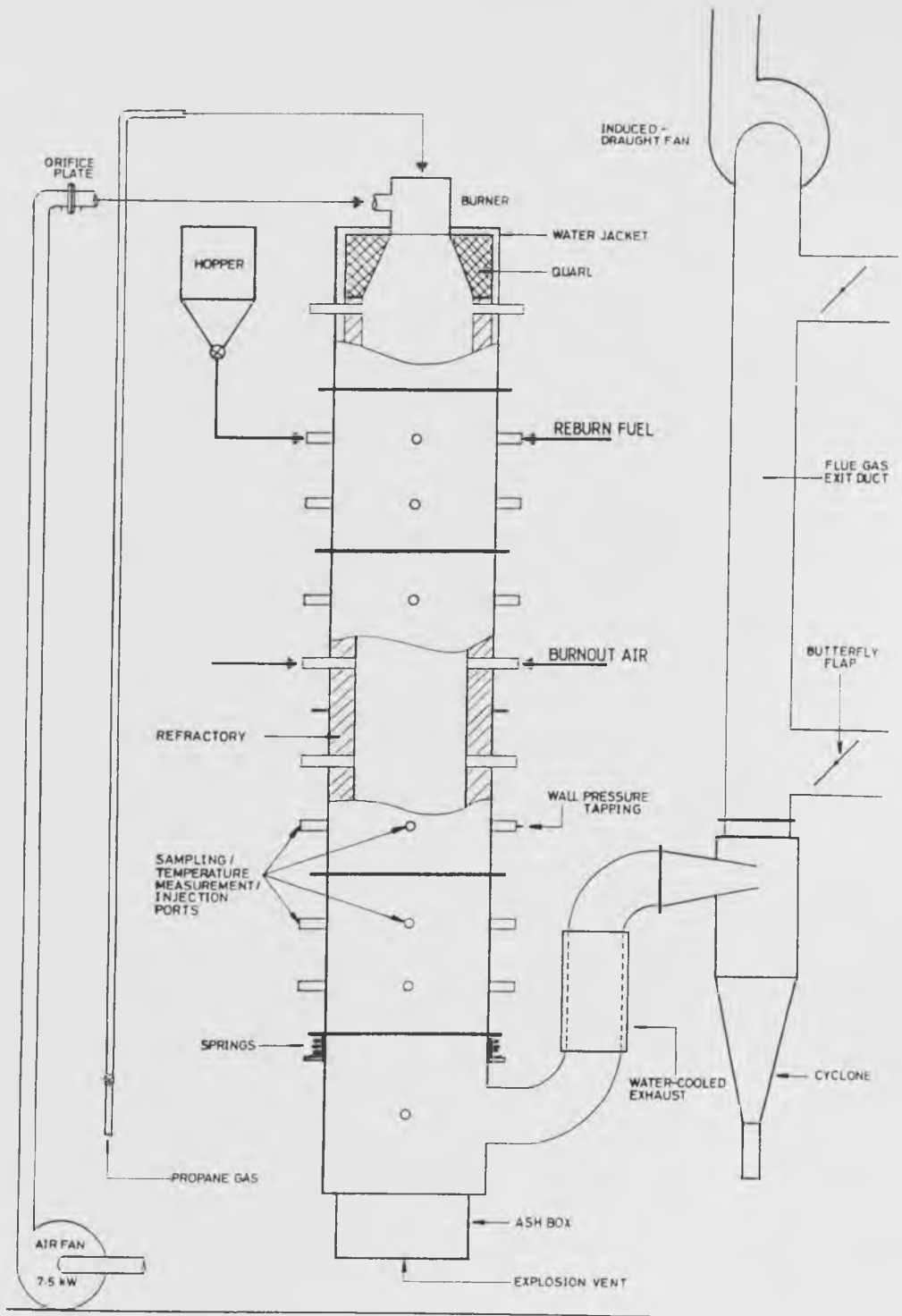


Figure 3.1 Schematic of the Reburn Furnace

Thirty seven utility ports were located along the length of the furnace for the injection of reburn fuel and burnout air; they were also used for gas sampling and temperature measurements. These ports consisted of 22 mm unions which were screwed into the exterior of the stainless steel shell. They allowed for the insertion of water cooled probes, thermocouples, and the reburn fuel and burnout air injector guns provided that they were equipped with the appropriate fitting.

The top section which essentially houses the burner quarl, and was therefore the hottest section, was surrounded by a 23 mm water jacket as well as being lined with an easily adjustable light weight ceramic fibre board (grade 1400). The ceramic fibre board was used to control the temperature in the primary combustion zone. The remaining sections were not water cooled, however, they were lined with 75 mm of ceramic fibre board grade 1400 for the top two sections and grade 1200 for the bottom three sections, giving roughly a 200 K drop in temperature along the 3 m long furnace as a result of heat losses and dilution by the cool burnout air. Details and composition of the furnace lining are given in Table 3.1.

The ash box was located at the bottom of the furnace along with an explosion vent as a safety measure. The bottom section was where the flue gases left the furnace after which they entered a water cooled exhaust pipe before exiting into a high efficiency cyclone which collected any remaining particles and then they were vented out through the roof with the aid of a fan. A general view of the reburn rig is shown in Plate 1.



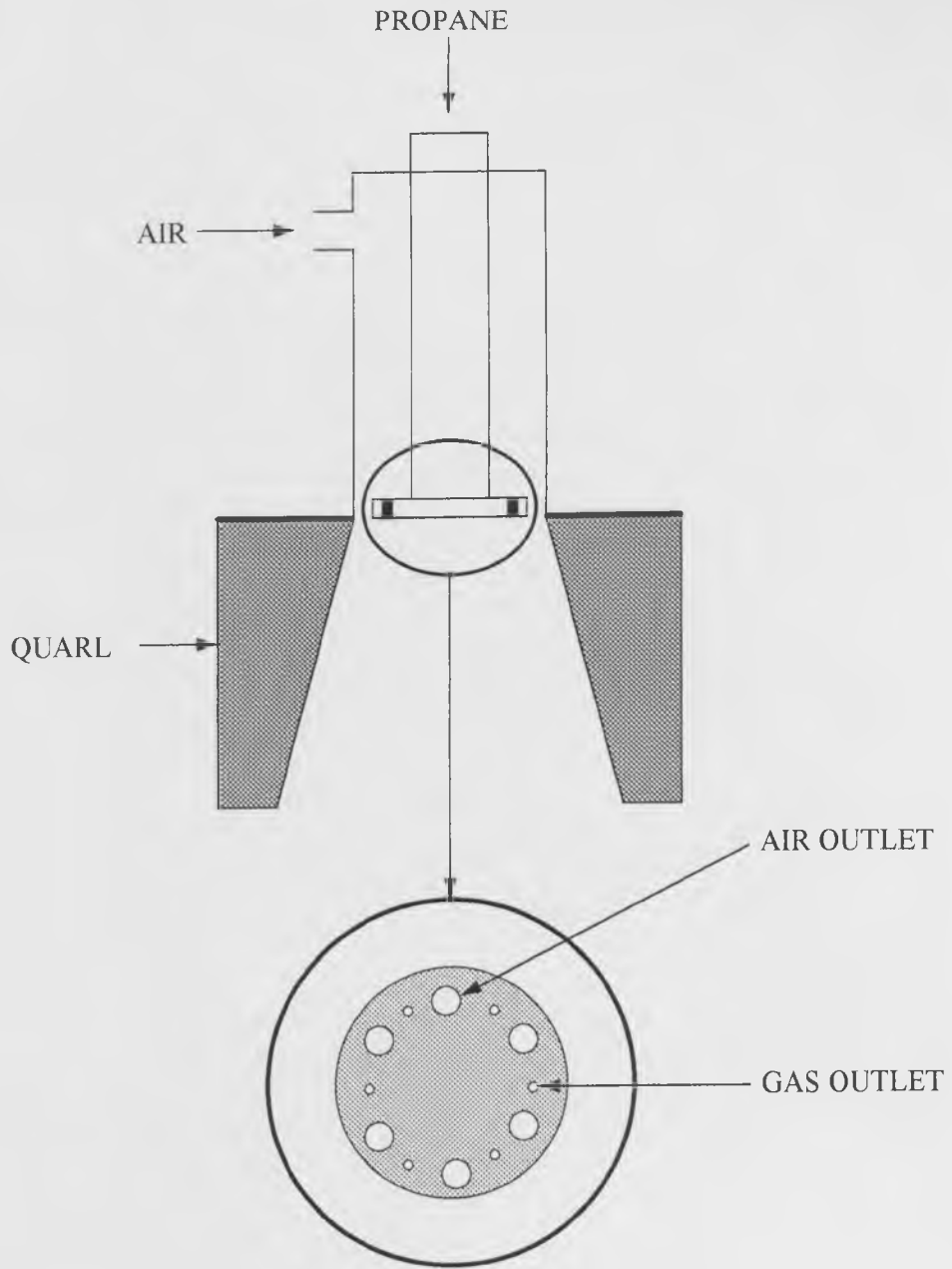
**Plate 1** A General View of the Reburn Rig

**Table 3.1** General Properties of Furnace Lining

Classification	1200	1400
Maximum surface temperature (°C)	1200	1400
Nominal density (kg/m <sup>3</sup> )	260	225
Approximate weight loss on firing (%)	5-7	5-10

### 3.1.2 Burner

Fitted on the top section of the furnace was a Stordy wall-hugger, nozzle-mixed gas burner (Fig. 3.2) type WHG 115 which was connected to a typical industrial automatic start-up/purge and flame failure detection control system which was designed to shut down in cases of loss of supply air pressure or loss of the combustion flame. The dual function of the burner was to deliver the fuel and combustion air into the furnace whilst acting as a shield to prevent pre-ignition of the fuel before entering the furnace. The flame was lit using an ignition rod and was constantly monitored by an ultra-violet photocell detector. The fuel and air flows were manually operated and controlled using rotameters. The burner itself produced a short round flame which adhered to the walls of the quarl exerting no forward velocity on the burner. It also had different thermal settings for variable load operations. The burner quarl which was essentially a cone made of a castable refractory provided a smooth expansion for the burning fuel at the entrance to the combustor and it is where simultaneous mixing and combustion occurred. The diameter of the cone extended from 105 mm to 220 mm over a length of 235 mm.



**Figure 3.2** Schematic of the WHG 115 Burner

### **3.1.3 Air and Fuel supply system**

A  $192 \times 10^{-3} \text{ m}^3/\text{s}$  and 7.5 kW (max. output) centrifugal fan was used to provide the air requirement for both the primary and burnout air. The coal carrier gas which was either air or air/nitrogen mixture was supplied using a compressed air system and nitrogen cylinders supplied by BOC Ltd. Both carrier air flows were regulated at a pressure of 2 bar to compensate for the large pressure drop in the coal feeding line. The burnout air was normally introduced into the furnace 700 mm downstream from the reburn fuel injectors using two 10 mm i.d. stainless steel nozzles. The reburn zone distance and hence residence time could be easily varied by moving the burnout air nozzles position. The various gas flows were individually regulated and measured using standard calibrated rotameters (KDG series 2000) and supplied at room temperature.

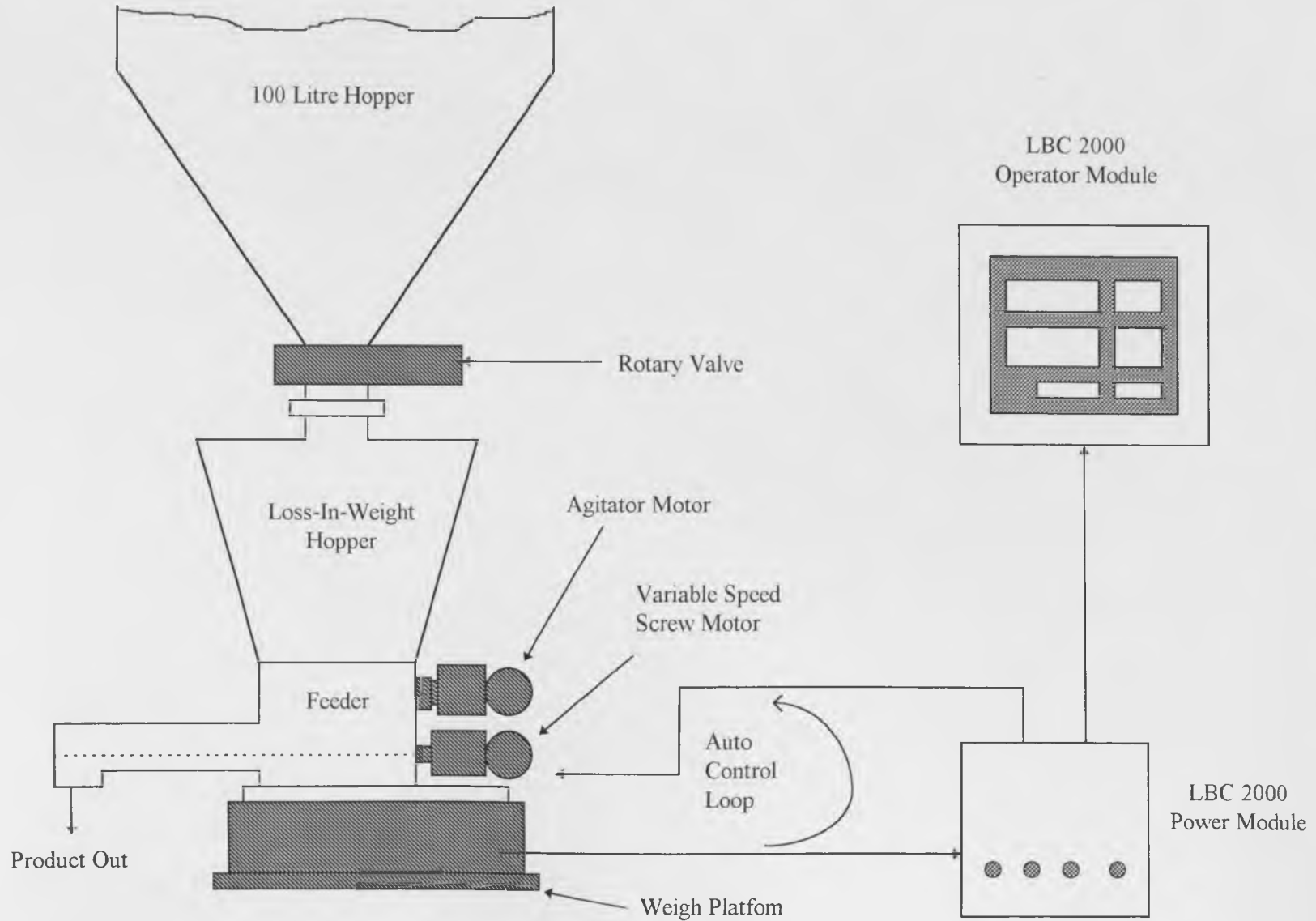
Propane gas to the rig was supplied using six propane cylinders (supplied by BOC Ltd.) which were regulated at a pressure of 55 mm water gauge. A calibrated series 2000 rotameter was also used to monitor the flow of the propane gas. Furthermore, three emergency stop were located around the rig to allow for immediate shut down of all fuel supplies by the operator when deemed necessary.

### **3.1.4 Coal feeding System (Reburn fuel supply and injection system)**

Located on the first platform was a loss-in-weight metering screw feeder (LBC 2000) which was used to supply the pre-pulverised coal from a hopper by a variable-speed twin-screw feeder with homogeniser, Fig. 3.3 (Rospen Ltd.). The coal then entered a vibrating chute and was conveyed pneumatically to the reburn section via



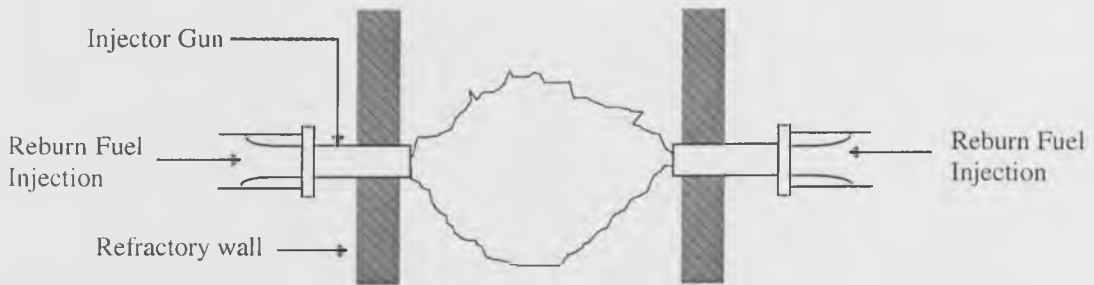
Figure 3.3 Schematic of the Loss-In-Weight Feeder



an air-mover in the secondary air line. Details of the air-mover's operation are given in Appendix B. The carrier gas line was a PTFE rubber tube of 12 mm inner diameter. It was electrically earthed to avoid the build-up of electrostatic charges that could cause irregular coal-feed rates as a result of particle accumulation inside the line. The line was also thermally insulated with a 3 mm thick fibre blanket. The coal-feed rate could be controlled to within 0.25-1% of the mean value. Compressed air or a mixture of air and nitrogen were used as carrier gases for the coal. The whole feeding system was repeatedly calibrated with each coal type to maintain an accurate flow rate for both coal and carrier gas.

Once the coal left the weigh platform it dropped into a vibrating feeder complete with a steel tray. The purpose of this was to spread the pulverised coal evenly across the tray thus ensuring uniform feeding takes place. The coal was then transported with the help of a pre-calibrated air-mover into a 12 mm inner diameter PTFE tube. A T-piece then split the flow and the pulverised coal was injected into the furnace at velocities of around 16 - 35 m/s using two 8 mm i.d. stainless steel injector guns positioned into ports on opposite sides of the furnace wall and perpendicular to the main gas flow. The resulting jets impinged on each other thus creating the mixing environment required for effective NO<sub>x</sub> reduction. The guns were situated at an axial distance of 40 cm from the burner exit; a point where the primary zone burnout was completed (confirmed by O<sub>2</sub> and CO measurements in the near burner region), and positioned in the furnace wall with only about 5 mm protruding into the furnace (Fig. 3.4). Each injector gun was thermally insulated using Kaowool mastic which was sandwiched between the injector and a 22 mm stainless steel tubing. This

arrangement was very beneficial in ensuring that the injector guns did not wear off in the very hot and reducing conditions of the reburn zone.



**Figure 3.4** Reburn Fuel Injector Guns Arrangement

An early attempt to use a Y-piece to divide the coal flow proved to be unsuccessful and caused a blockage in one of the tubes. This was due to the design of the Y-piece which was not exactly symmetrical and thus did not give an even split across the two channels. While one channel had a high flow rate the other channel's flow was reduced considerably to a point where hardly any flow was detected. The problem was resolved by using a T-piece. This slightly increased the pressure drop in the coal feeding line but gave an even split across the two channels.

To demonstrate the effect of mixing on reburning effectiveness, the two nozzle configuration was replaced with a four nozzle system. Carrier gas velocities were maintained as before by reducing the diameter of the PTFE tube to 8 mm and replacing the two 8 mm injector guns with four 5 mm injector guns.

The principle aim of the LBC 2000 is to weigh and control the coal feed rate thus regulating the quantity of coal according to the requirement of the operator. Details of the system is given in Appendix A.

### **3.1.5 Exhaust Gas Dilution System**

The exhaust system was designed to reduce the temperature of the large volume of exhaust gases and collect any particulate material whilst maintaining control of the furnace pressure. After leaving the furnace via the bottom section, the flue gases passed through a 75 cm long water-jacketed exhaust pipe, which in conjunction with a 45 degree water spray, helped to cool the gases. The 45 degree water spray also helped quench the char reaction so that any char collected after that point could be analysed to estimate burnout efficiency. The relatively cool gases then entered the cyclone where the centrifugal action caused any particles retained in the flue gases to deposit into a collector. Further cooling was now employed by means of entrainment of the surrounding air through two butterfly flaps located along the length of the exhaust. The cleaned and cooled (100 °C) gases were then vented out using an induced-draught fan.

As well as being designed to reduce the temperature of the large volume of flue gases, the exhaust system also helped maintain control of the furnace pressure. This was done with the aid of two butterfly flaps located along the length of the exhaust which served to regulate furnace pressure. The desired furnace pressure level could then be monitored using a micro-manometer and any variation corrected by adjusting the butterfly flaps.

### **3.1.6 Ammonia Supply System**

The ammonia doping system consisted of a 6 kg ammonia cylinder, a 0-5 l/min. mass flow controller and a transfer line. Ammonia was used to dope the propane gas in order to vary the NO<sub>x</sub> levels in the primary zone. The primary propane flame was doped with ammonia at a rate of 1.8 -2.0 l/min. and controlled using a mass flow controller. The doping resulted in an NO concentration at the exit of the primary zone of between 850-900 ppmv on a dry basis. This included the 100-120 ppmv background thermal and prompt NO. The diluted NO concentration due to the introduction of carrier gas and burnout air was around 600 ppmv. Ammonia slip was found to be less than 10 ppmv giving a 98% conversion efficiency under all burner operating conditions.

It should be noted that although ammonia was used to simulate fuel nitrogen it does not in any way simulate fuel nitrogen release during coal combustion and should not be mistaken as such. The use of propane gas flames laden with ammonia as fuel-N in this study enabled a straight forward assessment of each coal without the complexity and problems associated with pulverised coal firing on a smaller scale. It also enables the primary NO concentration to be varied more easily.

### **3.1.7 Sampling System**

The sampling system consisted of a probe, transfer line, filters, condensers and gas analysis instrumentation. A water-cooled stainless steel probe was used to extract gaseous samples through different ports along the furnace length. The probe consisted of three concentric stainless steel tubes, with an outside diameter of 16 mm

and an inside diameter of 6 mm. Cooling water circulated in between the two outer tubes forming a water jacket that allowed the introduction of the probe into the furnace. The probe tip was fitted with a quartz wool filter to minimise the influx of coal ash/particles into the sample line. The gas sample flowed through the water-cooled probe under vacuum generated by a sampling pump. The gas sample was then thoroughly cleaned and dehumidified using a mixture of water traps, filters and a refrigerator maintained at 2 °C before being fed to the analysing instruments through a 1/4 inch Teflon tubing. The concentrations of NO<sub>x</sub>, CO and O<sub>2</sub> were measured simultaneously by the following analysis equipment:

NO <sub>x</sub>	Analysis Automation Ltd Series 440 chemiluminescent Analyser
CO	Analytical Development Company (ADC) NDIR <sup>1</sup>
O <sub>2</sub>	Taylor-Servomex OA 570

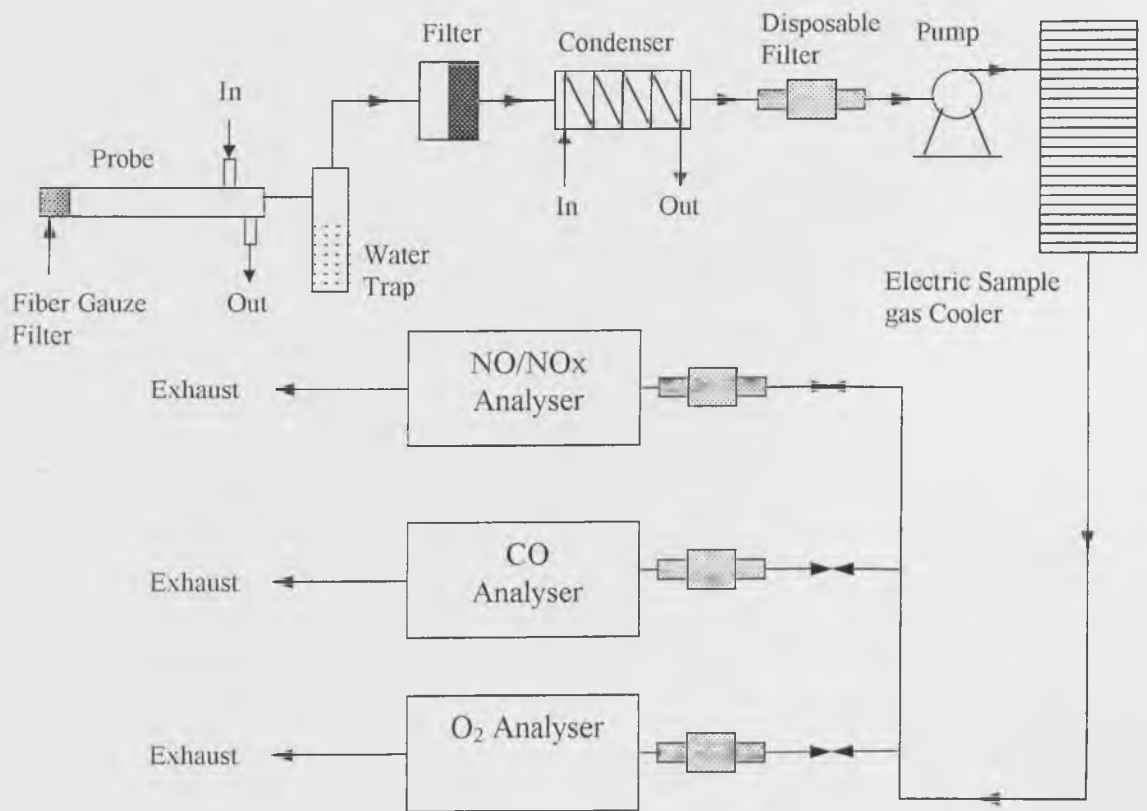
<sup>1</sup> Non-Dispersive Infra-Red

All the instruments were calibrated before and after any test. Detail of the gas analysis instrumentation is given in Appendix C. The flow diagram of the gas sampling system is shown in Fig. 3.5.

### 3.1.8 Temperature Measuring Devices

The following thermocouples were used to measure temperature.

A) A suction pyrometer equipped with an R-type (platinum-13% rhodium / platinum) thermocouple was used to take temperature profiles of the furnace at different loads. The R-type thermocouple was protected from chemical attack by



**Figure 3.5** Layout of Gas Sampling and Analysis System

an impermeable sheath and a radiation shield made of five concentric ceramic tubes which allowed the flue gas to pass through while helping to shield the thermocouple from the surrounding radiation.

B) Two sheathed R-type (platinum-13% rhodium / platinum) thermocouples with a 10 mm outside diameter and 400 mm length were used at fixed position in the furnace; normally at the entrance of the reburning zone and the end of the burnout zone. They were also used for radial measurements of temperature, however, temperature changes in the radial direction were less than 15 °C over a radial distance of 12 cm. Thus, in this study, it is assumed that temperature changes were in the axial direction only. Millivolt outputs from the R-type thermocouples were converted to temperature readings by a one channel digital display unit by Ancoms Ltd.

C) A series of sheathed K-type thermocouples of 3 mm o.d. were used at different positions within the furnace to give a rough indication of temperature. They were also utilised in monitoring combustion air temperature and final exhaust temperature. These thermocouples were connected to a 9-channel digital display model 2751-K by Digitron Instrumentation Ltd, of which data was selected by using a Digitron 12 way-type K Selector Unit.

An estimation of errors in temperature readings can be found in Appendix E.



## **3.2 Experimental Approach**

### **3.2.1 Coals Used**

The nine bituminous reburn coals used in this study were supplied by the former Coal Research Establishment (now CRE Group Ltd), Cheltenham, pre-pulverised with different particle size distribution, nitrogen content and volatile matter. They were supplied sealed under nitrogen gas in 25 kg containers. Table 3.2 lists the coals in order of increasing volatile matter content on a dry basis. The particle size distribution of all coals is given in Appendix F. The proximate and elemental analysis results as well as coal particle size analysis results were also supplied by CRE Group Ltd.

### **3.2.2 Experimental Procedure**

Before each run the following procedure was adopted :

- (i) the coal loss-in-weight feeding system was calibrated for the coal type to be used and the top hopper filled with the same coal. The feeding system was then switched on to allow the load cells to reach working temperature.
- (ii) the analysis instrumentation was turned on at least two hours before starting a run to warm-up and thus avoid any signal drift during the run. Once they reached working temperature they were first zeroed and then calibrated using the appropriate calibration gas.
- (iii) the gas sampling system was thoroughly cleaned and checked for leakage. The quartz wool filter at the probe end was changed and probe cleared of any

**Table 3.2** Details of Coal Used and Analysis

Commercial Name	Proximate Analysis % dry basis (d.b)				Ultimate Analysis % dry basis (d.b)					Gross Calorific Value (kJ/kg)
	Symbol	Ash	Volatile Matter	Fixed Carbon	C	H	N	S	O	
Betts Lane	▼	17	26.8	56.2	72.0	4.46	1.41	2.58	2.54	29563
Koonfonteine	*	13.9	27.0	59.0	71.0	4.37	1.74	0.55	8.42	28360
South Brandon	—	8.94	29.6	61.5	77.74	4.72	1.61	2.58	4.34	32450
Gascoige Wood	+	17.83	30.39	51.78	68.36	4.81	1.41	1.19	6.39	27180
Pittsburgh No. 8	×	11.5	31.5	57.0	73.3	4.5	1.45	1.78	7.47	30500
Thoresby	▲	16.3	30.9	52.9	71.2	4.15	1.60	1.37	5.43	28540
Hunters Valley	◆	12.3	31.4	56.3	72.8	4.75	1.61	0.45	8.06	29460
La Jagua	●	8.7	36.1	55.2	73.2	5.1	1.41	0.67	11.0	30063
Asfordby	■	10.1	37.7	52.2	72.8	5.8	1.39	0.87	9.0	29673

blockage. All other filters used in the sampling system were also checked and replaced with fresh ones when required.

- (iv) prior to preheating the furnace, the water supply to the top section as well as that to the exhaust and sample probes were turned on. The carrier gas and burnout air supply were also turned on.
- (v) the burner was then lit and the fuel to air ratio adjusted accordingly. The 45 degree spray shower was then employed to keep exhaust gas temperature below 300 °C.
- (vi) when the operating temperature was reached the ammonia doping system was then engaged to obtain the desired baseline NO level (normally ~ 600 ppm) with the carrier gas and burnout air passing through the furnace.
- (vii) the different operating parameters ( $SR_1$ ,  $SR_2$ ,  $SR_3$ , coal feed rate, residence time and primary NO level) were then set and varied accordingly.
- (viii) once all parameters were set and all the instruments indicated steady state baseline conditions of stable temperatures and exhaust gas concentrations, the reburning coal was injected into the furnace and the concentrations of CO, O<sub>2</sub> and NO were noted once the readings settled. Coal feeding was then stopped and baseline NO level checked for any fluctuations. Operating variables were again altered and the process repeated.

The variables were chosen to give the desired stoichiometry in each of the three zones. Burnout air injector positions were varied so that the effect of reburn zone

residence time could be observed. While the effect of primary NO level on reburning effectiveness was investigated by varying the amount of ammonia dopent.

### **3.2.3 Solid Sampling**

The coal burnout rate was estimated by collecting ash samples from the collector at the bottom of the cyclone after each run and determining the carbon conversion efficiency using ash as a tracer method. The carbon conversion efficiency was also obtained using results of gaseous measurements and the oxygen balance method according to equation 4.11.

# CHAPTER FOUR

## Experimental Results and Discussion

Nine bituminous power station coals were used to examine the effect of different process variables on the outcome of reburning. The parameters investigated include: the primary zone stoichiometry, the primary zone NO concentration, the reburn zone stoichiometry, the reburn zone residence time, the reburn zone temperature, reburn fuel carrier gas oxygen concentration, reburn fuel fraction, and the impact of mixing in the reburn zone. The effect of each of the above variables was examined separately over a range of conditions and the optimum or near optimum conditions identified under the experimental range specified. A multi-variate analysis was also undertaken to determine the importance of some of these variables on NO reduction observed, and the influence of reburn coal properties such as fuel nitrogen content and volatile matter. All reburning experiments were performed using a baseline NO concentration of 600 ppmv unless otherwise stated.

### 4.1 Introduction

Initial trials on the furnace were aimed at establishing baseline operating conditions for the burner, thus no reburn fuel was used. The uncontrolled NO<sub>x</sub> emissions for the propane-fired burner were typically around 110-140 ppmv at 3% excess air; increasing with an increase in temperature. The temperature profile at different burner loads can be seen in Fig. 4.1 where roughly, a 200 K drop in temperature was

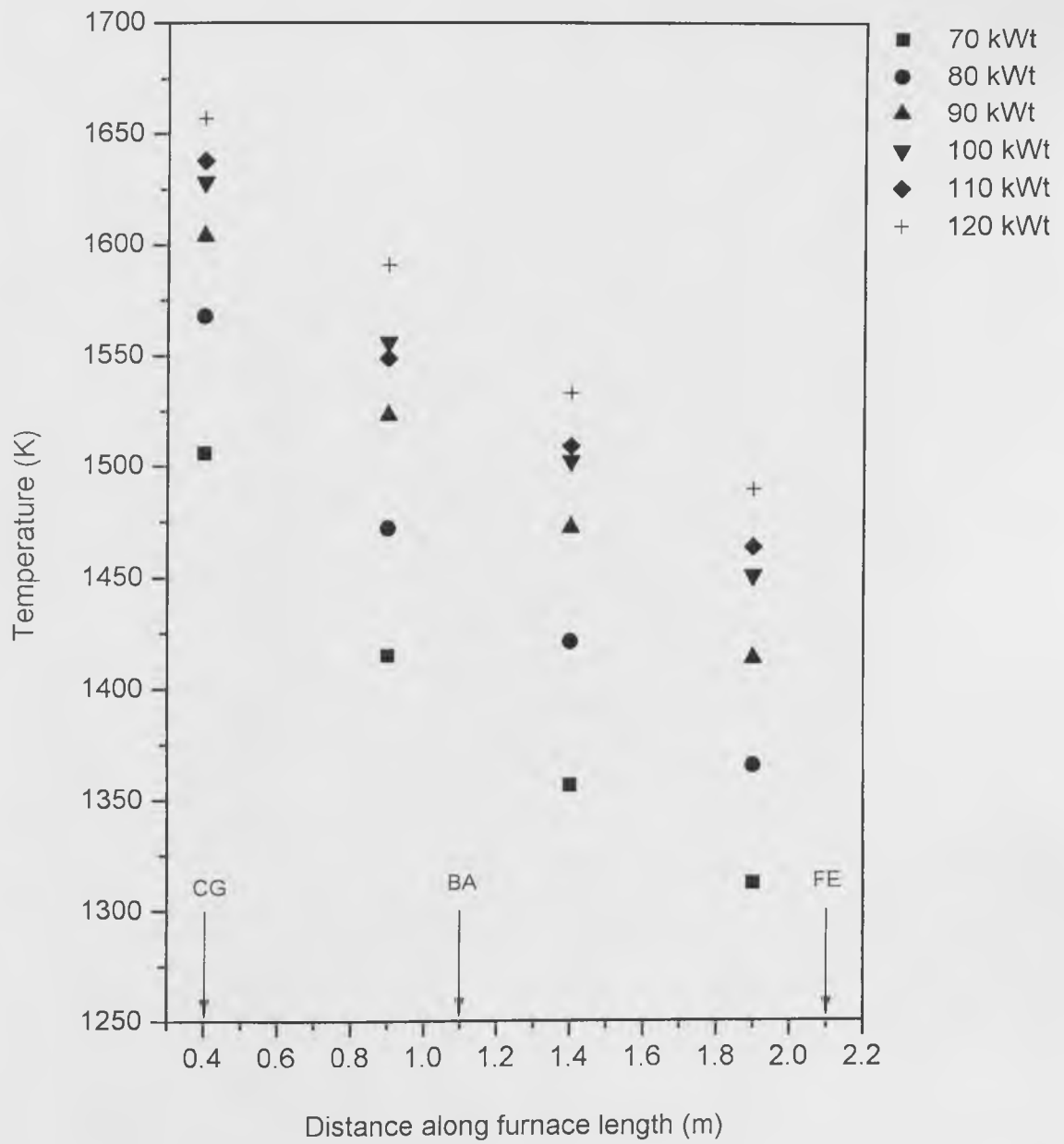


Figure 4.1 Typical temperature profiles for various burner loads

observed along the length of the furnace. This is mainly due to cooling from the carrier gas and burnout air. Equations 4.1 - 4.4 were used to calculate the stoichiometry in each of the combustion zones; the primary zone air/fuel stoichiometric ratio ( $SR_1$ ), the overall reburn zone air/fuel stoichiometric ratio ( $SR_2$ , including carrier-gas air) and the burnout zone stoichiometric ratio ( $SR_3$ ).

$$SR_1 = \frac{MA}{MF \times TA_M} \quad (4.1)$$

$$SR_2 = \frac{MA + CG_A}{(MF \times TA_M) + (RF \times TA_R)} \quad (4.2)$$

$$SR_3 = \frac{MA + CG_A + BA}{(MF \times TA_M) + (RF \times TA_R)} \quad (4.3)$$

MA Main air flow rate,  $m^3/\text{min}$ . @ STP (i.e. 298 K and 101.3 pa)

MF Main fuel flow rate,  $m^3/\text{min}$ . @ STP

RF Reburn fuel flow rate,  $\text{kg}/\text{min}$ .

BA Burnout air flow rate,  $m^3/\text{min}$ . @ STP

$CG_A$  Carrier- gas air flow rate,  $m^3/\text{min}$ . @ at STP

$TA_M$  Theoretical air requirement of main fuel (for propane =  $23.81 \text{ m}^3/\text{m}^3$  gas)

$TA_R$  Theoretical air requirement of reburn fuel ( $\text{m}^3/\text{kg}$  coal)

The reburn zone residence time,  $\tau_2$ , was varied by altering the position of the burnout air nozzles and calculated using equation (4.4).

$$\tau_2 = \frac{V_R \times T \times 60}{TVR_R \times T_0} \quad (4.4)$$

$V_R$  Volume of reburn zone,  $m^3$

$T$  Average gas temperature, K

$T_0$  Reference gas temperature, 298 K

$TVF_R$  Total volumetric flow rate of combustion gases entering the reburn zone,  $m^3/\text{min}$ .

The total volumetric flow rate of combustion gases entering the reburn zone were calculated by assuming that the primary fuel was completely burnt to  $CO_2$  and  $H_2O$  and by estimating the volume of combustion products produced per kg of coal burnt using equation (4.5).

$$V_C = V_{XO_2} + V_{N_2} + V_{H_2O} \quad Nm^3/kg \quad (4.5)$$

$Nm^3/kg$  = cubic meter per kilogram under standard temperature and pressure (298 K & 101.3 pa) conditions.

where,

$$V_{xO_2} = \frac{1.866}{100}(C + 0.375S) \quad Nm^3/kg \quad (4.6)$$

$$V_{N_2} = 0.79V_o + \frac{0.8}{100}N \quad Nm^3/kg \quad (4.7)$$



$$V_{H_2O} = 0.111H + 0.0124W + 0.0161V_o \quad \text{Nm}^3/\text{kg} \quad (4.8)$$

$$V_o = 0.0889(C + 0.375S) + 0.265H - 0.033O \quad \text{Nm}^3/\text{kg} \quad (4.9)$$

- C Carbon content of coal, % a.d. (a.d. denotes 'as received' basis)
- S Sulphur content of coal, % a.d.
- O Oxygen content of coal, % a.d.
- N Nitrogen content of coal, % a.d.
- H Hydrogen content of coal, % a.d.
- W Moisture content of coal, % a.d.
- $V_o$  Theoretical air requirement,  $\text{Nm}^3/\text{kg}$  coal
- $V_C$  Volume of combustion product,  $\text{Nm}^3/\text{kg}$  coal
- $V_{N_2}$  Volume of nitrogen produced,  $\text{Nm}^3/\text{kg}$  coal
- $V_{XO_2}$  Volume of  $\text{SO}_2$  and  $\text{CO}_2$  produced,  $\text{Nm}^3/\text{kg}$  coal
- $V_{H_2O}$  Volume of water vapour produced,  $\text{Nm}^3/\text{kg}$  coal

In reburning, the failure to completely oxidise the fuel in the final combustion stage is a major concern. Poor combustion can result in higher CO emissions in the exhaust, relative to the uncontrolled emissions, as well as a reduction in carbon burnout. In this study, the carbon burnout efficiency,  $\eta_c$ , was determined from the results of solid sampling analysis, using the ash as a tracer method.

$$\eta_c = 1 - \frac{C_s}{C} \times \frac{\text{Ash}}{\text{Ash}_s} \quad (4.10)$$

- C Carbon content of the reburning coal, %.
- C<sub>s</sub> Carbon content of the solid sample taken from the ash trap, %.
- Ash Ash content of the reburning coal, %.
- Ash<sub>s</sub> Ash content of the solid sample taken from the ash trap, %.

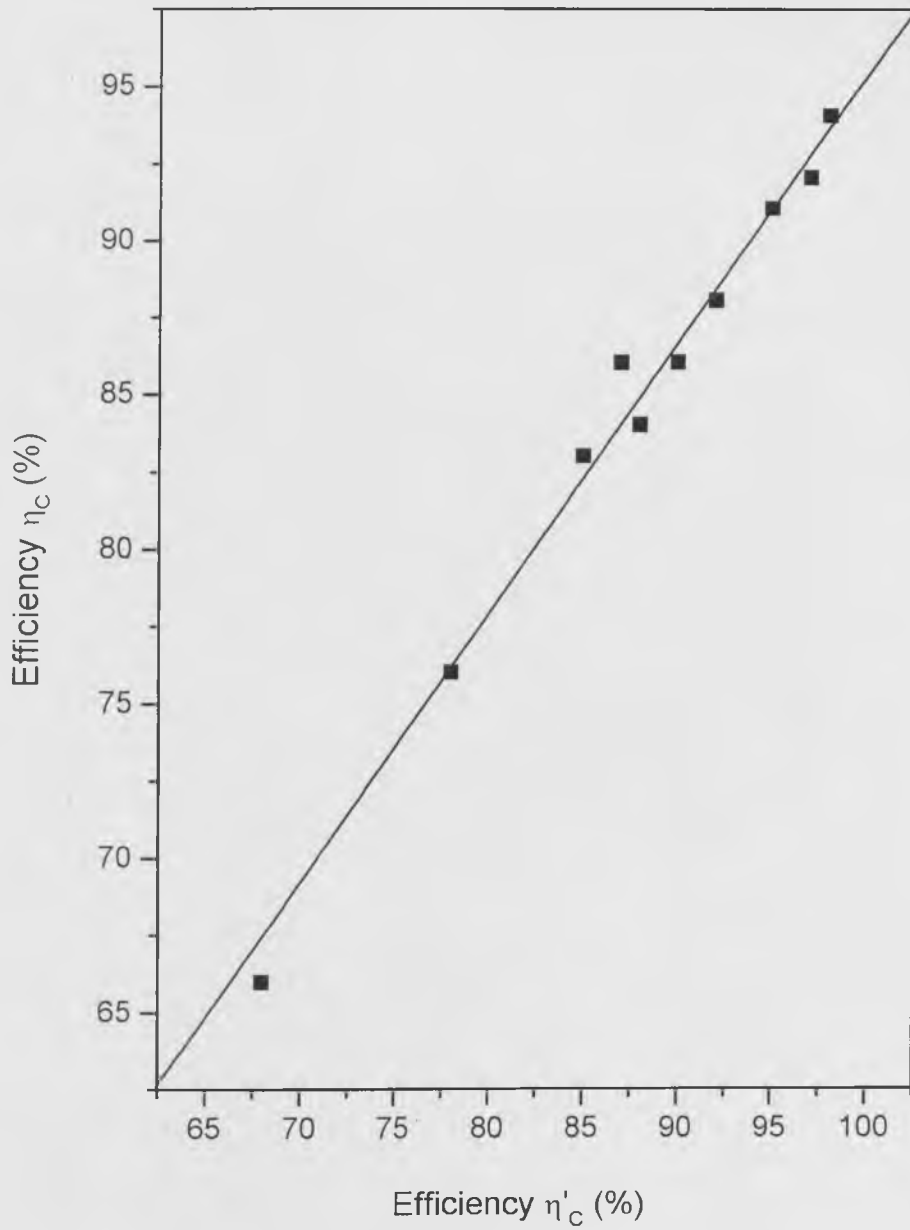
The carbon burnout efficiency was also obtained by an oxygen balance. This was achieved by calculating the theoretical O<sub>2</sub> for both complete combustion (100% burnout) and no combustion (0% burnout). These values together with the measured O<sub>2</sub> reading during reburning were used in the following equation to calculate carbon burnout.

$$\eta'_c = \frac{[\text{O}_2 \text{ 0\% burnout}] - [\text{O}_2 \text{ measured}]}{[\text{O}_2 \text{ 0\% burnout}] - [\text{O}_2 \text{ 100\% burnout}]} \times 100\% \quad (4.11)$$

The good agreement between the carbon burnout efficiencies obtained using both methods is illustrated in Fig. 4.2. Thus, for convenience, the carbon conversion efficiency was usually determined from gas phase measurements and an oxygen balance.

The NO<sub>x</sub> reduction efficiency was calculated based on NO measurement alone; NO<sub>2</sub> was only 5 to 10 ppm of the total NO<sub>x</sub> under all operating conditions and was not included in the results. Equation (4.12) was used to calculate the NO reduction efficiency.

$$\eta_{\text{NO}} = \frac{\text{NO} - \text{NO}_0}{\text{NO}_0} \times 100 \quad (4.12)$$



**Figure 4.2** Comparison of carbon burnout efficiency using two different methods  
 All coals, SR1=1.03, SR2= 0.89 - 0.99,  $T_{pr}$ =1573 K

where,

- $\eta_{\text{NO}}$  NO reduction efficiency or reburning efficiency, %
- NO measured volumetric NO concentration at the furnace exit during reburning, ppmv (dry basis)
- NO<sub>0</sub> primary zone NO concentration measured at the furnace exit, i.e. the measured volumetric fraction of NO before the addition of the reburning fuel but with the introduction carrier gas and burnout air, ppmv (dry basis).

## 4.2 Parametric Study of Reburning

Reburning is a complex process involving a large number of operational variables that are associated with each of the three combustion zones. These variables play a significant role in determining the outcome of reburning i.e. the degree of NO<sub>x</sub> reduction or reburning effectiveness. However, since most of these variables are interdependent, assessing the effect of one variable in isolation is not always possible. Nevertheless, in order to compare the reburning results of this investigation to those of others, it is important to identify the significant variables that affect the reburning process and to examine the effect of each variable separately. The experimental tests were conducted over the following ranges of operating conditions:

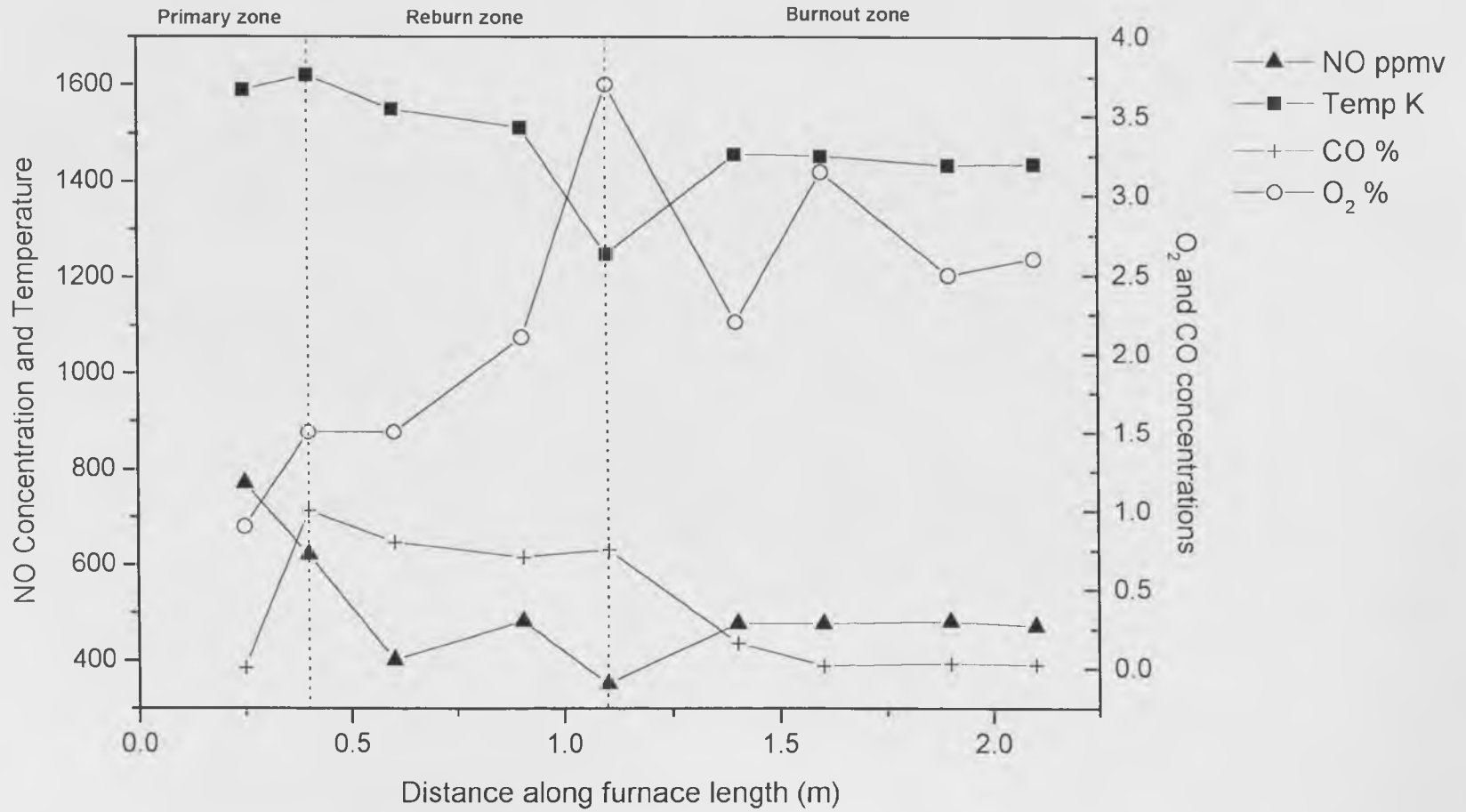
- Furnace load, 100 - 120 kW
- Reburn fuel fraction ( $R_{\text{ff}}$ , ratio of thermal contribution made by the reburn coal to the primary fuel), 9 - 35%
- Reburn zone air/fuel stoichiometric ratio ( $SR_2$ ), 0.83 - 1.03
- Primary zone air/fuel stoichiometric ratio ( $SR_1$ ), 1.0 - 1.18
- Reburn zone residence time, 120 - 840 ms
- Reburn zone inlet NO concentration, 137 - 1150 ppmv

- Reburn coal carrier gas oxygen concentration, 12% and 21%
- Burnout zone air/fuel stoichiometric ratio ( $SR_3$ ), 1.04 - 1.11

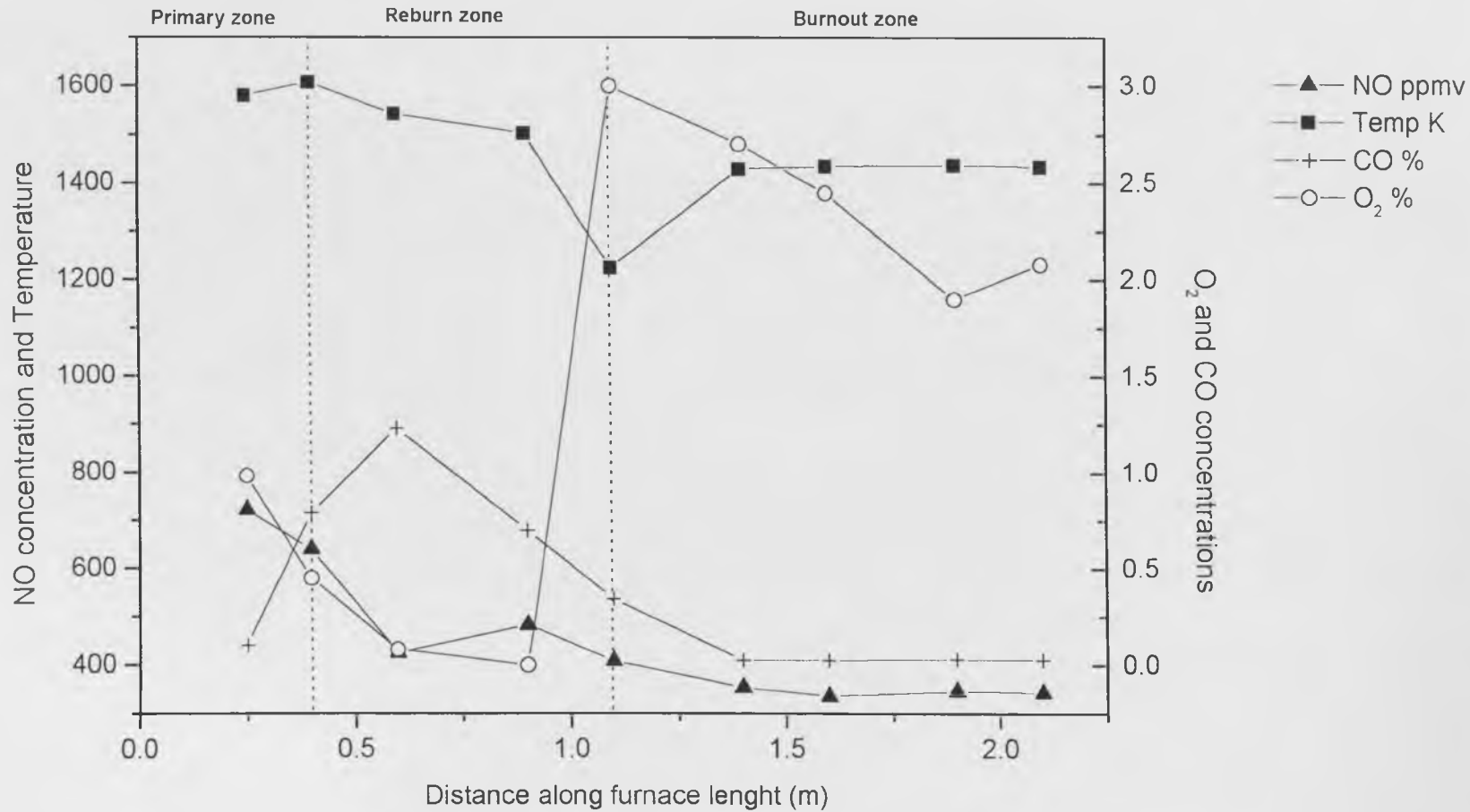
The following subsections will present and analyse the results of the different process variables investigated in this study. Residence times in the primary zone and in the burnout zone, and the stoichiometry after the burnout air addition are not included in the analysis since these variables have been shown to have only a minor or no effect on reburning effectiveness under practical conditions (Greene *et al.*, 1986).

#### 4.2.1 Detailed Furnace Measurements

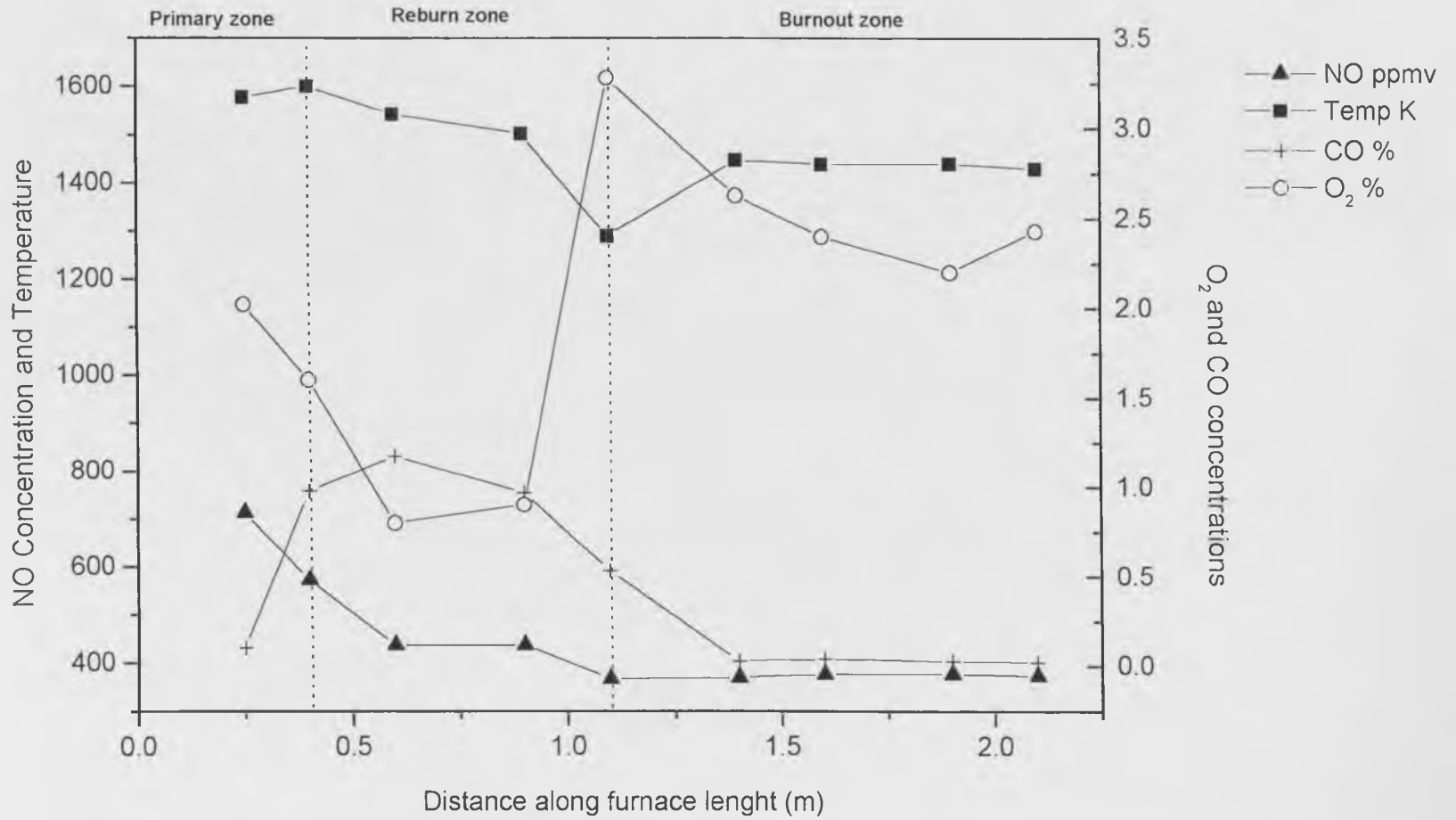
Figures 4.3 to 4.7 show the typical axial variation in temperature, NO, CO and O<sub>2</sub> for operation with five different coals. The measurements were taken from the start of the primary zone, along the centre line of the furnace, to the end of the burnout zone. The points at which reburn coal and burnout air were introduced are indicated by the dotted lines. The gas temperature increases slightly to a peak value of about 1600 K near the reburn coal injection point due mainly to volatile combustion. Further downstream, the temperature fell to a minimum of around 1100 K for Koonfonteine, as a result of heat losses and dilution by the cool burnout air before increasing again in the burnout zone due to the combustion of char and any remaining volatiles. The carbon monoxide concentration varied from 0.5 - 1.0 in the fuel rich reburn zone, but CO was quickly consumed in the burnout zone and was between 400 - 200 ppmv in the exit flue. The NO fell rapidly from an initial value of around 800 ppmv at the start of the reburn zone (corresponding to a baseline NO concentration at the exit of 600 ppmv) to a minimum of 300 - 400 ppm just prior to



**Figure 4.3** Axial distribution of temperature, oxygen, NO and CO  
 Gascoigne Wood, SR1=1.03, SR2=0.96, SR3=1.07, Rff=17%

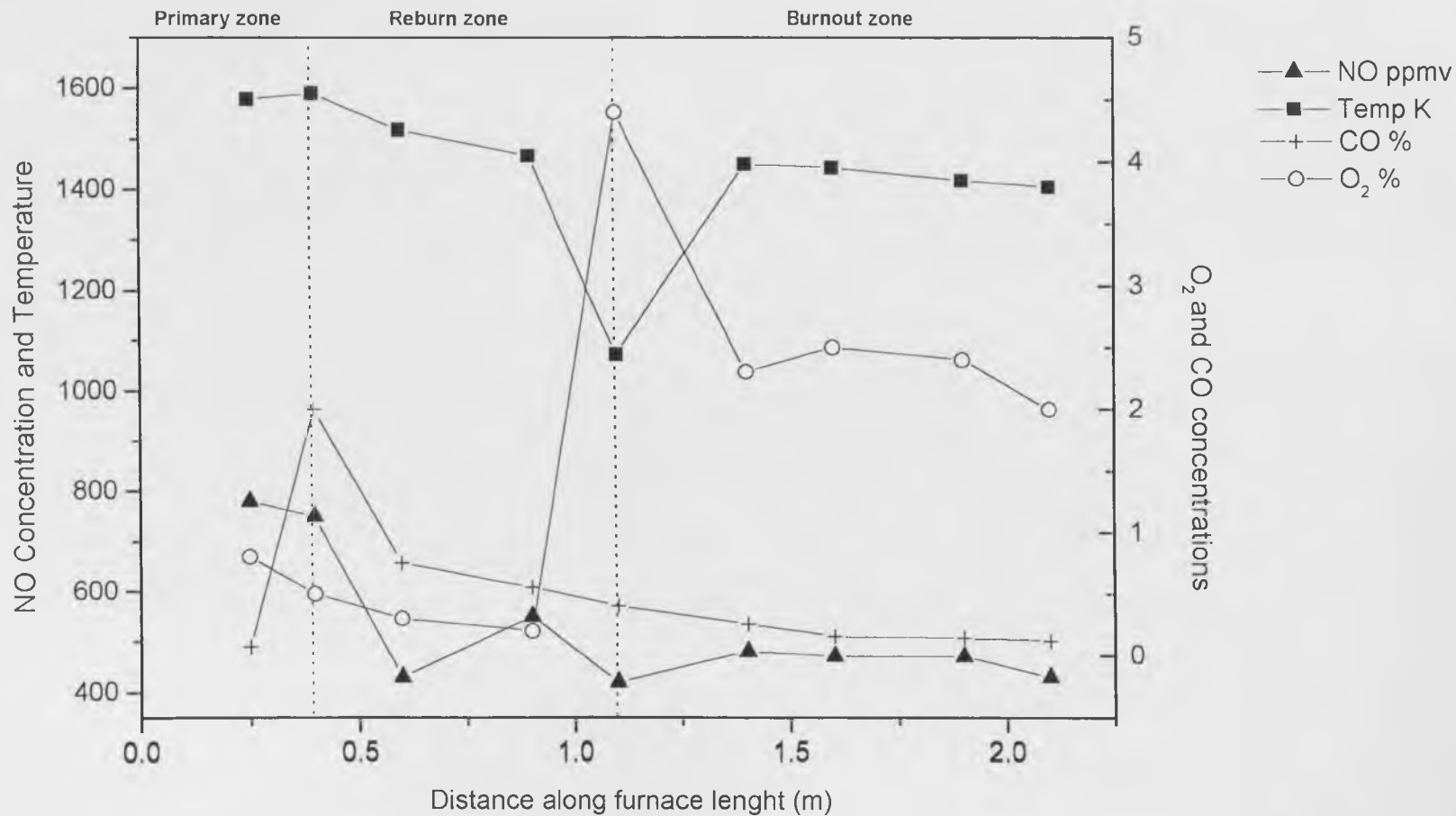


**Figure 4.4** Axial distribution of temperature, oxygen, NO and CO  
 Hunters Valley, SR1=1.03, SR2=0.92, SR3=1.08, Rff=22%

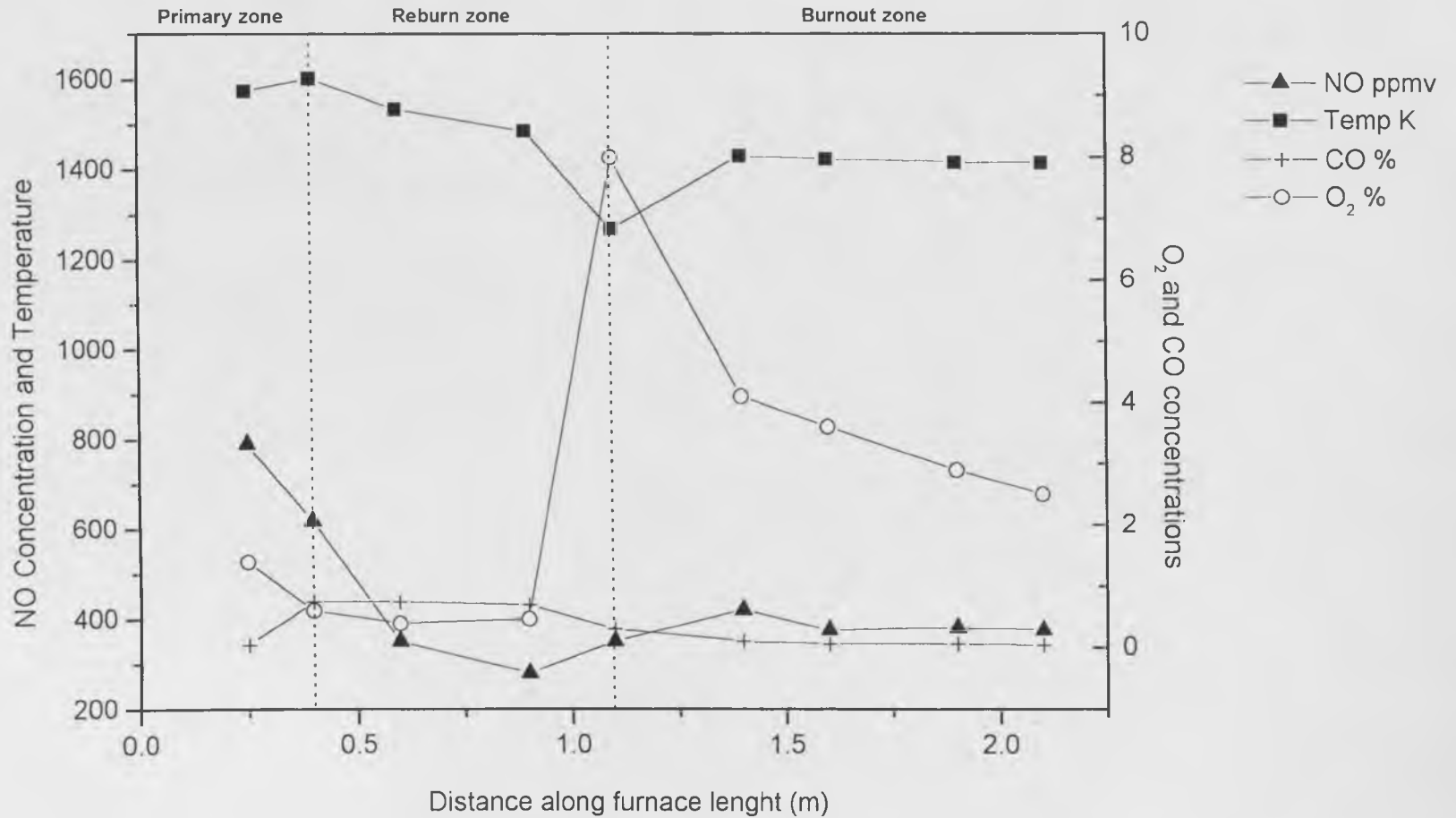


**Figure 4.5** Axial distribution of temperature, oxygen, NO and CO  
 La Jagua, SR1=1.03, SR2=0.95, SR3=1.08, Rff=19%





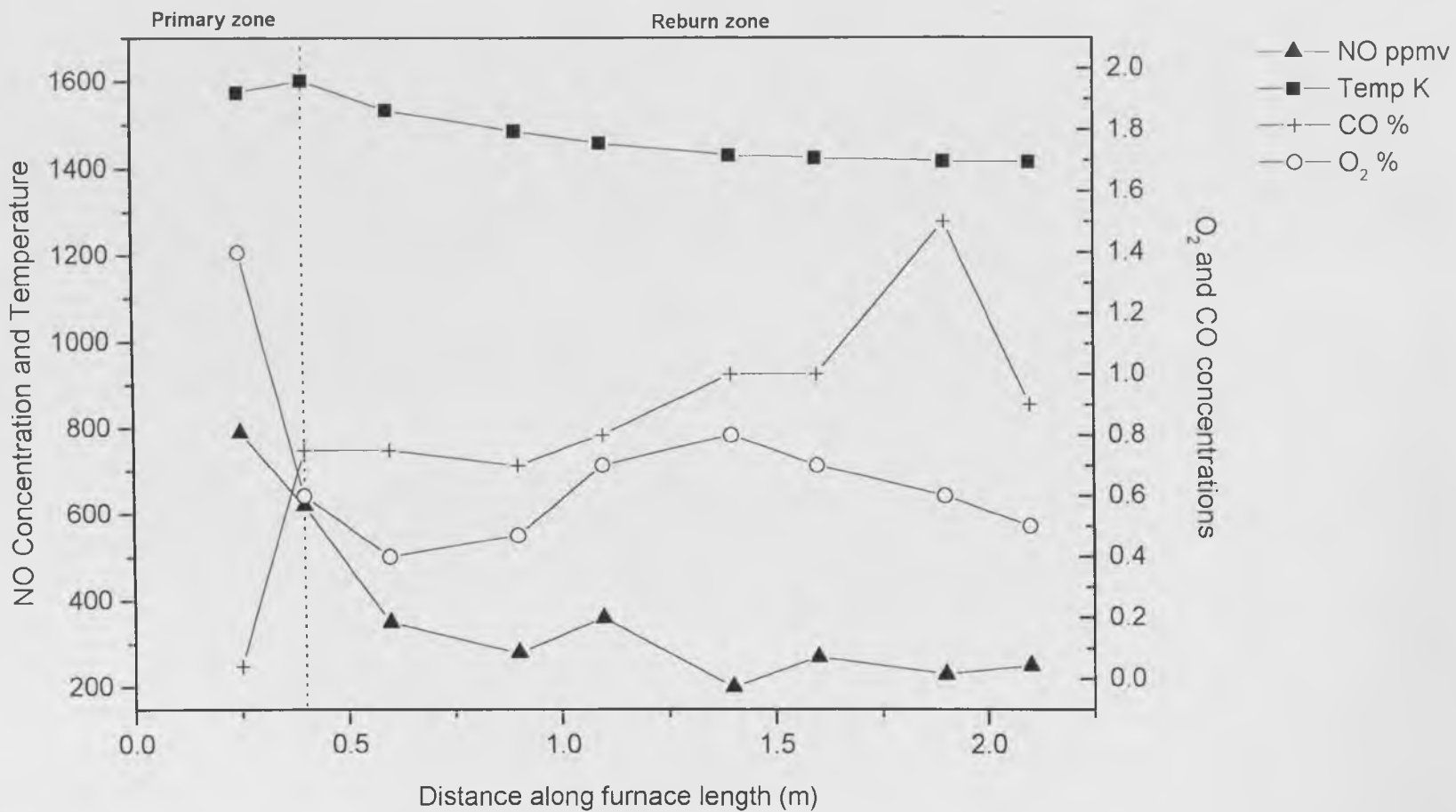
**Figure 4.6** Axial distribution of temperature, oxygen, NO and CO  
Koonfonteine, SR1=1.03, SR2=0.95, SR3=1.10, Rff=18%



**Figure 4.7** Axial distribution of temperature, oxygen, NO and CO  
 Thoresby, SR1=1.03, SR2=0.936, SR3=1.09, Rff=21%

the burnout air injection. Beyond this point, the concentration rose to about 400 - 450 ppmv before reducing slightly and leveling off to the exit value.

The NO concentration profile shown in Figs. 4.3 to 4.7 demonstrates the effectiveness of coal to reduce NO in the reburn zone. The major NO reduction processes take place in the reburn zone where the important reducing species such as CO, CH<sub>i</sub>, NH<sub>i</sub> and HCN, derived from the devolatilisation of the reburn coal, react with and reduce primary NO to N<sub>2</sub>. However, as soon as the burnout air is introduced new NO is formed by the residual nitrogen in the char together with any unconsumed volatile nitrogenous fragments (HCN and NH<sub>3</sub>), which may possibly escape into the burnout zone, and as a result are easily oxidised to NO by the additional O<sub>2</sub> in the burnout air. This is illustrated in Figs. 4.7 and 4.8 where Thoresby coal was used as a reburn fuel, with and without burnout air respectively. In Fig. 4.7 where burnout air was used the NO level rose from 350 ppmv to 420 ppmv in the burnout zone before leveling off at 375 ppmv at the exit as the oxygen is consumed. This exit concentration is still above the minimum value reached at the exit of the reburn zone (280 ppmv) and this increase is due to the oxidation of residual char-N and other TFN species. However, when no burnout air was used, as in Fig. 4.8, the NO concentration drops to a minimum of 200 ppmv before rising to 250 ppmv at the exit. The increased NO reduction efficiency achieved in Fig. 4.8 is due to three main factors: the increased reburn zone residence time which allows for the TFN species to decay in a reducing environment, the reduction of NO by the char via reactions (R4.3 - R4.5), and the reduced heterogeneous oxidation of char-N due to the fuel rich conditions in place. Nevertheless, since it is crucial to complete the



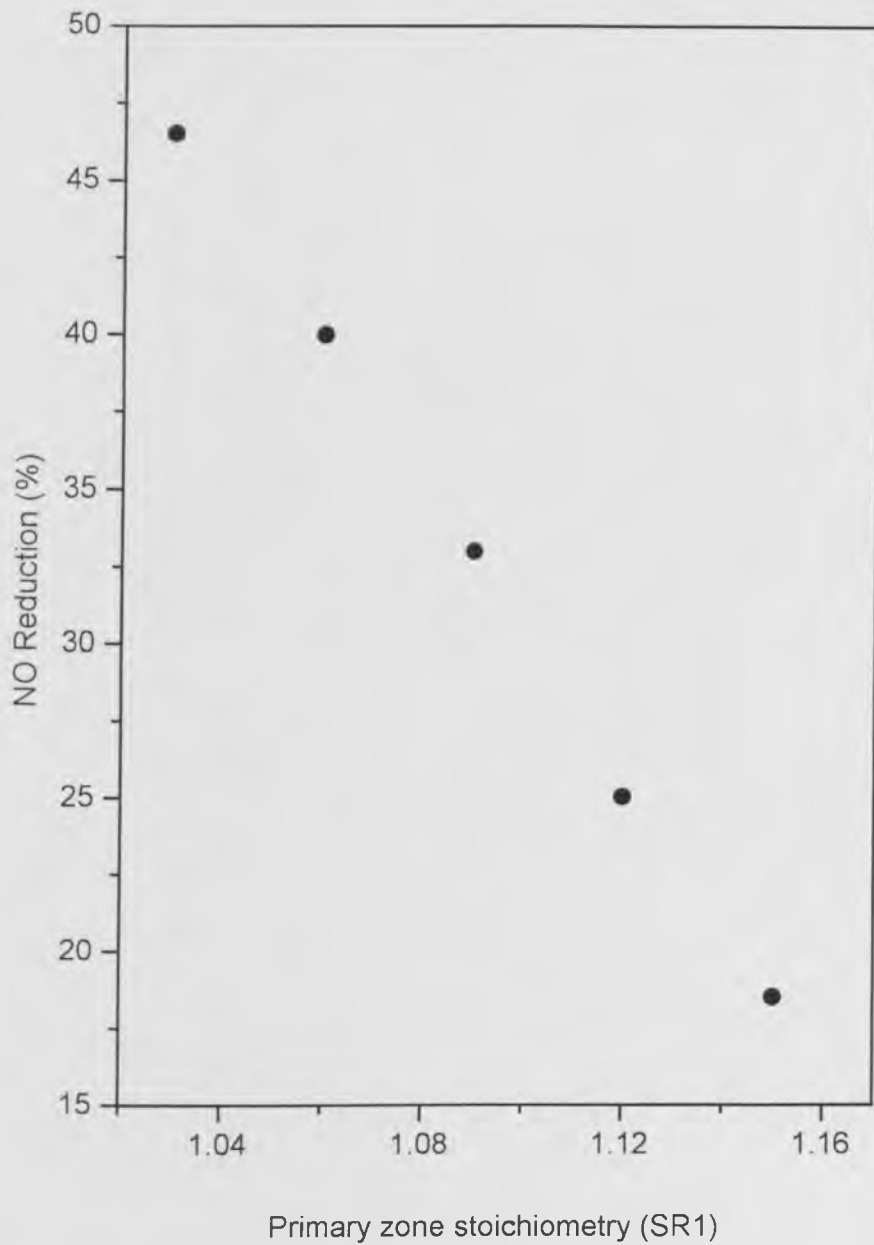
**Figure 4.8** Axial distribution of temperature, oxygen, NO and CO  
 Thoresby, SR1=1.03, SR2=0.936, Rff=21%, No burnout air

oxidation of the fuel in any reburning operation the introduction of the burnout air is an important factor which helps reduce exhaust CO emissions and improve carbon burnout.

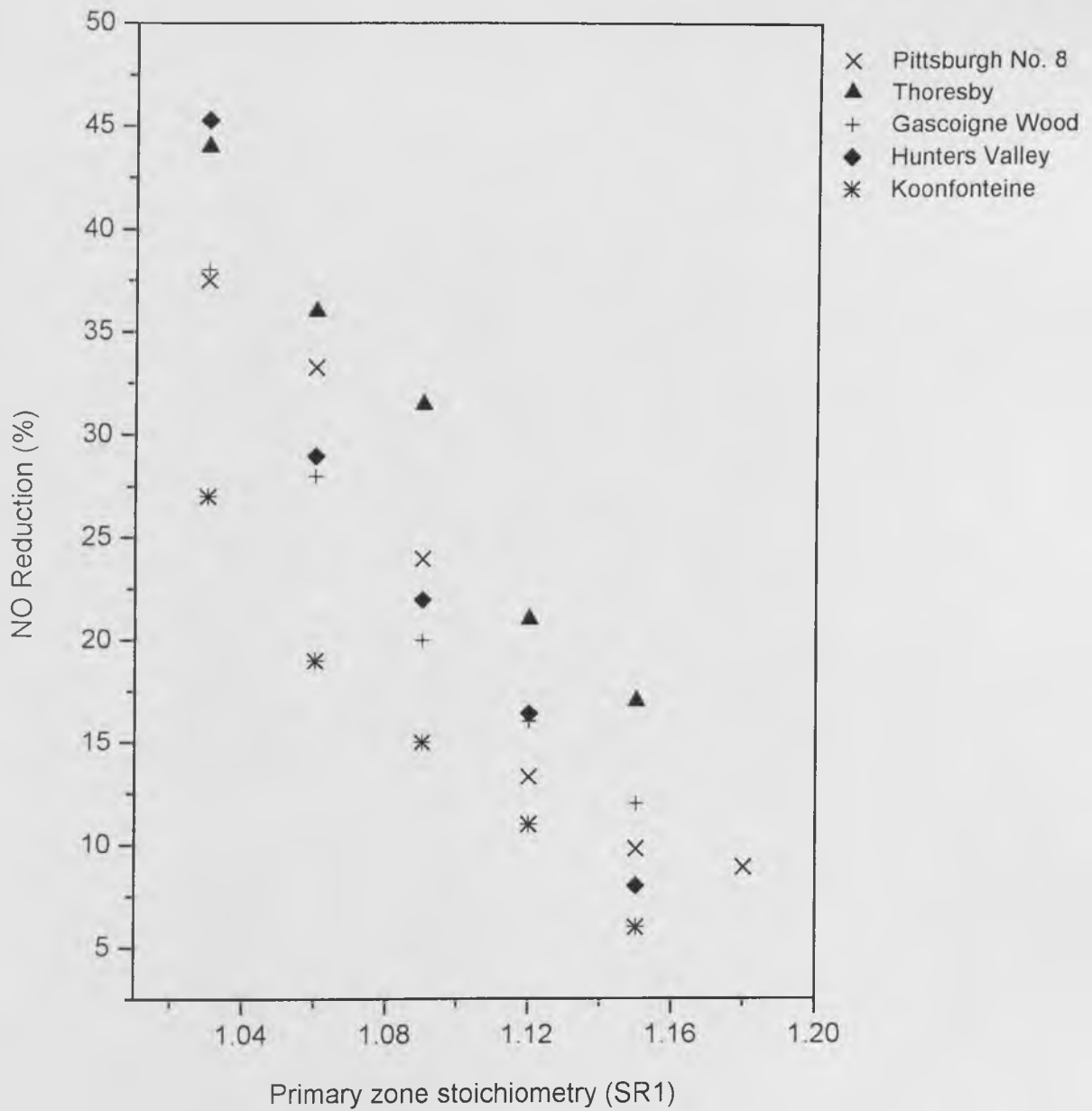
#### 4.2.2 Effect of Primary Zone Stoichiometry

The primary zone stoichiometry,  $SR_1$ , was varied by changing the primary air flow rate for a constant coal-feed rate and carrier-gas air flow. Figure 4.9 shows the typical NO reduction obtained from La Jagua. Five other different coals are shown in Fig. 4.10. It can be seen that NO reduction decreased as  $SR_1$  increased. This is expected since the reburn fuel fraction,  $R_{ff}$  (expressed as a percentage of the primary fuel thermal input), is constant at 18 % and the carrier-gas stoichiometry,  $SR_r$ , is also fixed. Therefore, the net effect of increasing  $SR_1$  is increasing the oxygen concentration in the reburn zone and hence the secondary stoichiometry,  $SR_2$ . The trends indicated in Figs. 4.9 and 4.10 suggest that the optimum amount of oxidant required in the reburn zone, to initiate the generation of hydrocarbon radicals from the reburn fuel and to promote the conversion of HCN to  $N_2$  has been exceeded, as the NO reduction efficiency rapidly deteriorates with increasing  $SR_1$ . Another possible explanation is that as  $SR_1$  is increased the residence time in the reburn zone, which enhances the destruction of nitrogenous species, is decreased.

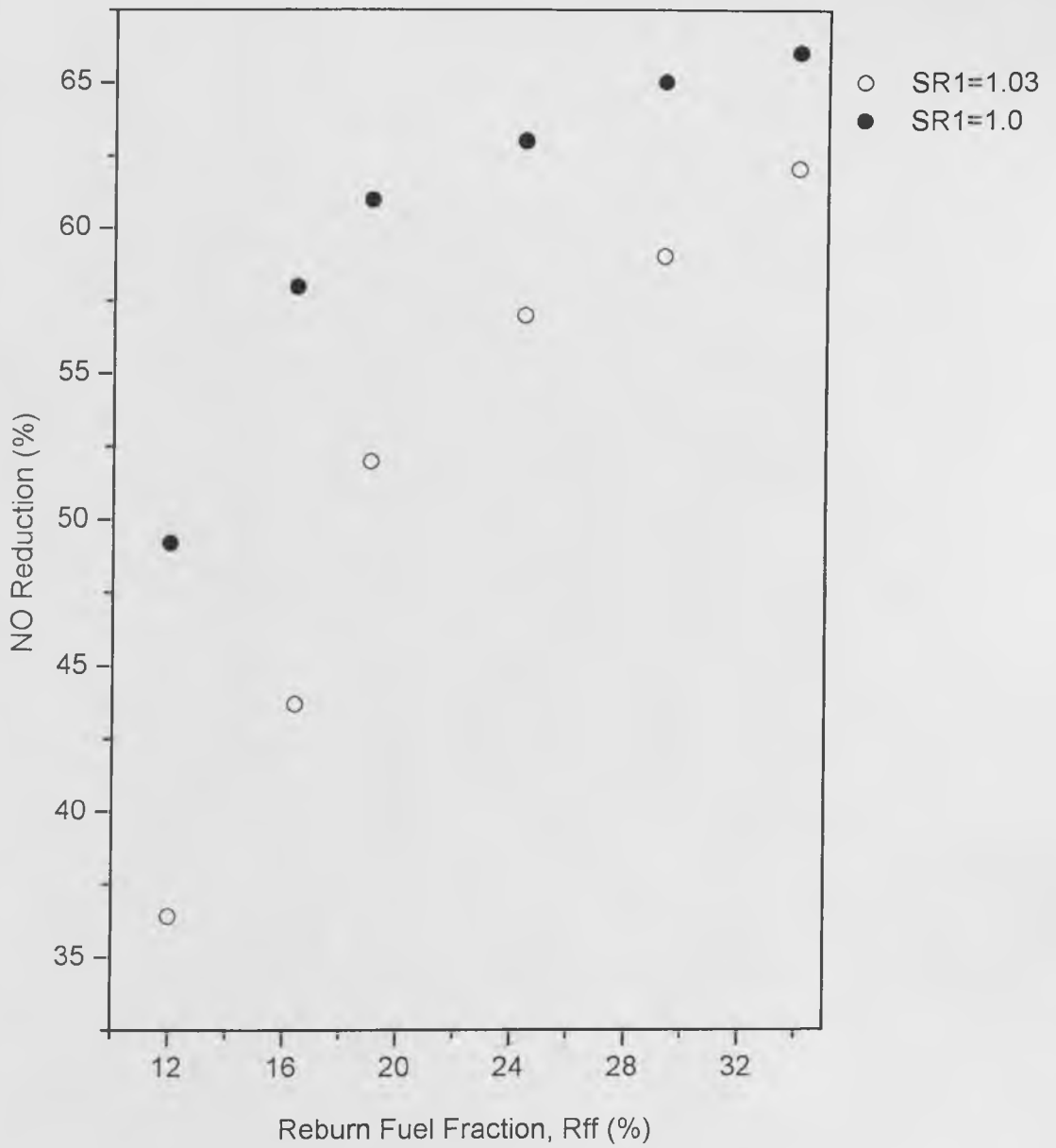
Figure 4.11 compares NO reduction efficiencies of two different primary zone stoichiometries,  $SR_1 = 1.03$  and  $SR_1 = 1.0$ , for a range of  $R_{ff}$ . The reburning carrier gas stoichiometry,  $SR_r$  was kept constant for all values of  $R_{ff}$ , and the results further illustrate that for the typical operating range of  $SR_2$  (0.94 - 0.80) lower values of  $SR_1$  enhance reburning effectiveness.



**Figure 4.9** Effect of SR1 on NO reduction  
La Jagua, SR2=0.93-1.03, SR3=1.09-1.19, Rff=22%

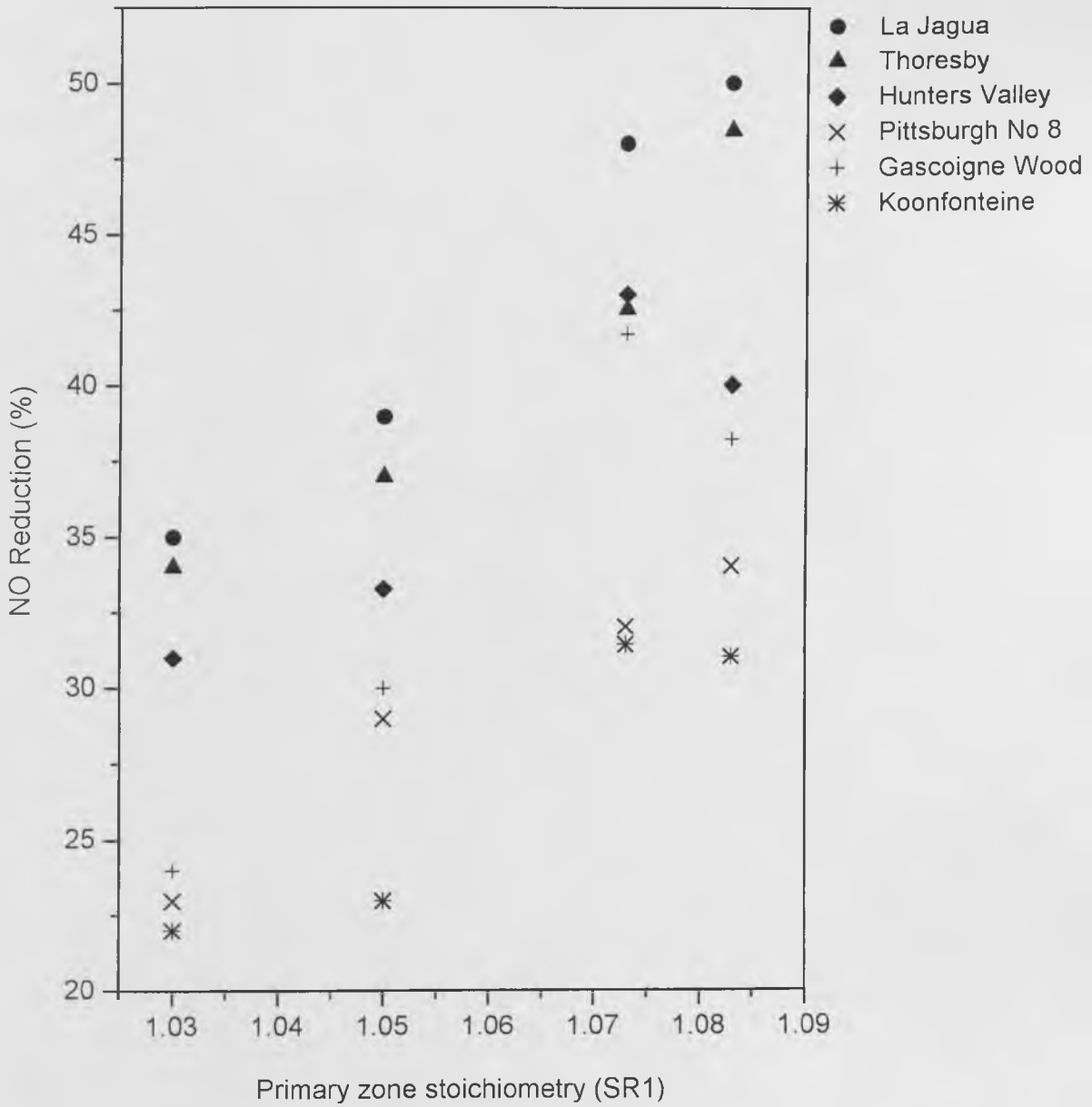


**Figure 4.10** Effect of SR1 on NO reduction  
 SR2=0.92-1.04, SR3=1.09-1.16, Rff=22%



**Figure 4.11** Effect of SR1 on NO reduction  
La Jagua, SR3=1.09,  $T_{pr} = 1573$  K





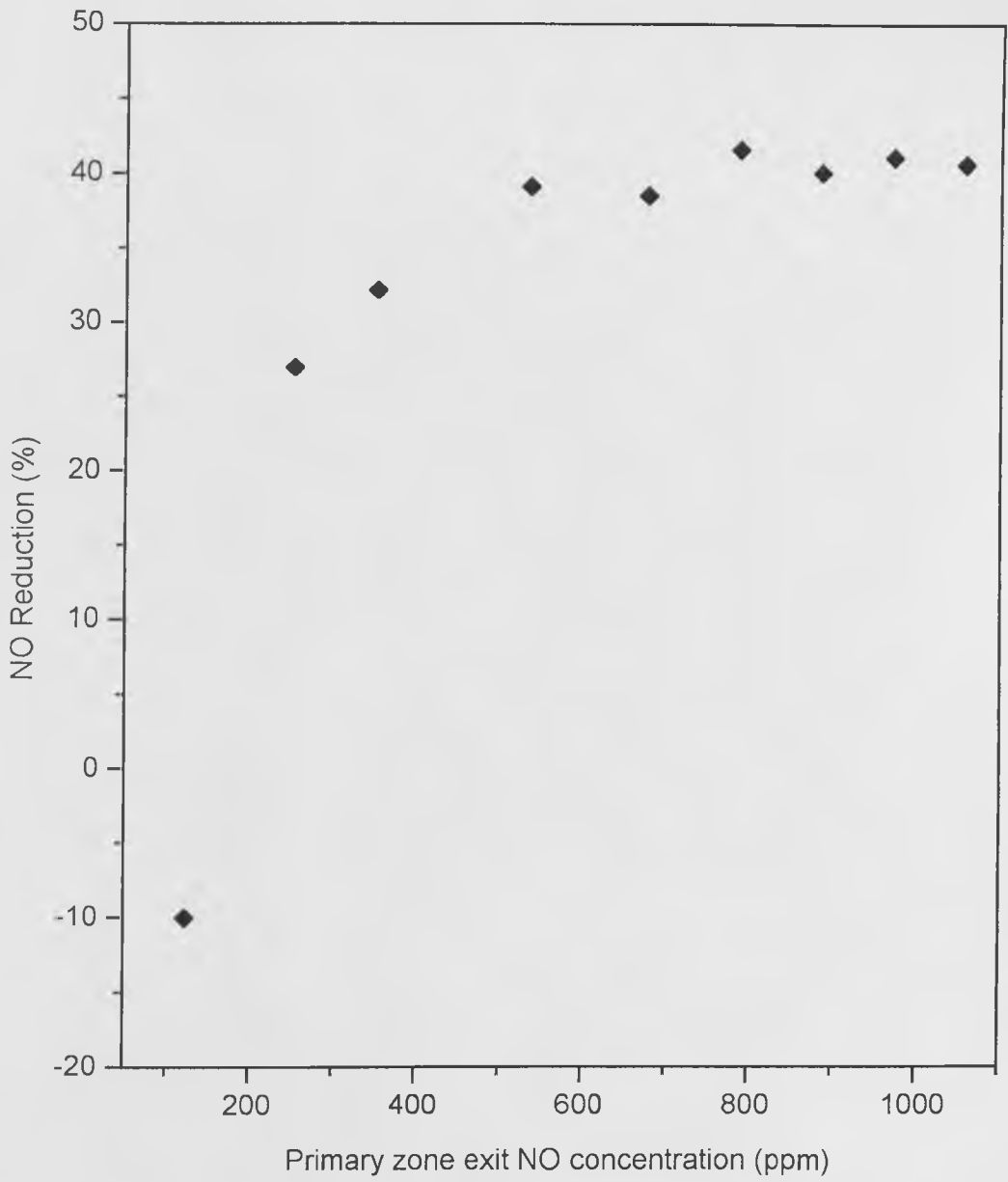
**Figure 4.12** Effect of SR1 on NO reduction  
 SR2=0.95, SR3=1.09, Rff=22%,  $T_{pr}=1573$  K

In order to investigate the effect of  $SR_1$  without affecting other parameters, especially  $SR_2$ , the  $R_{fl}$  was kept constant while the primary and carrier-gas air were varied so as to keep  $SR_2$  constant. In this way, it was possible to vary  $SR_1$  while keeping  $SR_2$  constant. Figure 4.12 shows the results of these tests where an increase in NO reduction with increasing primary stoichiometry was seen for most of the coals. This result must be treated with caution as the carrier-gas air must be reduced as the primary air is increased, hence  $SR_r$  was also reduced. Consequently, the increase in NO reduction efficiency shown in Fig. 4.12 can be attributed to the fact that the fuel transport gas becoming more fuel rich which leads to reduced oxygen concentration in the vicinity of the reburning coal flame and thus better NO reduction.

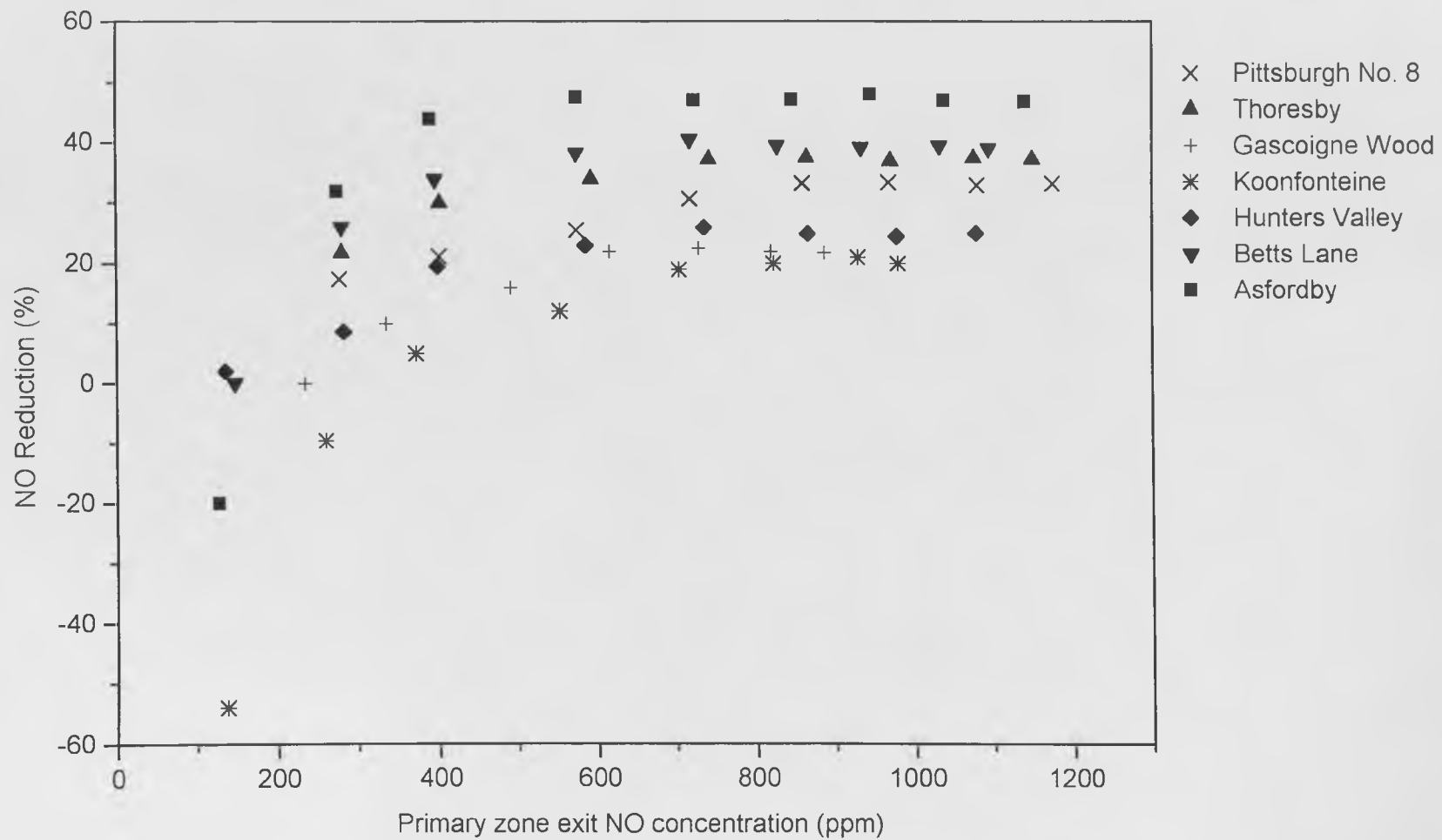
#### 4.2.3 Effect of Primary Zone NO

Figure 4.13 shows the typical effect of varying the primary zone NO concentration, as measured at the exit of the primary zone, on NO reduction. For the experimental range specified ( $NO_0 = 137 - 1150$  ppmv), the NO reduction efficiency increases significantly with increasing initial NO up to around 600 - 700 ppmv after which the trend levels off. Beyond 800 ppmv the NO reduction efficiency remained constant. These observations are consistent with those of Greene *et al.* (1986) and Chen *et al.* (1983, 1986). The effect is similar for all coals (Fig. 4.14).

At low primary NO concentrations (<200 ppm) the NO reduction efficiency of three coals, namely Asfordby, La Jagau and Koonfontiene containing 1.39%, 1.41 and 1.74% (by weight, dry basis) fuel nitrogen respectively resulted in an increase in the exit NO emissions (indicated by the negative values in Figs. 4.13 & 4.14). This is in



**Figure 4.13** Influence of reburn zone inlet NO concentration  
La Jagua, SR1=1.03, SR2=0.944, SR3=1.075, Rff=19%,  $T_{pr}$ =1573 K

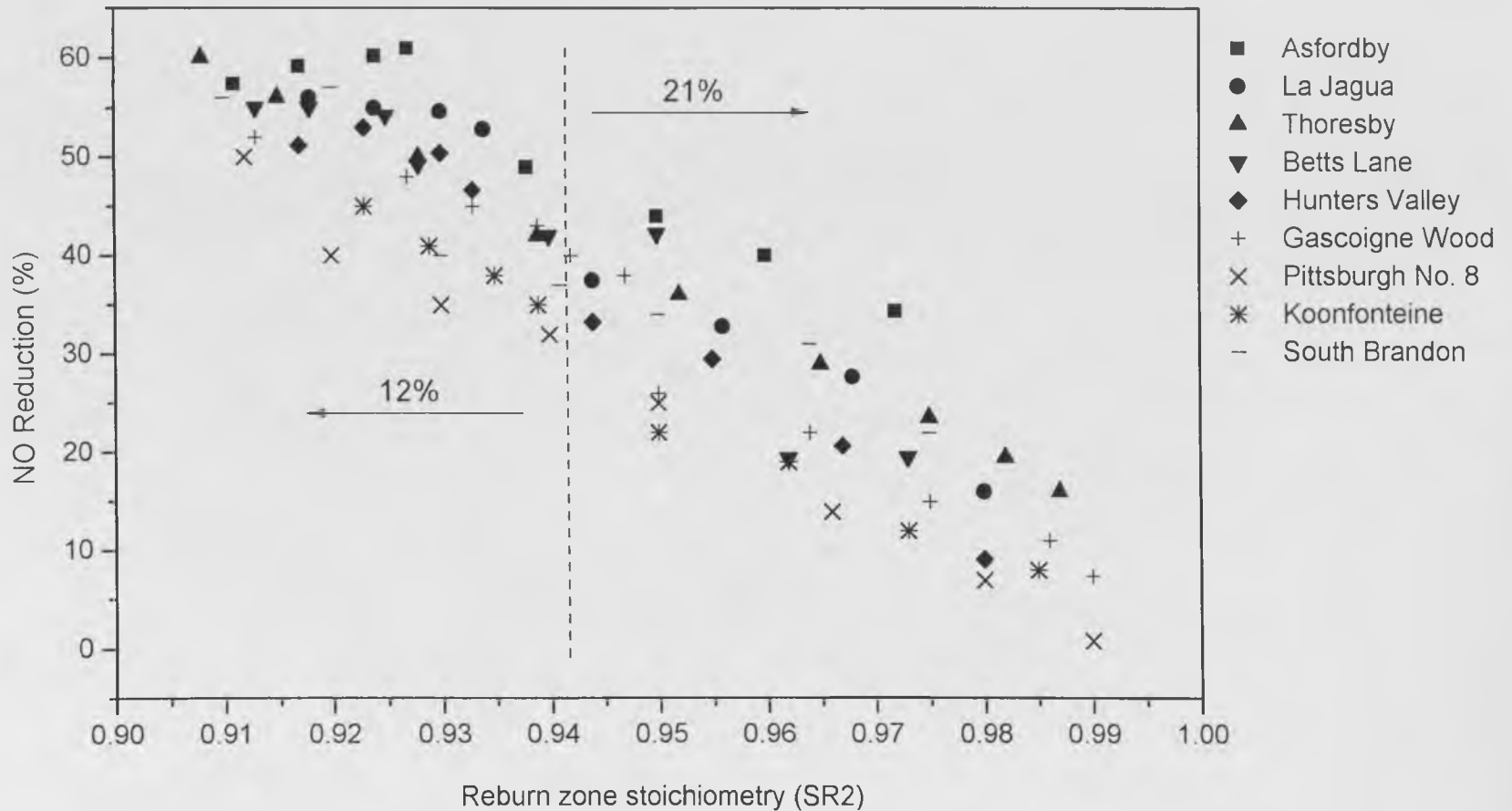


**Figure 4.14** Influence of reburn zone inlet NO concentration  
 SR1=1.03, SR2=0.944-0.955, SR3=1.07, Rff=19%, Tpr=1573 K

agreement with the work of Mullholland and Hall (1986, 1987) who found that for an initial NO concentration of less than 200 ppm, reburning fuel nitrogen exceeding 1% resulted in an increase in NO emissions. Greene *et al.* (1986), using a bituminous coal containing 1.54% (dry basis) fuel nitrogen with an initial NO level of 190 ppm, also reported an increase in NO emissions. In this study Koonfonteine produced a 54% increase in NO emissions at a primary NO level of 137 ppm.

#### 4.2.4 Effect of Reburn Zone Stoichiometry

The effect of varying the overall reburn zone stoichiometric ratio ( $SR_2$ ) on NO reduction efficiency for all eight coals is shown in Fig. 4.15. The reburn fuel fraction was kept constant at 19% for all coals, however, due to the limitations of the coal feeding system the lowest possible reburn zone stoichiometric ratio attained was 0.91. The variation in  $SR_2$  was achieved by adjusting the coal carrier-gas (air) flow rate or / and oxygen concentration for a constant coal feed rate and primary air flow. All coals showed a strong sensitivity to changes in  $SR_2$  over the range investigated, with the NO reduction efficiency decreasing nearly linearly as  $SR_2$  was increased. However, it was not possible to operated the reburn zone at a fuel-lean ( $SR_2 \geq 1.05$ ) and still achieve an overall NO reduction efficiency at the exit. The highest NO reductions achieved, over the investigated range, were between 50 and 60% at  $SR_2 \leq 0.92$ . This further highlights the conflicting results found in the literature where the optimum  $SR_2$  ranged from 0.7 to 0.94 (Mulholland and Hall, 1986; Miyamae *et al.*, 1986), and supports the notion that the optimum stoichiometry is greatly influenced by the size of the combustor, mixing behaviour and other factors such as residence time, temperature and coal properties.



**Figure 4.15** Overall NO reduction efficiency as a function of reburn zone stoichiometry for all nine coals  
 Rff=19%, SR1=1.03, SR3=1.07-1.09, carrier gas air (21%O<sub>2</sub>) or air plus nitrogen (12%O<sub>2</sub>) as indicated, T<sub>pr</sub>=1573 K

The data also provided an indication of the variability in the extent of NO reduction associated with the use of a range of coals of similar rank. Since no discontinuity can be observed in the NO reduction trend between corresponding data in Fig. 4.15 for the same coal at the two carrier gas oxygen concentrations used (21% and 12%), the implication is that given good mixing at the injection point, the oxygen concentration of the reburn coal carrier gas can be assumed to exert an influence mainly through subsequent change in  $SR_2$ .

#### **4.2.5 Effect of Reburn Fuel Fraction ( $R_{ff}$ )**

The  $R_{ff}$  is defined as the ratio (expressed in percentage) of the thermal contribution made by the reburn coal to that of the primary fuel. Figures 4.16 - 4.22 show the effect of varying  $R_{ff}$  on NO reduction efficiency for each of the eight coals. The  $R_{ff}$  was varied between 9-35% by increasing the coal feed rate, and for each  $R_{ff}$  value the possible reburn zone stoichiometric ratios were restricted to a narrow band due to the operational limits of the coal-feeder. The results obtained clearly show that as the  $R_{ff}$  is increased the NO emission is decreased, however, closer examination indicates that for a fixed  $SR_2$  lower values of  $R_{ff}$  are favoured; with the best NO reductions generally obtained for lower  $R_{ff}$  values at a particular value of  $SR_2$ .

#### **4.2.6 Effect of Reburn Zone Residence Time**

The influence of increasing reburn zone residence time on NO reduction efficiency is shown in Fig. 4.23. The general trend exhibited by the three coals indicate an increase in NO reduction with increasing residence time up to a maximum at around

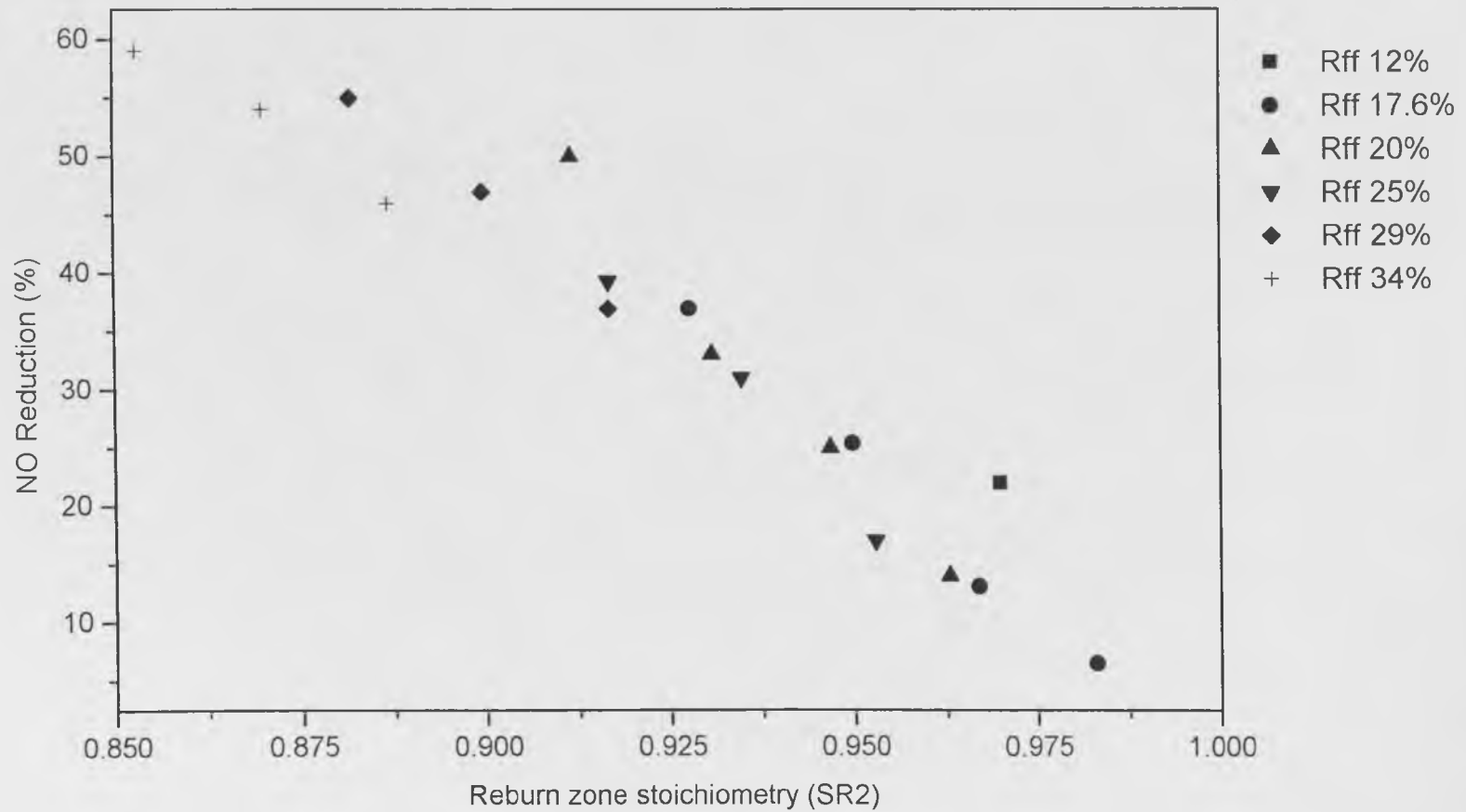
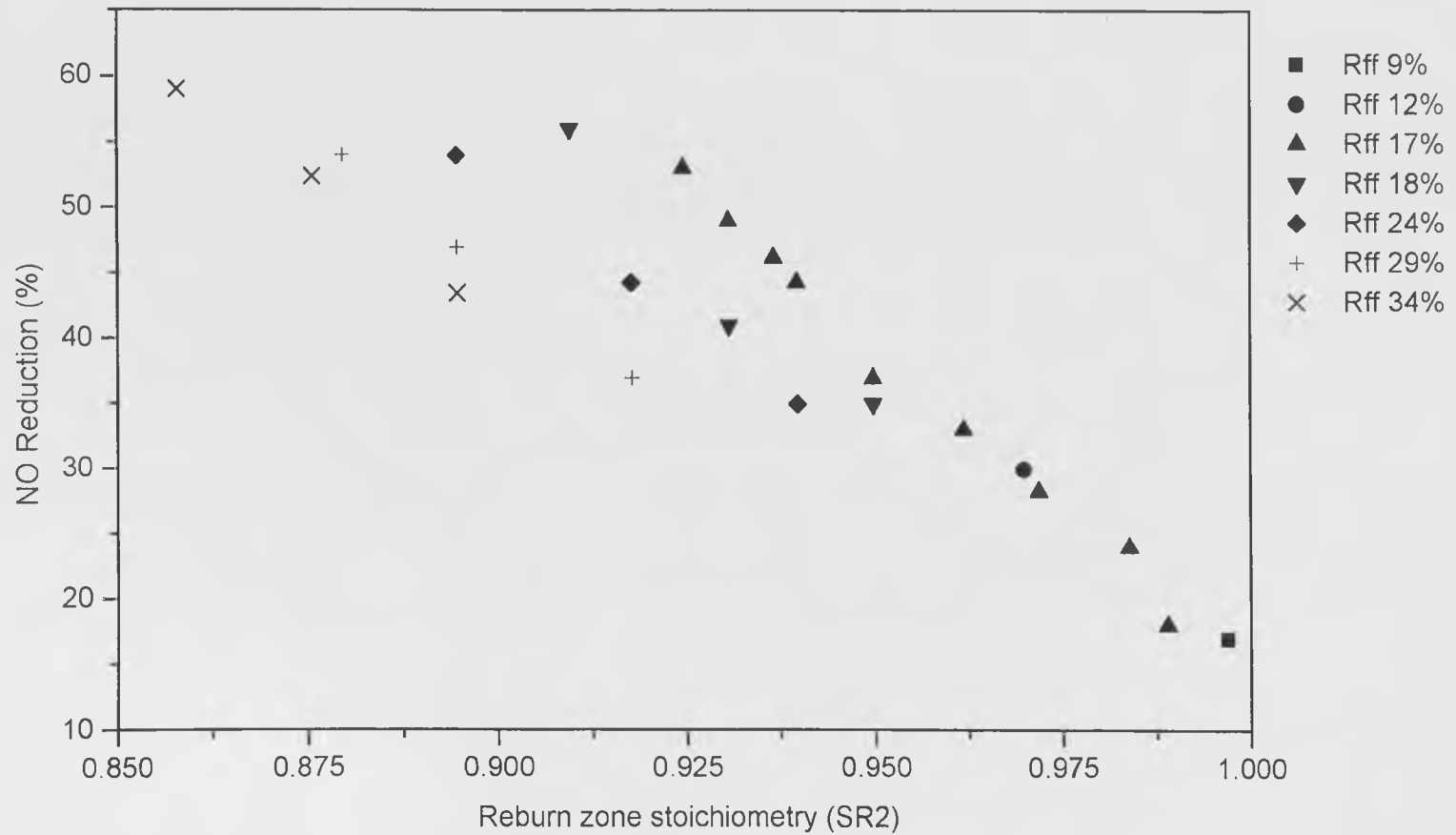
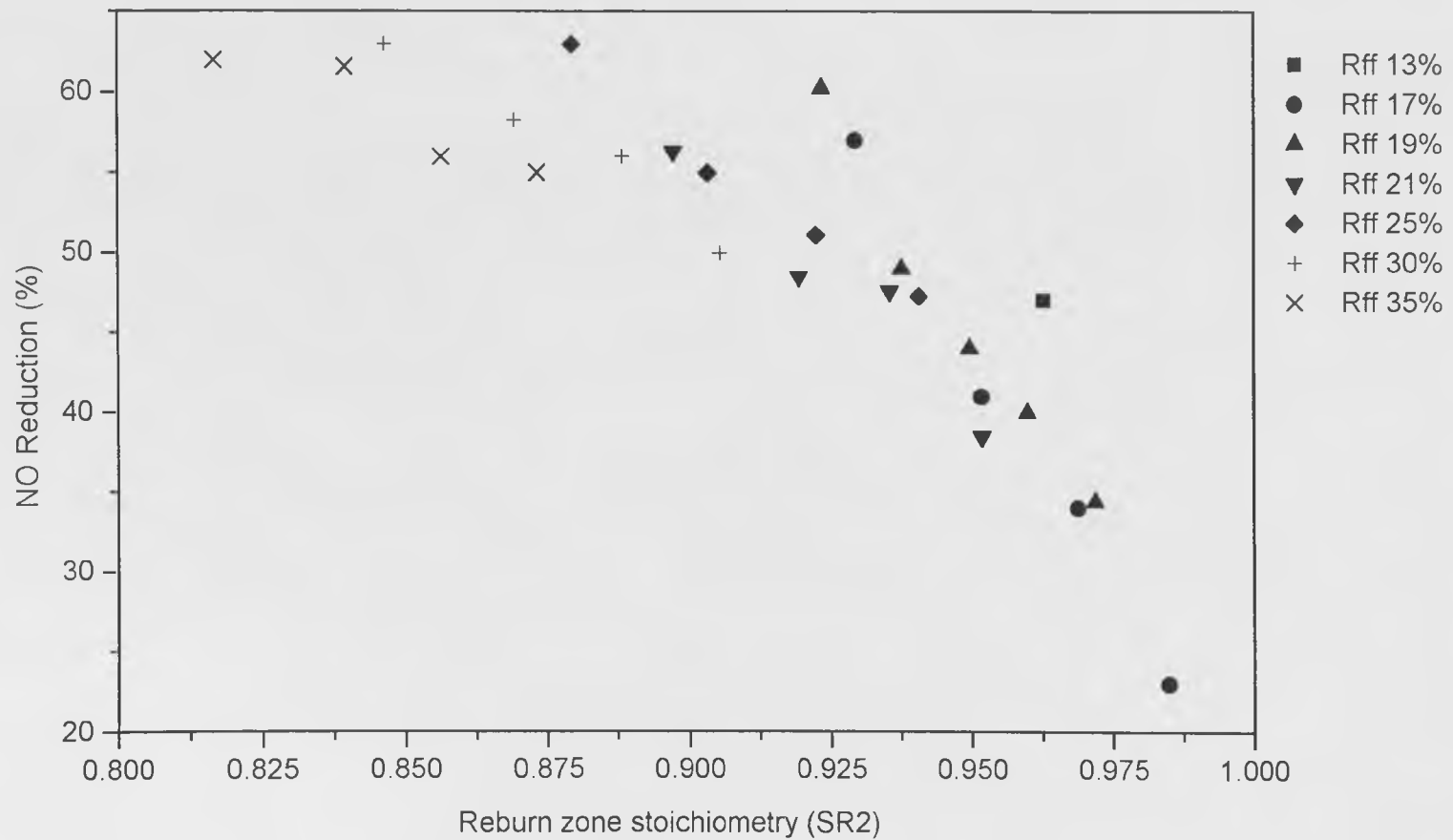


Figure 4.16 Effect of reburn fraction on NO reduction efficiency  
 Pittsburgh No. 8, SR1=1.03, SR3=1.05-1.10,  $T_{pr}$ =1573 K

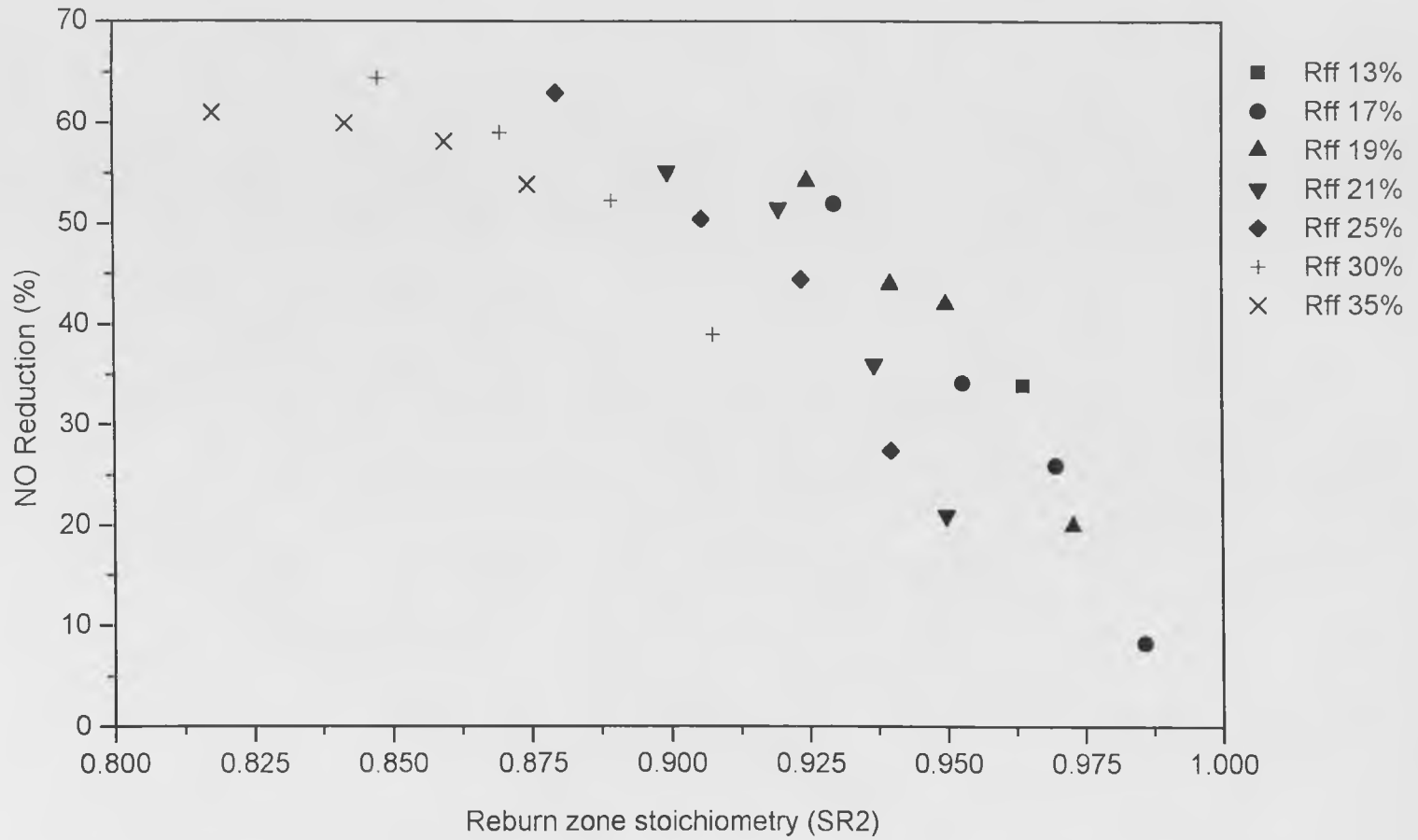




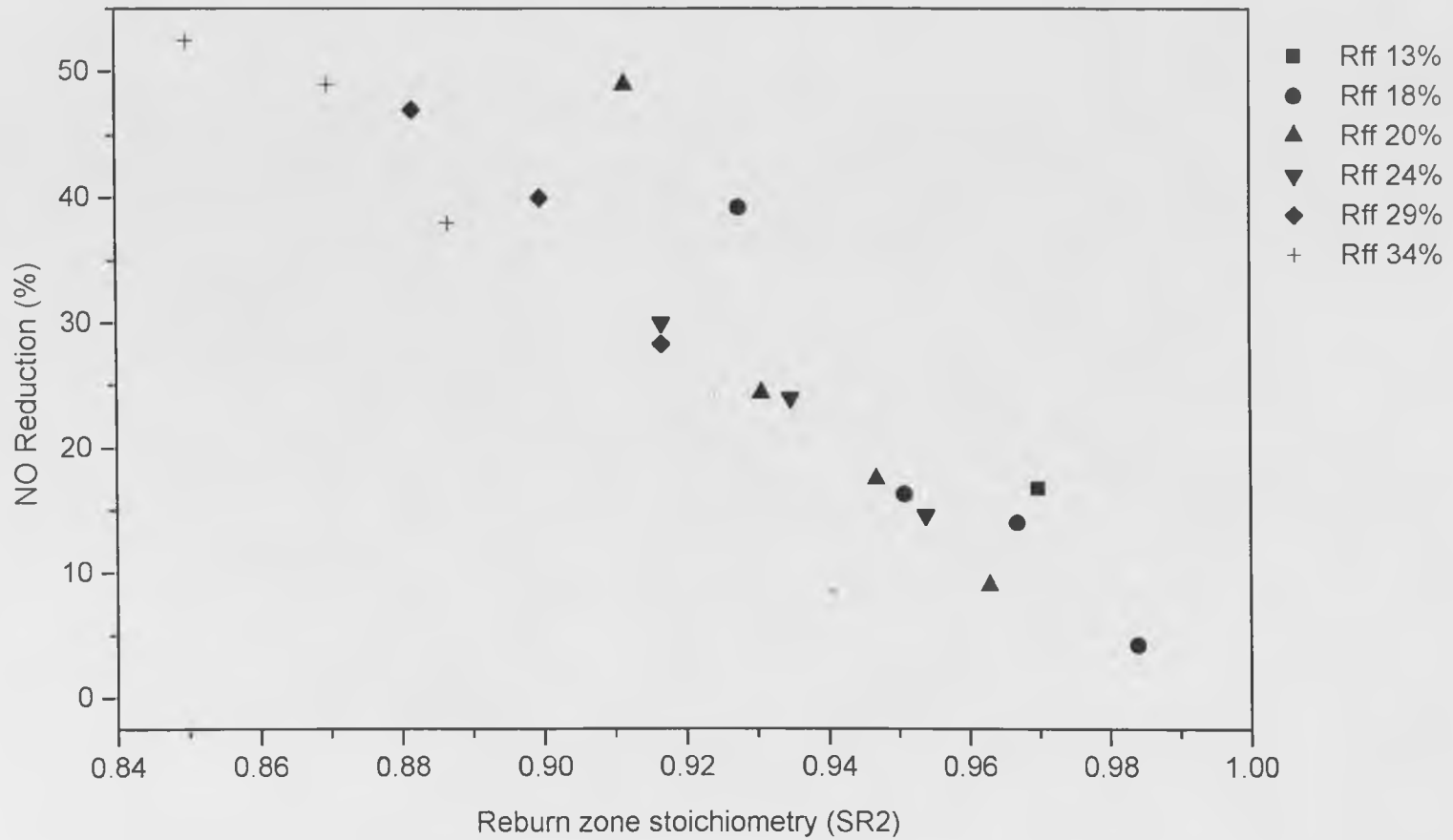
**Figure 4.17** Effect of reburn fuel fraction on NO reduction efficiency  
 Thoresby, SR1=1.03, SR3=1.05 - 1.10,  $T_{pr} = 1573$  K



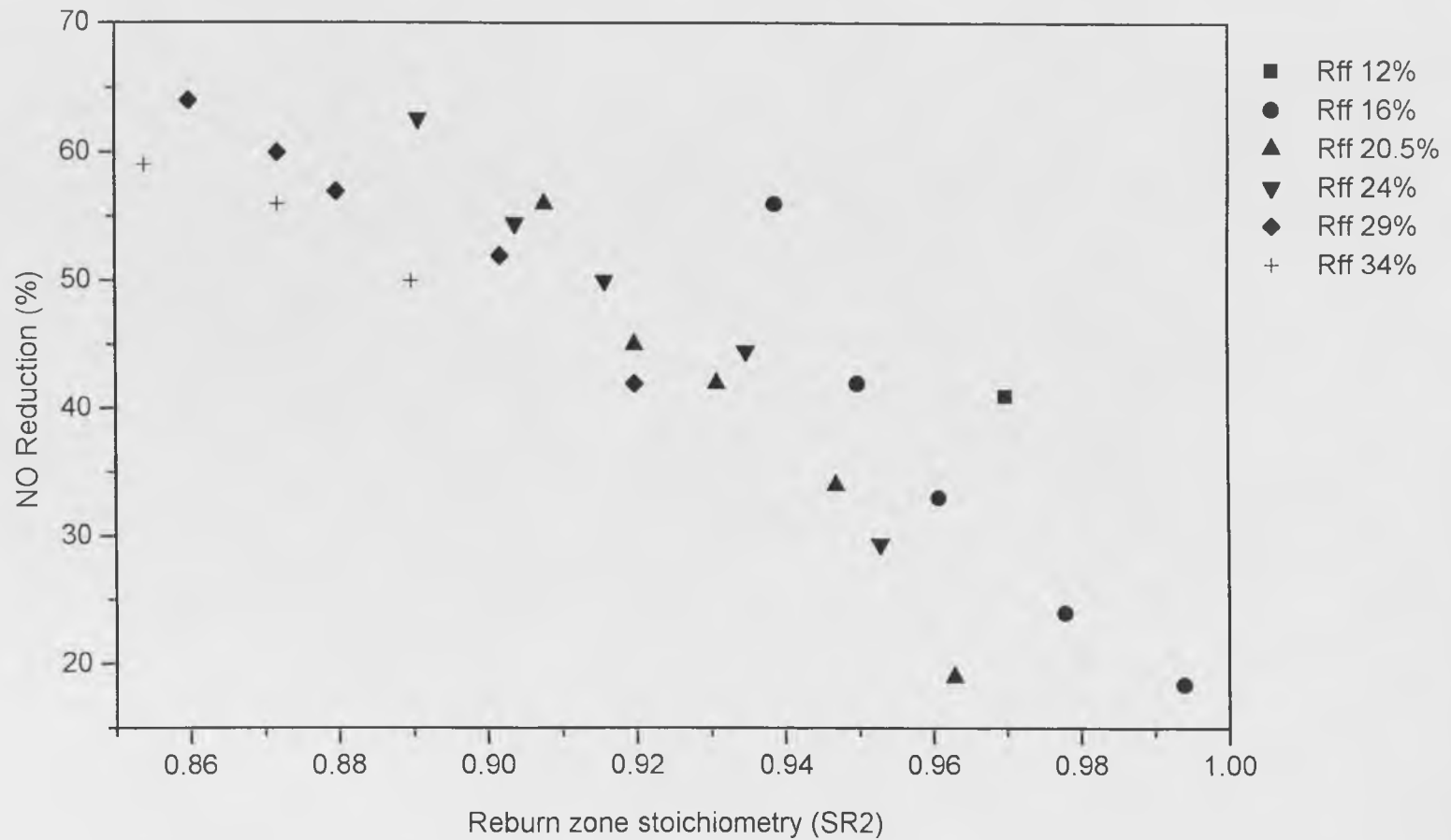
**Figure 4.18** Effect of reburn fuel fraction on NO reduction efficiency  
 Asfordby, SR1= 1.03, SR3= 1.04 - 1.10,  $T_p = 1573$  K



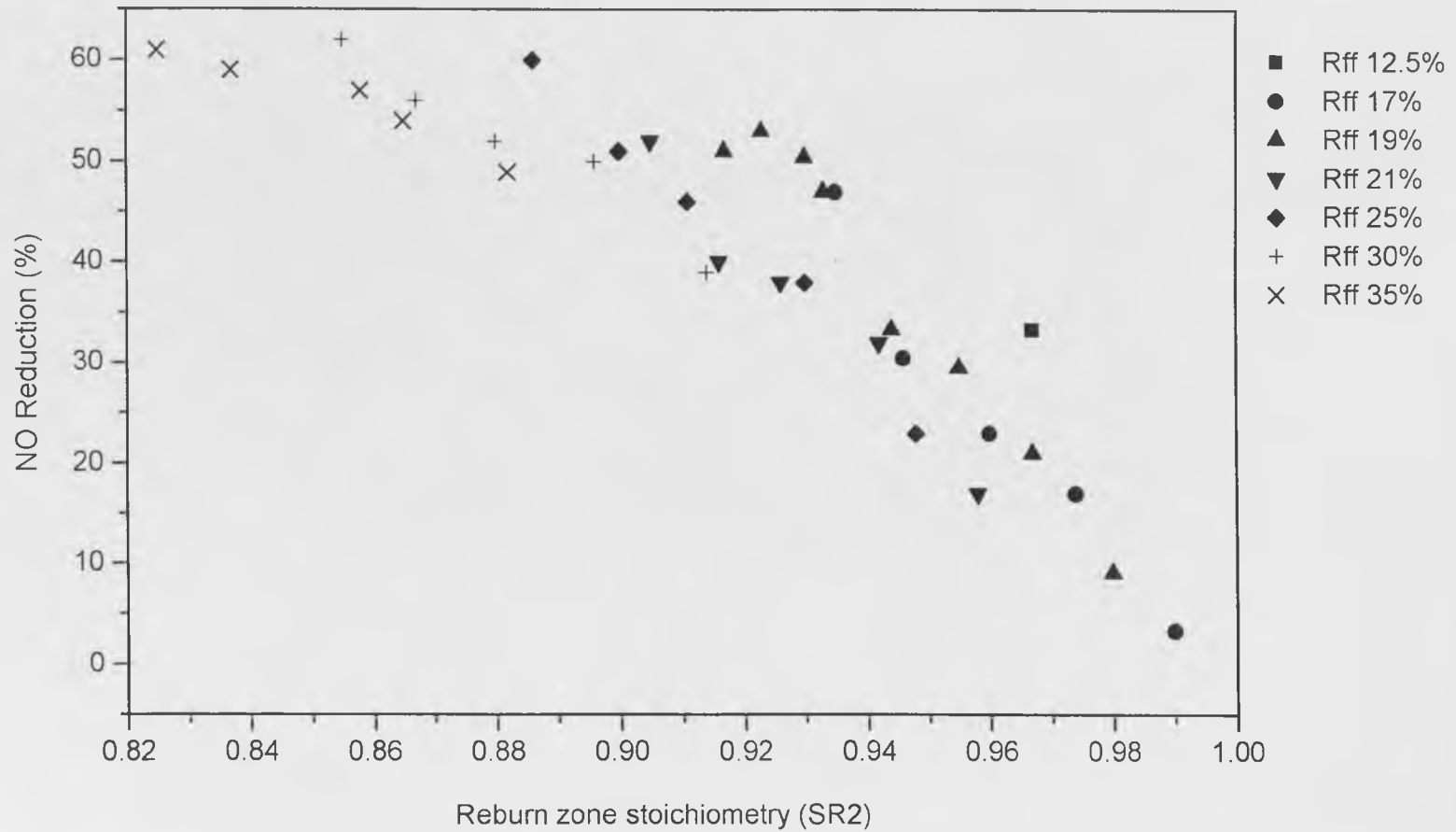
**Figure 4.19** Effect of reburn fuel fraction on NO reduction efficiency  
 Betts Lane, SR1= 1.03, SR3= 1.04 - 1.10,  $T_{pr}$  = 1573 K



**Figure 4.20** Effect of reburn fuel fraction on NO reduction efficiency  
 Koonfonteine, SR1= 1.03, SR3= 1.046 - 1.10,  $T_{pr} = 1573$  K



**Figure 4.21** Effect of reburn fuel fraction on NO reduction efficiency  
 La Jagua, SR1= 1.03, SR3= 1.05 - 1.098,  $T_{pr}$  = 1573 K



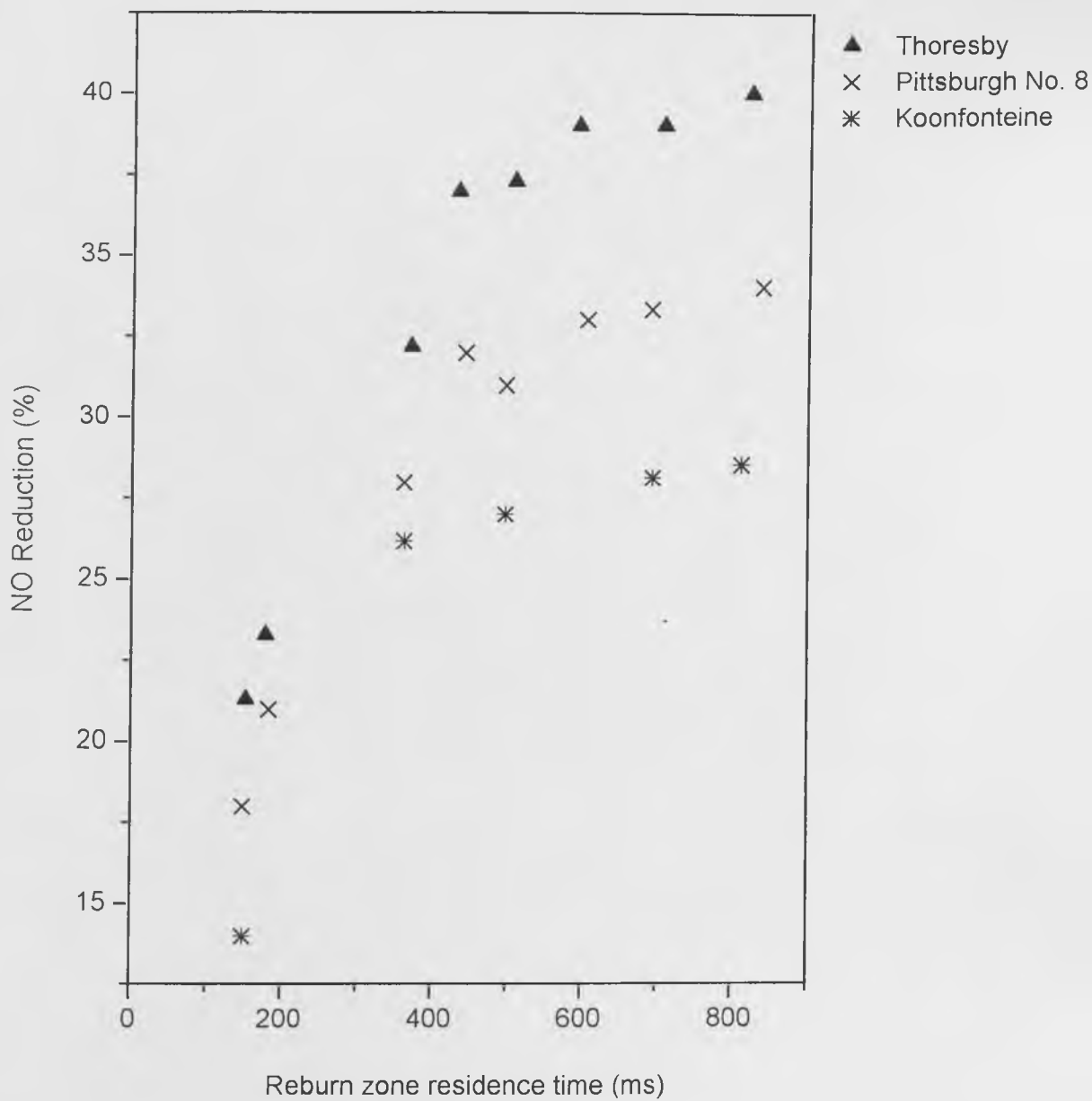
**Figure 4.22** Effect of reburn fuel fraction on NO reduction efficiency  
 Hunter Valley, SR1= 1.03, SR3= 1.03 - 1.11,  $T_{pr}$  = 1573 K

450 ms, beyond which only marginal gains in NO reduction were obtained. These trends support earlier work by Liu (1995c) on a drop tube furnace.

The results obtained by Mereb and Wendt (1994) using a bituminous coal as reburn fuel revealed an almost linear relationship between NO reduction and increasing reburn zone residence time up to 800 ms at a reburn zone stoichiometry of 0.9. A similar linear relationship was observed by Kircherer *et al.* (1994) up to 1300 ms of residence time. The reason for this difference could be due to both studies having a coal-fired primary flame which lasts longer than a gas primary flame and could overlap the reburn zone. The primary combustion would thus interfere with the reburn zone especially by the continued burning and reacting in the reburn zone of large quantities of residual char particles from the primary zone. Also, the optimum residence time is coupled to the different mixing conditions prevailing in the reburn zone. Rapid mixing would enhance the reaction processes so that the time to equilibrium is reduced; but rapid mixing may also prove to be a disadvantage, since poorer mixing of coal and combustion products may form fuel rich pockets in the reburn zone, which can therefore improve NO reduction and prevent the oxidation of nitrogen in the reburn fuel to NO. In this study, mixing and reaction was completed within 450-500 ms which is typical of the required reaction time for a pulverised coal fired boiler using reburn for NO reduction (Miyamae *et al.*, 1986; Chen *et al.*, 1986; Bortz and Offen, 1988) .

#### **4.2.7 Effect of Carrier Gas Oxygen Concentration**

Reburning with coal requires the use of a transport medium to carry the coal, and the impacts of the transport medium are of primary importance in commercial



**Figure 4.23** Effect of residence time on NO reduction efficiency  
 SR1=1.03, SR2=0.94, SR3=1.09, Rff=21%  $T_{pr}$  =1573 K

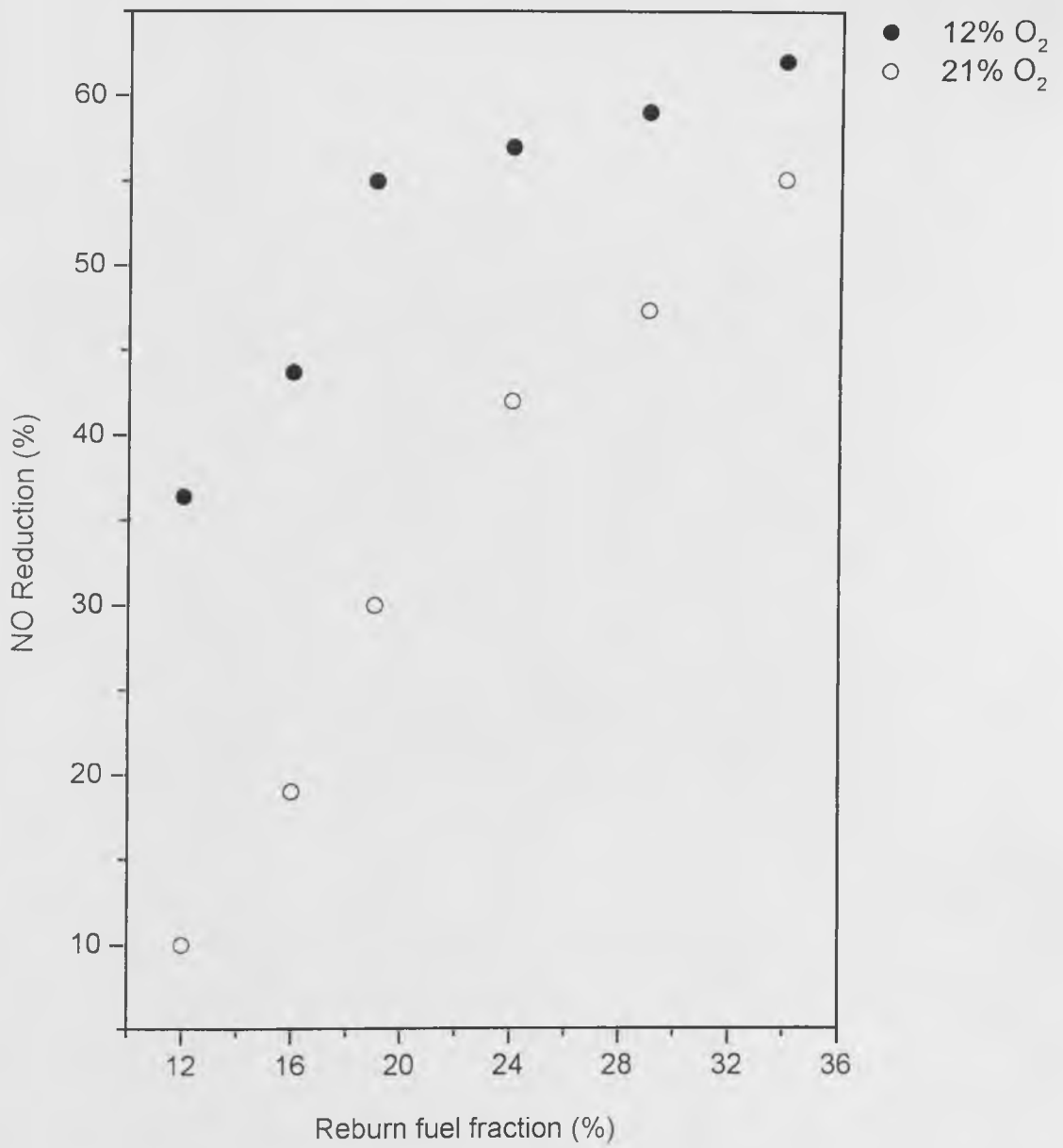


application. The ratio of the oxygen present in the reburning coal transport line to the theoretical oxygen required for complete combustion of the reburning coal is referred to as the reburning carrier gas stoichiometry or  $SR_r$ . Ideally, an inert transport medium ( $SR_r = 0$ ) is desirable both for safety and process economy since less reburning fuel is required to attain optimum stoichiometry. However, in many pilot-scale systems flue gas recirculation (FGR) is used to transport the reburning coal (Overmoe *et al.*, 1986; McCarthy *et al.*, 1988).

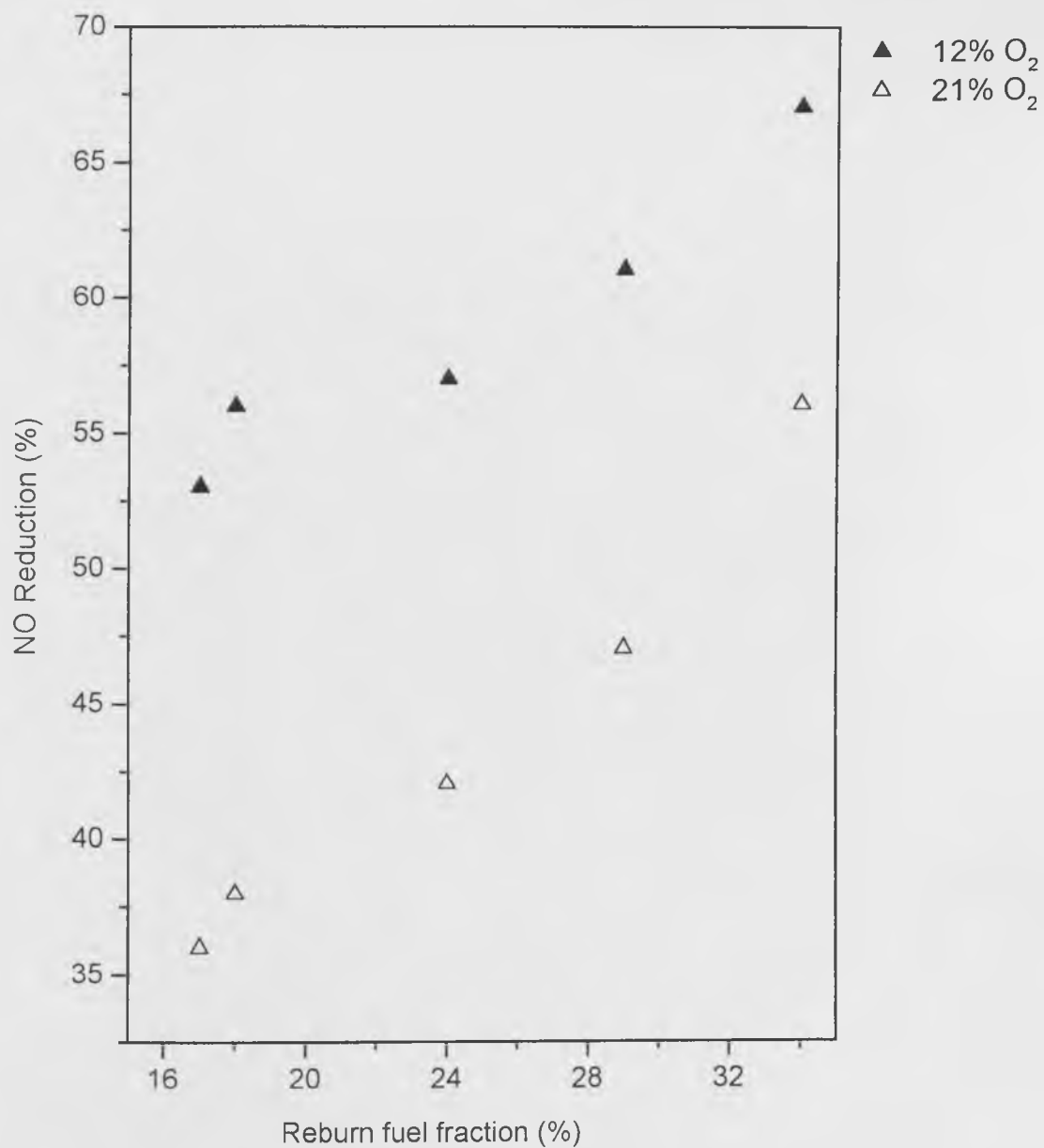
The results of the tests designed to investigate the effect of oxygen concentration in the carrier gas on NO emission are shown in Figs. 4.24 - 4.26. Two different oxygen concentrations (12% and 21% with balances of nitrogen) were used for fixed flow rates of carrier gas injected through a constant reburning injector configuration thereby matching jet velocities and negating the effect of mixing in the reburn zone. The results in Figs. 4.24 - 4.26 indicate that for a given  $R_{ff}$ , the NO reduction efficiencies with the 12%  $O_2$  are well above those with 21%  $O_2$ . The results also show that the influence of carrier gas oxygen concentration on NO emissions becomes less important as the reburning zone grows more fuel rich. As  $SR_2$  decreases the influence of the premixing becomes secondary to the effect of the overall rich reburning zone environment. Similar results were reported by Greene *et al.* (1985) and Overmoe *et al.* (1986).

#### **4.2.8 Effect of Temperature**

The effect of the thermal environment on NO reduction efficiency was investigated at two inlet gas temperature levels, 1573 K and 1773 K (measured at the inlet of the reburning zone). The two temperature levels were achieved by varying the cooling



**Figure 4.24** Effect of carrier gas O<sub>2</sub> concentration on NO reduction  
 La Jagua, SR1=1.03, SR2=0.97 - 0.83, SR3=1.03 - 1.09, T<sub>pl</sub>=1773 K



**Figure 4.25** Effect of carrier gas O<sub>2</sub> concentration on NO reduction  
Thoresby, SR1=1.03, SR2=0.95 - 0.84, SR3=1.05 - 1.09, T<sub>pr</sub>=1573 K

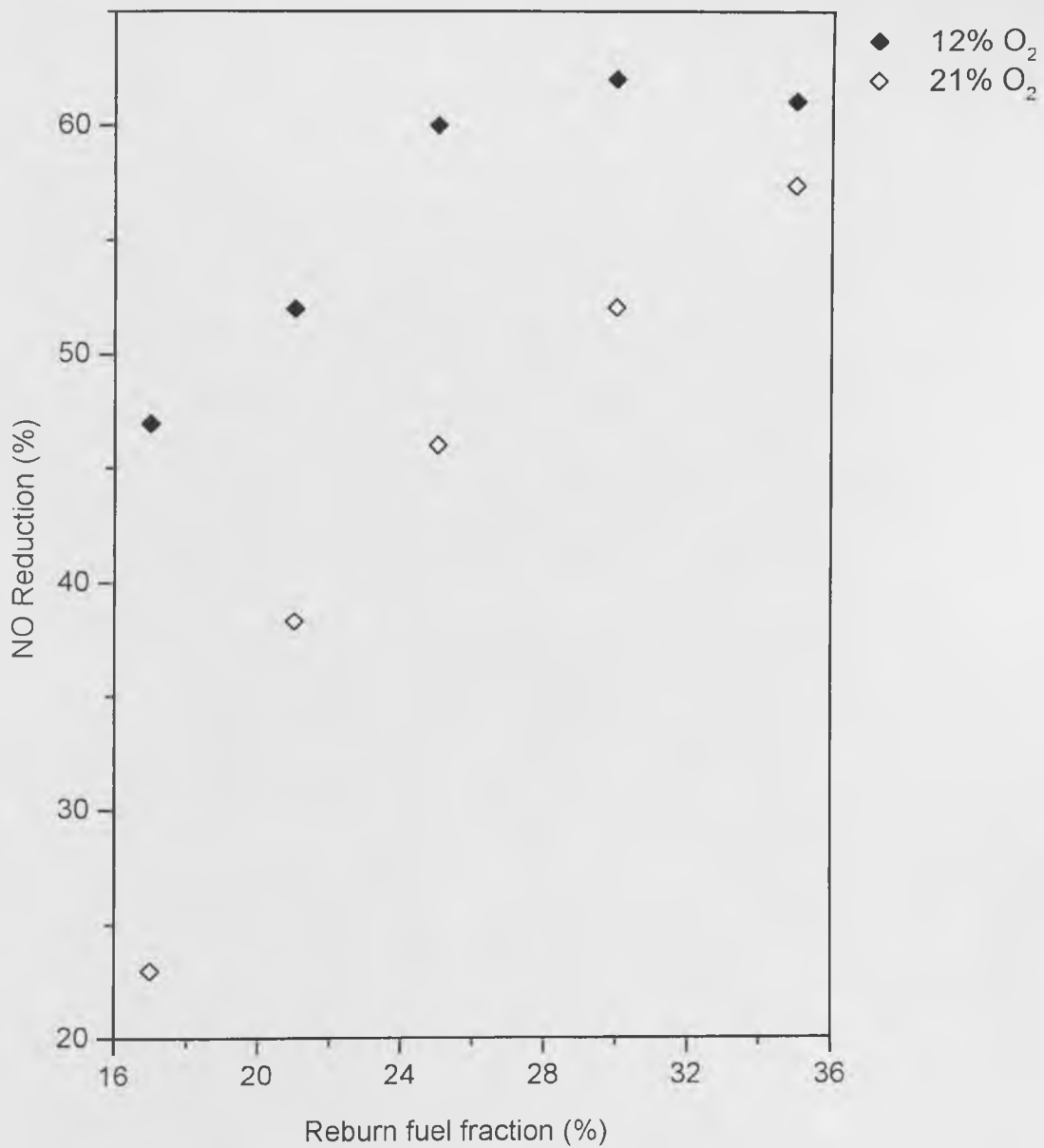
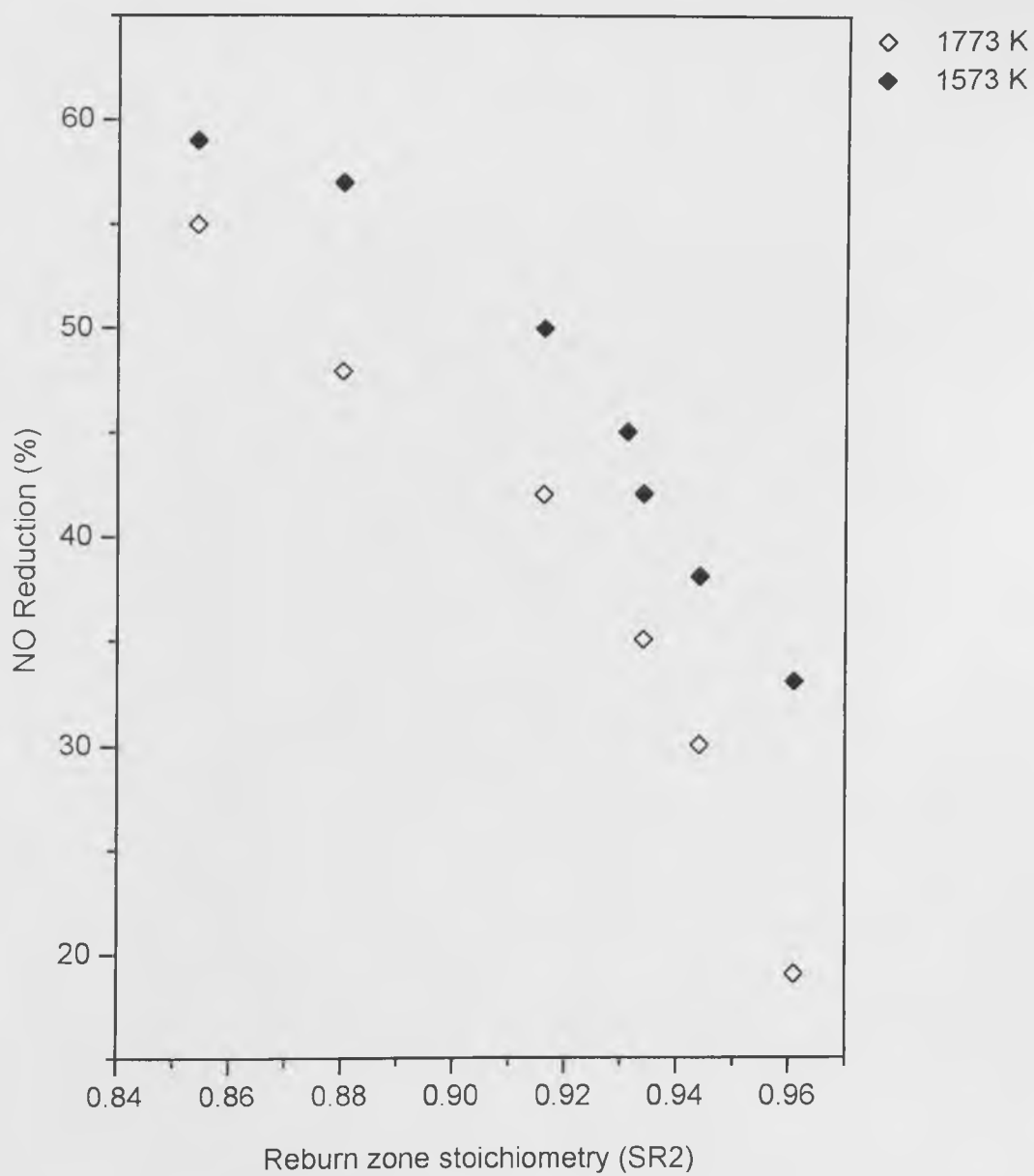


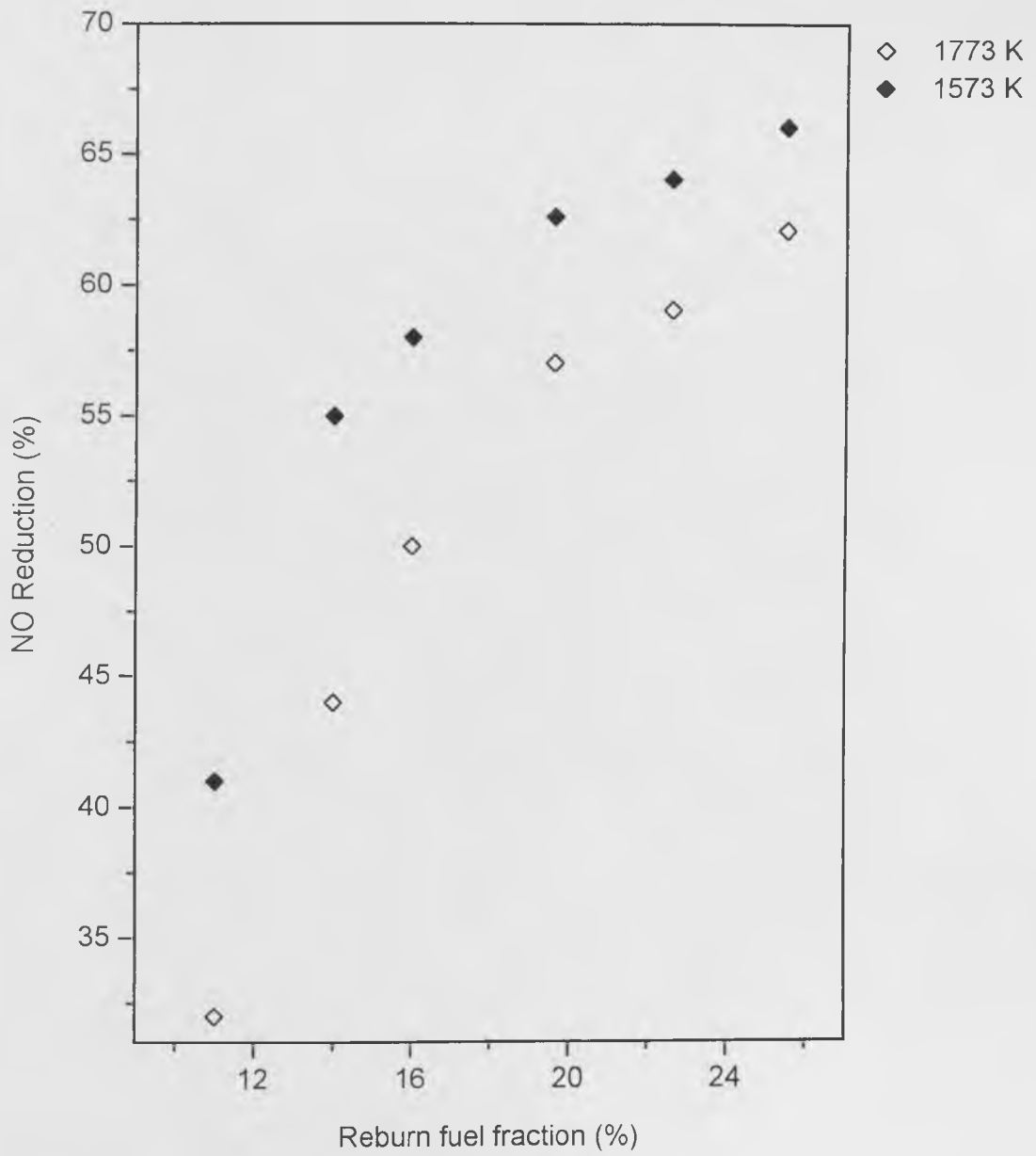
Figure 4.26 Effect of carrier gas O<sub>2</sub> concentration on NO reduction  
 Hunters Valley, SR1=1.03, SR2=0.935 - 0.825, SR3=1.04 - 1.09, T<sub>pr</sub>=1573 K

area in the primary combustion zone. From the results presented in Figs. 4.27 - 4.30, the general trend indicates that the low inlet gas temperature (1573 K) is more beneficial than the high inlet gas temperature (1773 K) in the tested range, especially at high  $SR_2$ . However, as  $SR_2$  is decreased the deviation between the two temperature levels diminishes and no obvious difference in NO reduction was observed. Similar results were obtained by Chen *et al.* (1986) where significant heat removal from the reburn zone using cooling coils resulted in a dramatic reduction in NO emissions when reburning with a low rank coal. Conversely, when reburning with propane this resulted in an increase in NO emissions and detailed measurements indicated that this was directly attributable to an increase in total fixed nitrogen species ( $TFN = NH_3 + HCN + NO + Char\ N$ ) existing in the fuel rich zone.

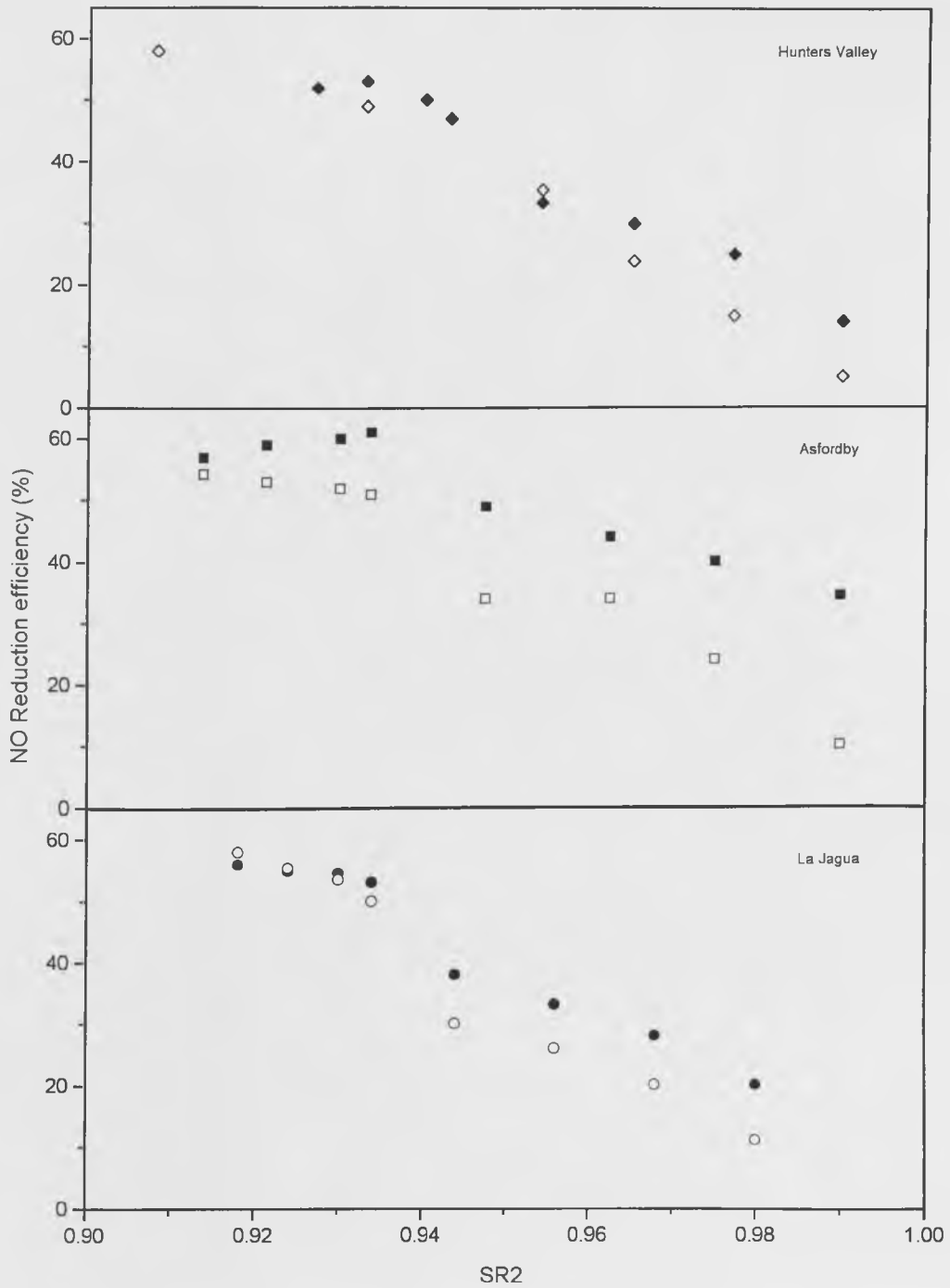
Figure 4.31 shows the NO reduction efficiency at the two temperature levels (1573 and 1773 K) over a range of residence times. It is difficult to isolate the effect of temperature since the change in temperature is accompanied by other changes such as residence times and primary NO concentration. Nevertheless, a comparison of the profiles in Fig. 4.31 suggests a minor effect of temperature at residence time less than 500 ms. At longer residence times (600 - 800 ms), however, the higher temperature seems to enhance NO destruction. Detailed measurements by Greene *et al.* (1986) indicated that at high temperature (1833 K) and long residence time (750 ms), the destruction of NO was accelerated resulting in an improved reburning effectiveness. The higher temperature also promoted the rapid decay of HCN and



**Figure 4.27** Influence of temperature on NO reduction  
La Jagau, SR1=1.03, SR3=1.05 - 1.09, carrier gas: air

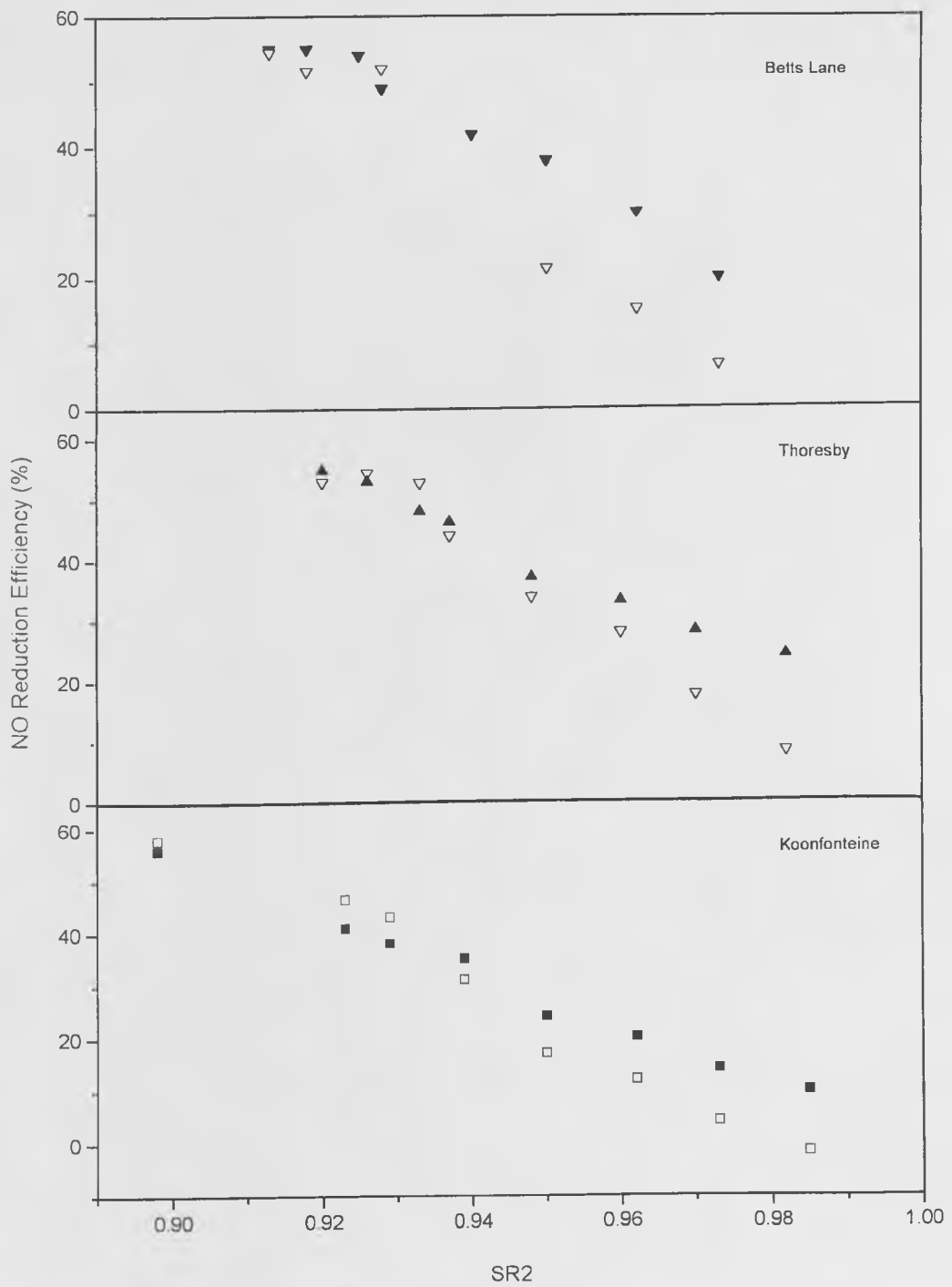


**Figure 4.28** Influence of temperature on NO reduction  
La Jagua, SR1=1.03, SR3=1.05 - 1.09, carrier gas: 12%O<sub>2</sub>

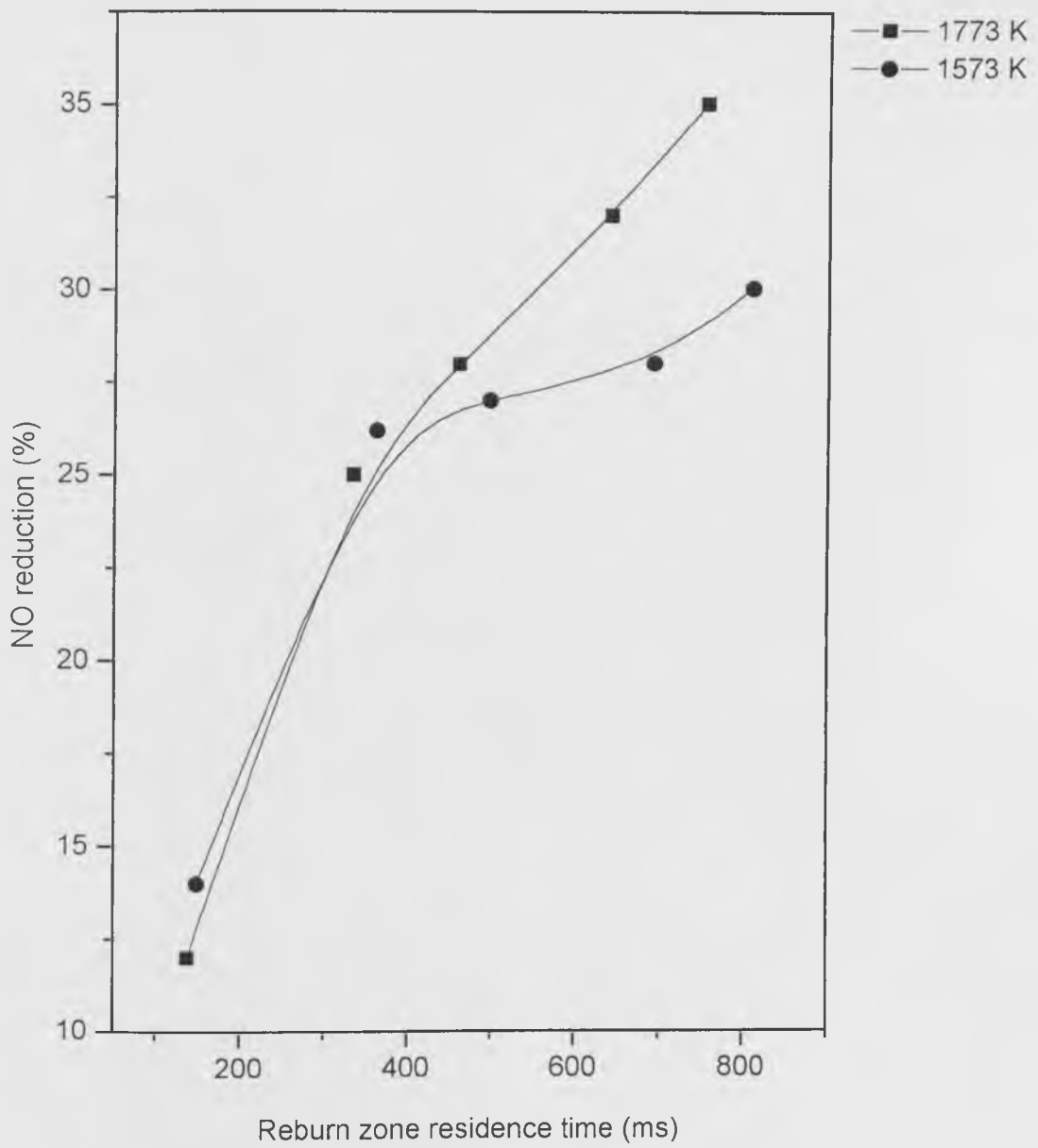


**Figure 4.29** Influence of temperature on NO reduction  
 SR1=1.03, SR3=1.075, Rff=19%,  $T_{pr}$  =1573 K (solid) and 1773 K (open)





**Figure 4.30** Influence of temperature on NO reduction  
 SR=1.03, SR3=1.07, Rff=19%,  $T_{pr}$ =1573 K (solid) and 1773 K (open)



**Figure 4.31** Influence of temprature on NO reduction for a range of residence times  
Koonfonteine, SR1=1.03, SR2=0.93, SR3=1.09, Rff=21%

$\text{NH}_3$  to  $\text{N}_2$  as suggested by the mechanisms of Glass and Wendt (1982) for the rich post-flame decay of nitrogenous species during coal combustion.

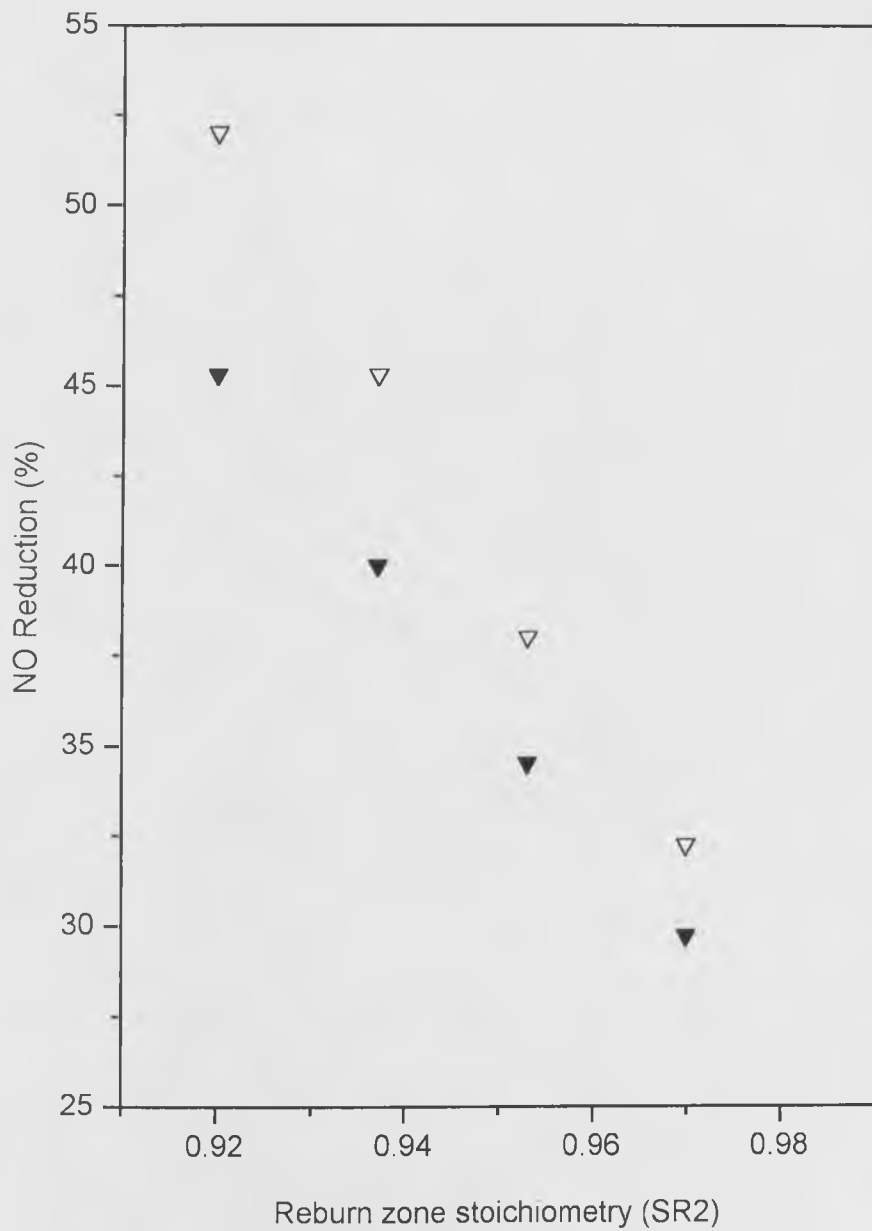
#### **4.2.9 Effect of Coal Particle Size**

The influence of reburn coal particle size distribution on reburning effectiveness was investigated by sieving out all particles larger than  $63\ \mu\text{m}$  from the 'as received' pulverised coal to produce two particle size distribution from the same coal. Figure 4.32 shows that finer particle size distribution produced a higher NO reduction, a confirmation of the results obtained by Liu *et al.* (1995c) and Kirherer *et al.* (1994). The increased NO reduction is mainly due to the fact that finer coal particles have a higher heating rate than coarse particles and thus have a greater volatile yield. This enhances their ability to produce more hydrocarbon radicals which in turn help reduce NO. The results also indicate that the effect of particle size is larger at lower values of  $\text{SR}_2$ . This is not surprising, because the yield of volatile reducing species is more effective due to the lower oxygen environment.

The improved burnout efficiency (typically 10% ) exhibited by finer coal particles can be attributed to the enhanced char reactivity (due to faster reaction rate) owing to a larger surface area, and better oxygen diffusion to the surface.

#### **4.2.10 Effect of Mixing in the Reburn Zone**

Experiments were conducted to test the effect of splitting the reburning fuel into more than one stream. In these experiments the total amount of fuel at a certain reburn zone stoichiometry was kept constant.



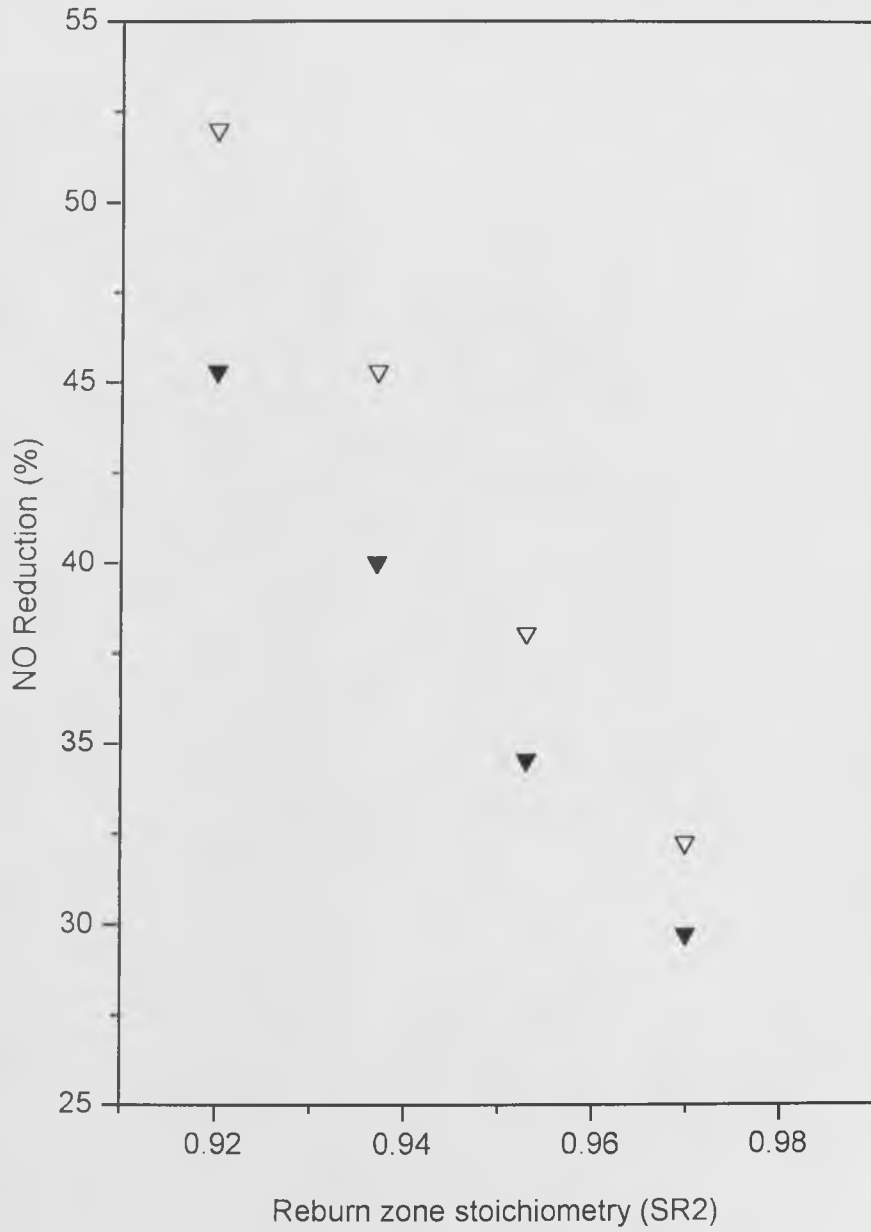
**Figure 4.32** Effect of particle size on NO reduction  
Betts Lane, SR1=1.03, Rff=19%,  $T_{pr}=1773$  K

- ▼ Particle size (75% wt. < 0.063 mm)
- ▽ Particle size (100% wt. < 0.063 mm)

The effect of mixing on reburning effectiveness can be seen in Fig. 4.33 and 4.34. The nozzle systems used (single nozzle, double nozzle and a four nozzle configuration) reflect the degree of mixing in the reburn zone, with the single nozzle being the worst and the four nozzle system giving the best mixing. The results indicate that when air is used as carrier gas for the range of stoichiometries ( $SR_2$ ) between 0.925 and 0.99 the single nozzle system is most beneficial in terms of NO reduction, with no great difference between the two and four nozzle configurations. Figure 4.33 also shows that at  $SR_2 = 0.99$  the two and four nozzle systems resulted in an increase in NO emissions of 2% and 5% respectively.

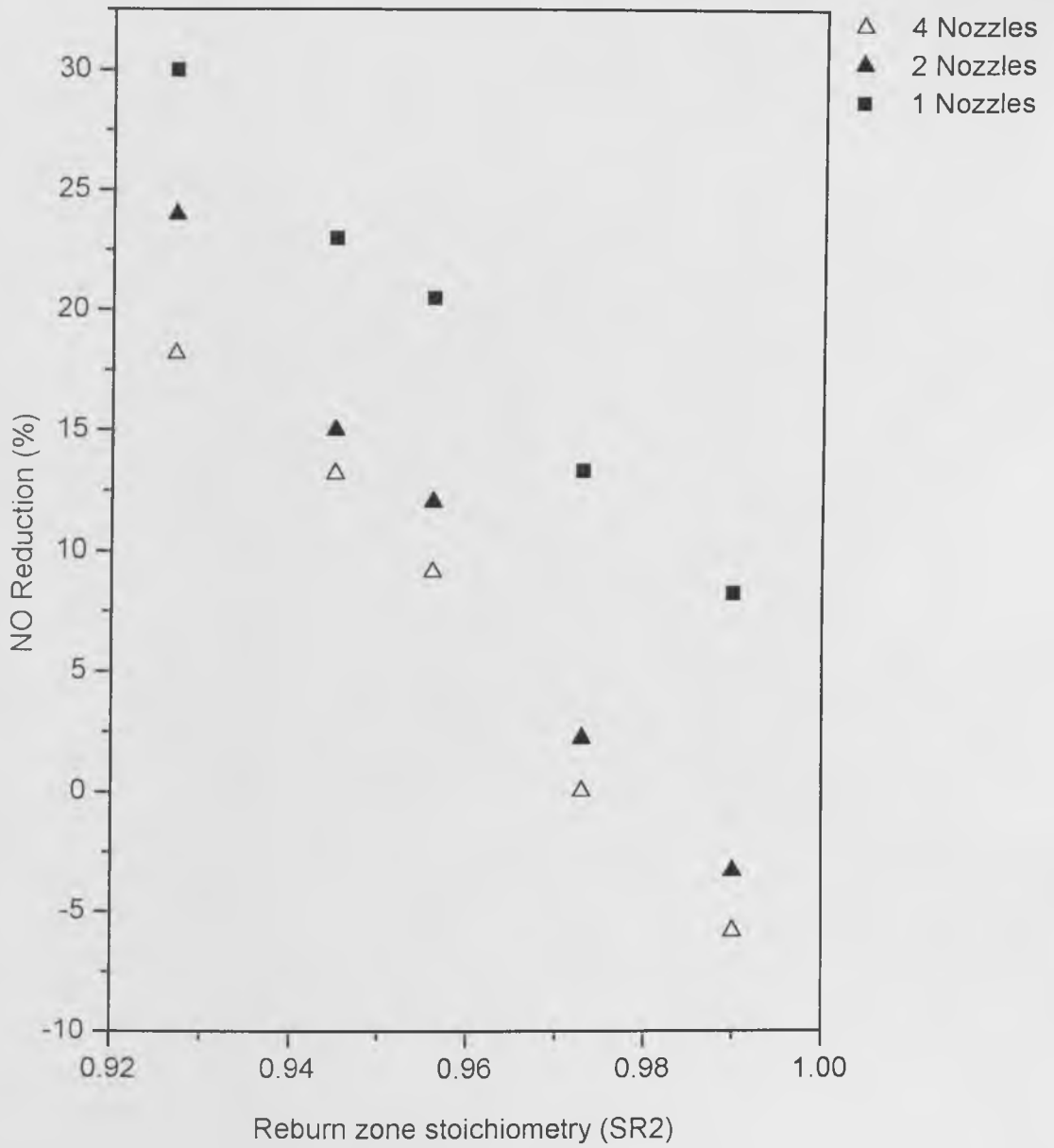
On the other hand, when a mixture of air and nitrogen (12%  $O_2$ ) is used as carrier gas for the range of  $SR_2$  between 0.86 and 0.91, the four nozzle configuration resulted in significantly improved NO reduction, achieving a 62% efficiency at  $SR_2 = 0.86$  as shown in Fig 4.34. The two and one nozzle systems were progressively less effective.

Figure 4.35 demonstrates the effect of  $R_{ff}$  on NO reduction for all three nozzle arrangements, using air as carrier gas. It is clear that NO reduction increases rapidly as  $R_{ff}$  increases, with the difference between the four and two systems increasing also. Only one reading was taken using the single nozzle due to severe impingement by the jet on the opposite wall. Nevertheless, the single reading confirms earlier results in Fig. 4.33 and shows that better NO reduction efficiencies can be achieved by insufficient mixing which can create local fuel rich regions in a near fuel lean environment ( $SR_2 = 0.98$ ).

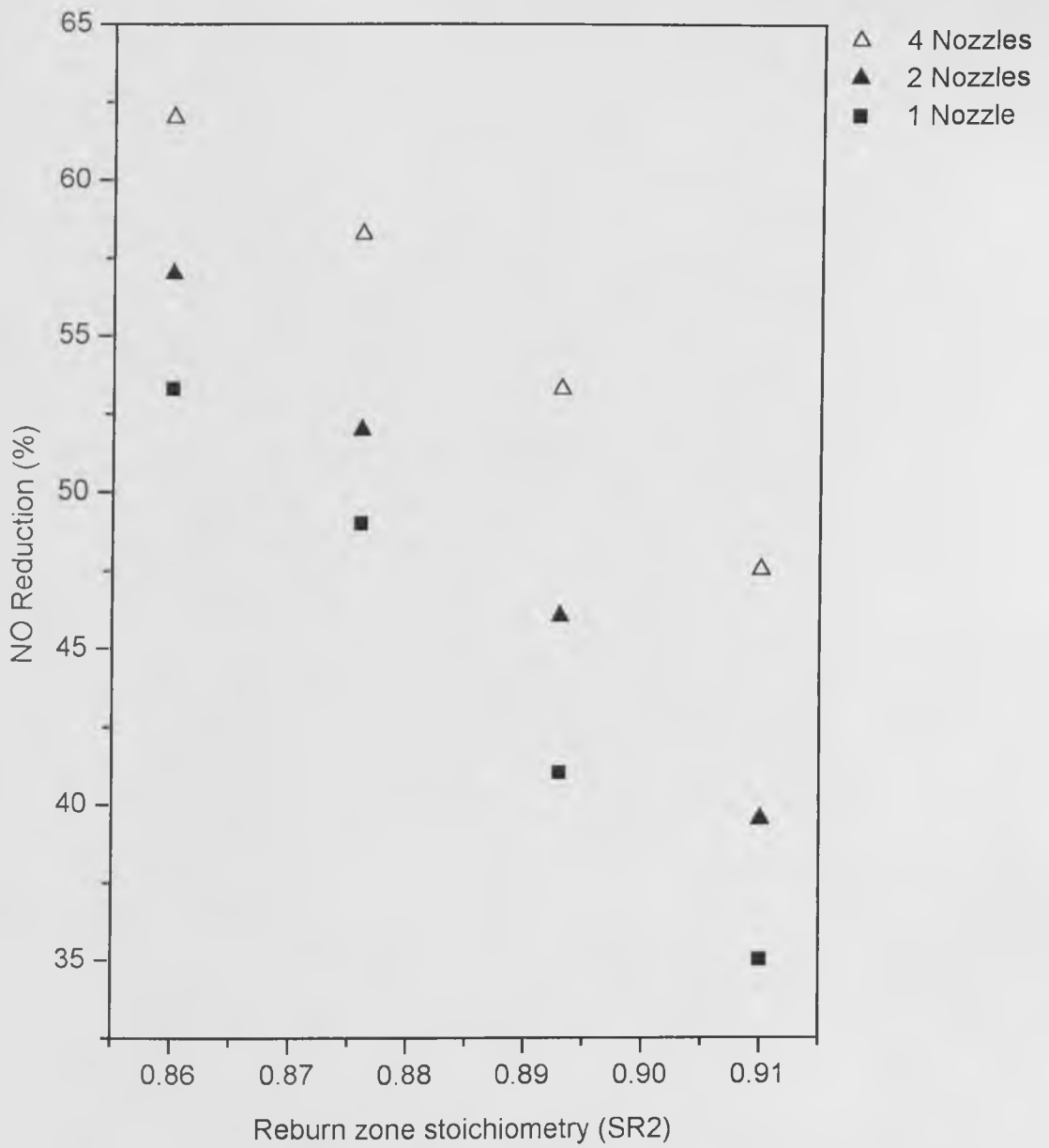


**Figure 4.32** Effect of particle size on NO reduction  
Betts Lane, SR1=1.03, Rff=19%,  $T_{pr}=1773$  K

- ▼ Particle size (75% wt. < 0.063 mm)
- ▽ Particle size (100% wt. < 0.063 mm)

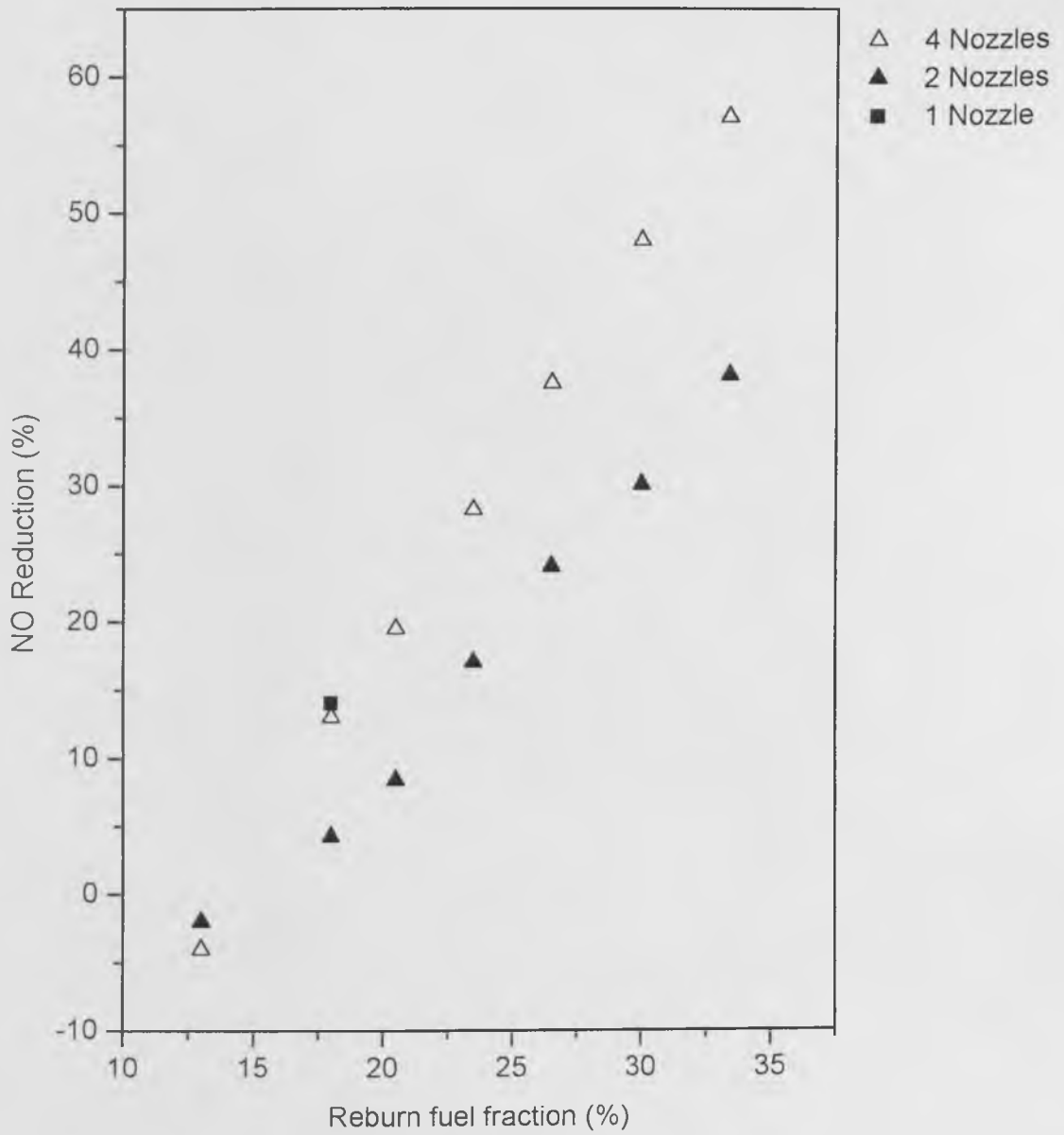


**Figure 4.33** Effect of mixing in the reburn zone on NO reduction  
 Thoresby, SR1=1.03, SR3=1.075, Rff=18%, Carrier gas : Air

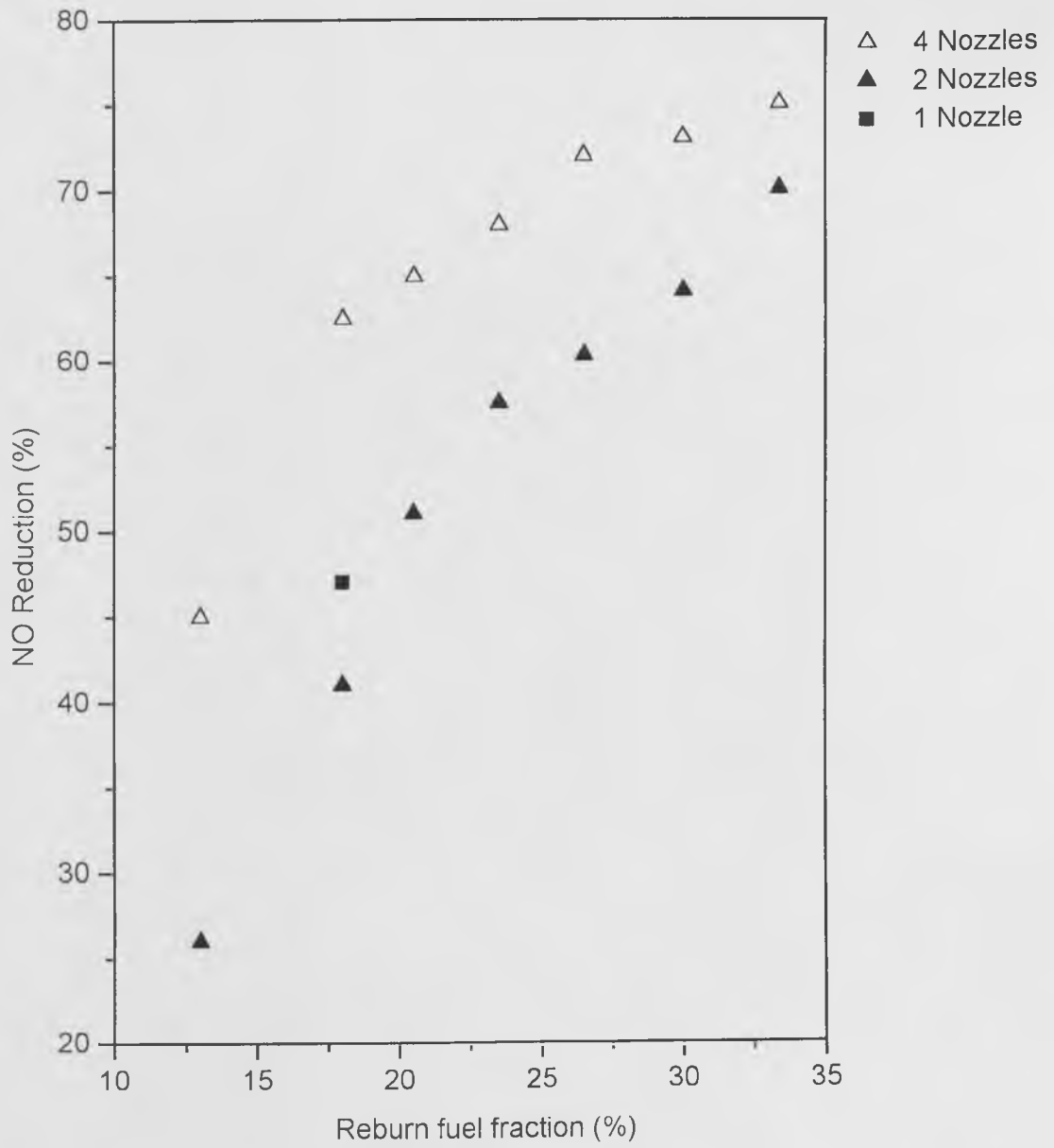


**Figure 4.34** Effect of mixing in the reburn zone on NO reduction  
Thoresby, SR1=1.03, SR3=1.075, Rff=18%, Carrier gas : 12% O<sub>2</sub>





**Figure 4.35** Effect of mixing in the reburn zone on NO reduction  
 Thoresby, SR1=1.03, SR2=0.88 - 1.03, SR3=1.09, carrier gas: Air



**Figure 4.36** Effect of mixing in the reburn on NO reduction  
Thoresby, SR1=1.03, SR2=0.82 - 0.956, SR3=1.07, carrier gas: 12% O<sub>2</sub>

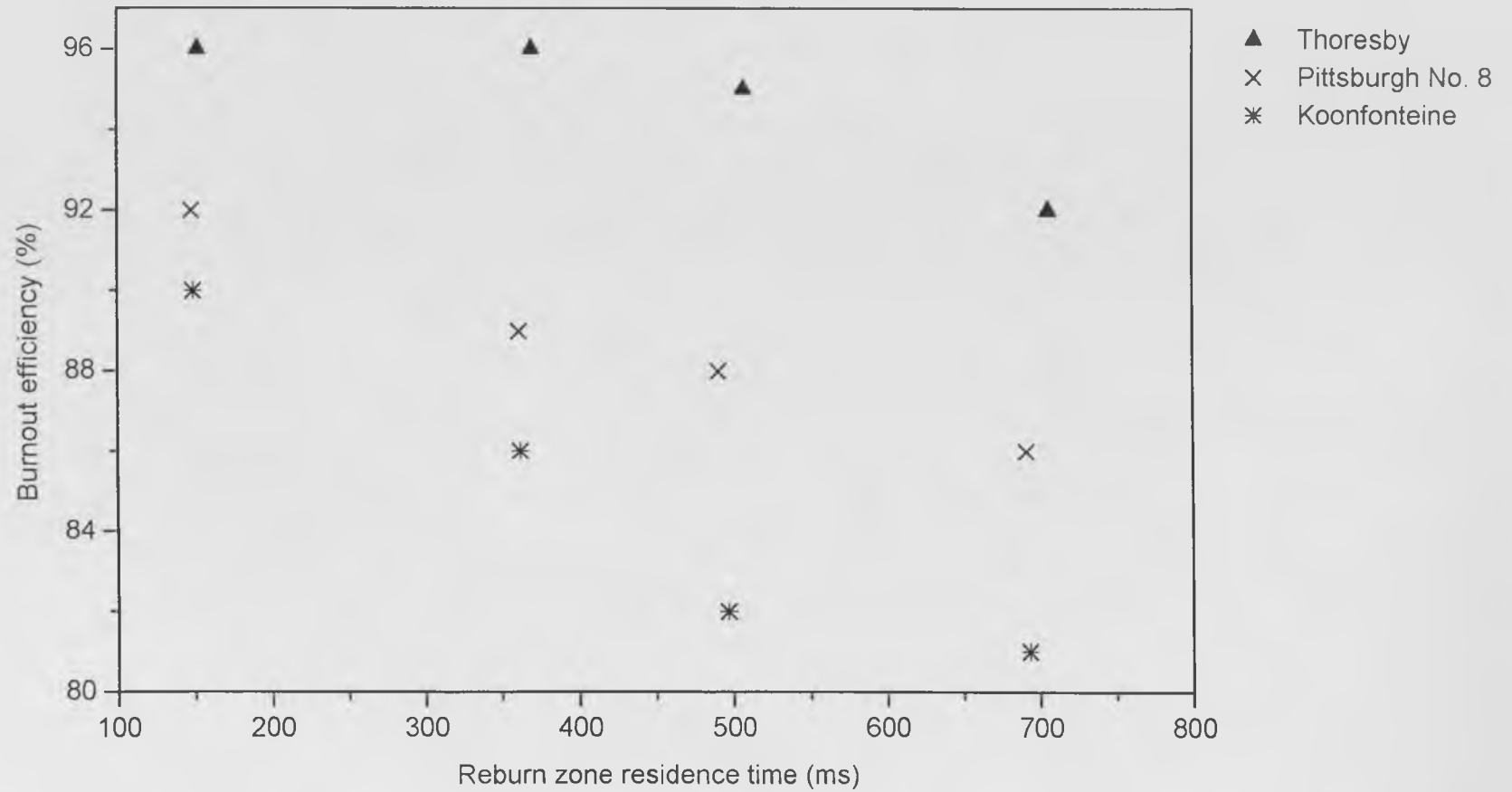
Figure 4.36 shows the same results but with a mixture of nitrogen and air (12% O<sub>2</sub>) as carrier gas. The results demonstrate that the improved mixing generated by the four nozzle configuration coupled with the relatively low oxygen concentration of the carrier gas can result in an NO reduction of up to 75%.

#### 4.2.11 Carbon Burnout

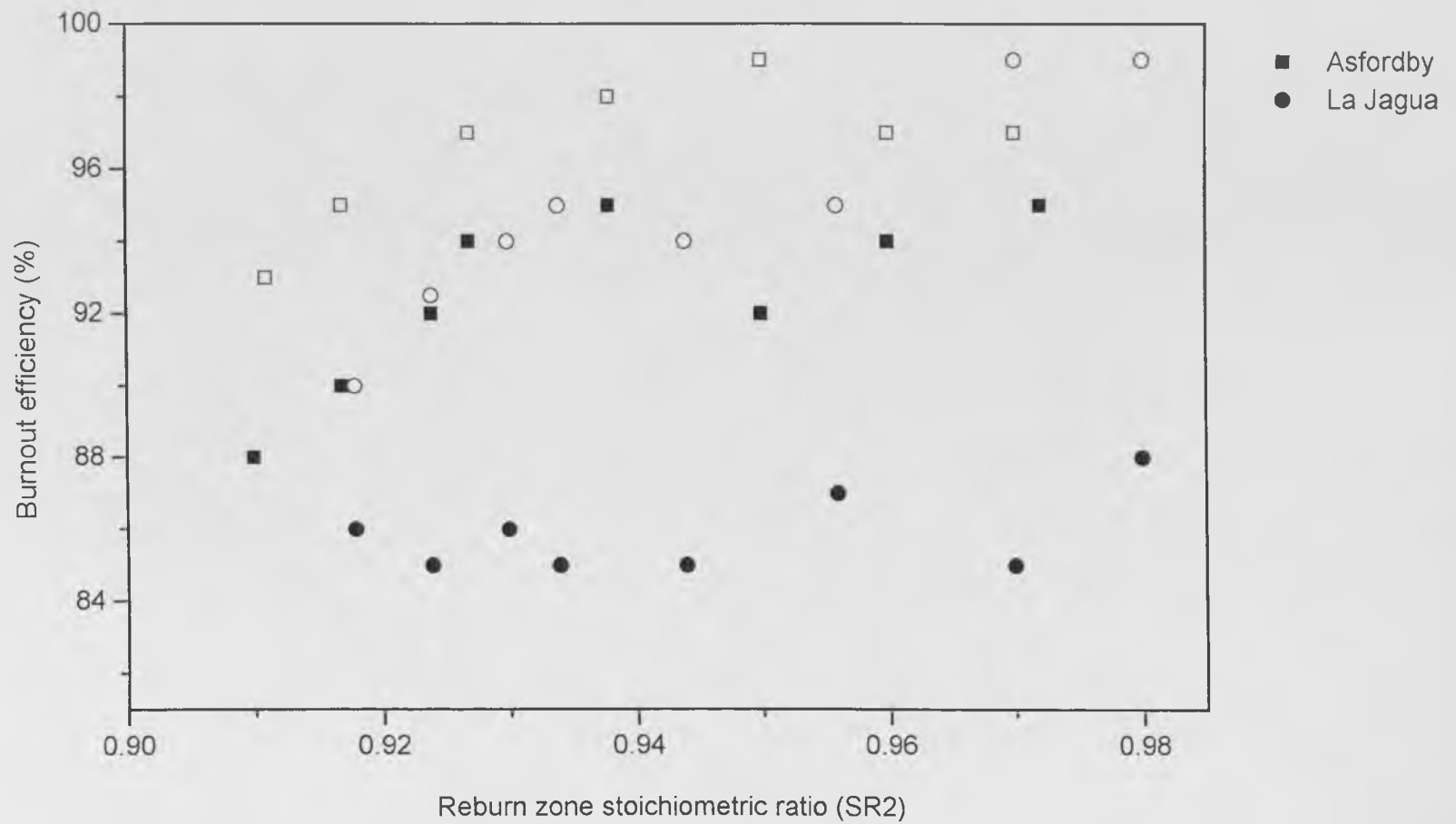
The carbon burnout efficiencies,  $\eta_c$ , of all the reburning coals were generally very good, ranging between 85% and 95%. The carbon burnout efficiency of each of the reburning coals is shown in Appendix D (Figs. D1 to D9).

The effect of reburn zone residence time on carbon burnout efficiency is shown in Fig. 4.37. It is clear that as the reburn zone residence time increased the burnout efficiency dropped. This is understandable since the total gas flow residence time of the furnace is limited to between 1.2 and 1.8 seconds depending on operating conditions, and an increase in reburn zone residence time will thus result in a shorter residence time in the burnout zone i.e. a reduced burnout time for the char particles thus resulting in a diminished burnout efficiency. The drop in burnout efficiency was only marginal for the high volatile coals and the maximum drop in efficiency among all tested coals was 8% for Koonfonteine which had the lowest content volatile matter and was the least effective coal in terms of NO reduction and combustion efficiency.

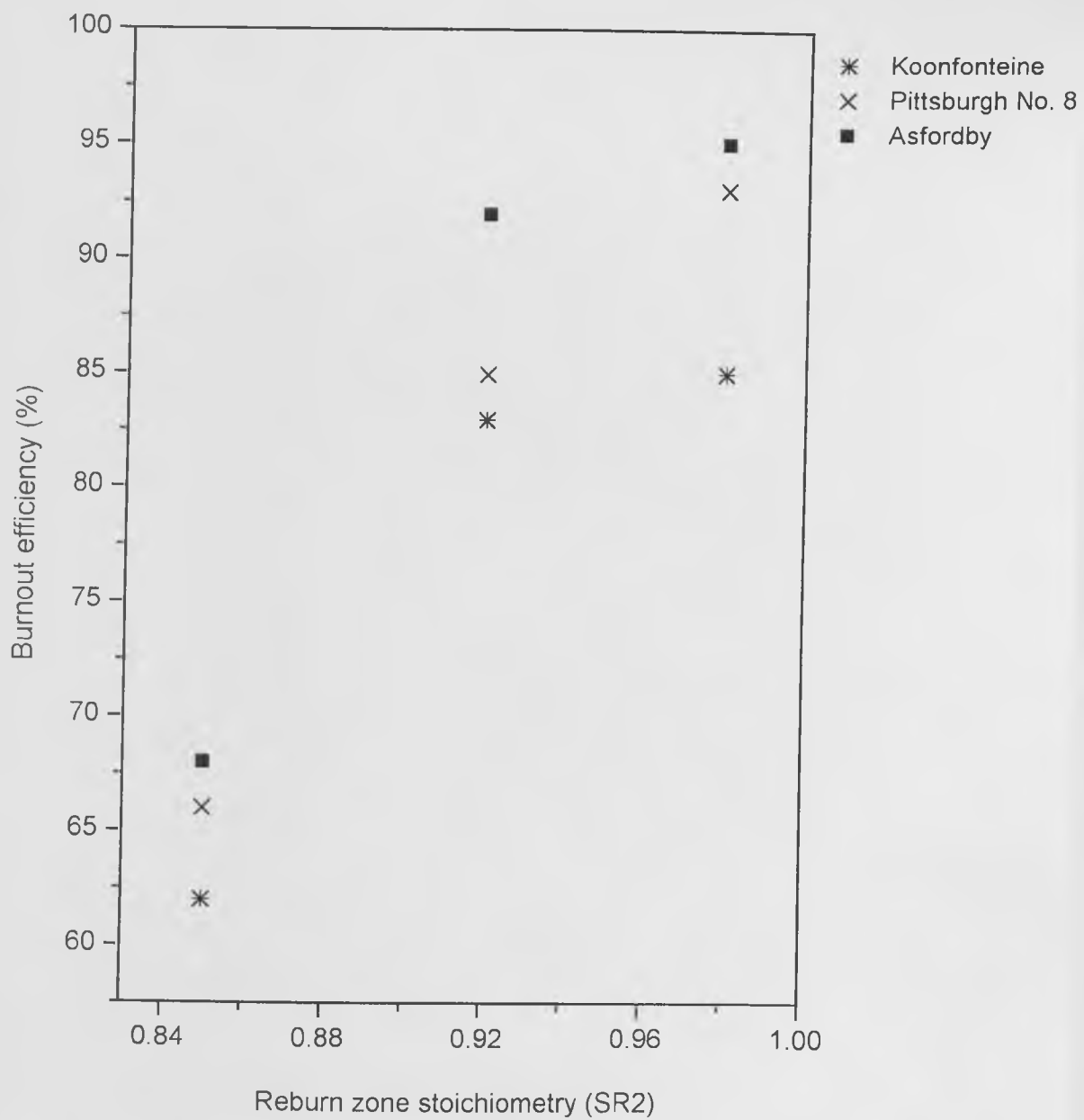
Primary zone gas temperature is another factor affecting the degree of carbon burnout. Figure 4.38 illustrates the effect of gas temperature entering the reburn zone on carbon burnout and shows that the higher temperature (1773 K) level can result in



**Figure 4.37** Effect of reburn zone residence time on burnout  
SR1=1.03, SR2=0.93, SR3=1.09, Rff=20%,  $T_{pr}=1573$  K



**Figure 4.38** Effect of temperature on burnout  
 SR1=1.03, Rff=19%, symbols: open - T<sub>pr</sub>=1773 K; solid - T<sub>pr</sub>=1573 K



**Figure 4.39** Effect of SR2 on Burnout  
 SR1=1.03, Rff=19-35%,  $T_{pr}$ =1573 K

a 5 - 10 % increase in burnout efficiency. This is because the higher temperature can accelerate the overall combustion process thus resulting in a rapid decay of fuel fragments and a high degree of burnout as a result, provided other conditions remain the same.

However, the overriding factor affecting carbon burnout efficiency appears to be the stoichiometry in the reburn zone. A comparison of the carbon burnout efficiency for three reburn zone stoichiometries (0.98, 0.92 and 0.85) shown in Fig. 4.39 suggests that problems with carbon burnout could occur under fuel rich conditions ( $SR_2=0.85$ ). This is the consequence of hindered combustion in the reburn zone as a result of low oxygen concentration.

### **4.3 Discussion of Results**

#### **4.3.1 Operating Stoichiometry**

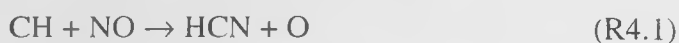
The most critical operating parameter controlling NO reduction efficiency (assuming ideal mixing) was the reburn zone air/fuel stoichiometric ratio,  $SR_2$ . In the reburn zone the mechanism of homogenous NO reduction to  $N_2$  involves species such as CO,  $C_mH_n$ ,  $NH_3$  and HCN, which are produced during the devolatilisation and combustion stages of the reburn coal. Consequently, any operating condition that serves to increase the concentration of these species in the reaction zone and, in the case where nitrogenous species are formed, prevent their oxidation to NO before they can react to form nitrogen, will help to improve reburn performance. Figure 4.15 demonstrated the sensitivity of the NO reduction efficiency to  $SR_2$ , however in contrast to other studies where the optimum value for  $SR_2$  was between 0.8 and 0.9

(Liu *et al.*, 1995a & 1995b; Chen *et al.*, 1986; Greene *et al.*, 1996), in this work no optimum value was found over the range of conditions investigated ( $SR_2 = 0.8 - 1.0$ ), as shown in Figs. 4.15 and 4.16 - 4.22. The best NO reductions were always obtained at the lowest values of  $SR_2$ , irrespective of the reburn fuel fraction. Similar findings were reported by Kicherer *et al.* (1994) using a 0.5 MWt test facility.

The extent of NO reduction is also affected by the primary zone stoichiometric ratio ( $SR_1$ ), but only through its influence on other reburning parameters, mainly  $SR_2$  and to a lesser degree temperature and residence time. Thus, the effect of  $SR_1$  is of minor significance and is attributed mostly to mixing inhomogeneities which create variations in the local stoichiometry of the reburn zone. These observations are in agreement with those of Greene *et al.* (1986) and Chen *et al.* (1986). In a practical system, however, the primary zone oxygen concentration and mixing can to some extent control the conversion of fuel-nitrogen to NO and the formation of thermal NO. Consequently the NO concentration at the start of the reburn zone will also vary with  $SR_1$ , unlike the present system where it was possible to maintain a constant NO concentration using the ammonia doping system.

#### 4.3.2 NO Concentration in the Primary Zone

The reason for the trends in Figs. 4.13 and 4.14 lies behind two competing pathways which occur in the fuel rich reburn zone; one that forms  $N_2$ , R4.1, suggested by Chen *et al.* (1986), and that which destroys  $N_2$ , R4.2, suggested by Lanier *et al.* (1986).







Lanier *et al.* (1986) showed, by detailed analysis of flame species, that R4.1 dominates at high primary zone NO concentration and while R4.2 dominates at low primary zone NO concentration. Thus, under low primary NO conditions, the N<sub>2</sub> destruction process (Fenimore mechanism) competes with NO for the consumption of hydrocarbon radicals which leads to a diminished NO reduction, resulting in a reduced reburning effectiveness. The situation is made worse if the reburn fuel contains inherent fuel nitrogen and the balance between NO-forming reactions (from the fuel-N) and the NO-reducing reactions (with fuel nitrogen derived species) tilts in favour of NO formation, so the NO reduction efficiency falls, leading eventually to the net production of NO if conditions are suitable (Fig. 4.14). This may impose a practical limitation on the use of coal or oil reburn technology when combined with low-NO<sub>x</sub> burner systems that produce less than around 150-170 ppm NO.

### 4.3.3 Reburn Fuel Fraction

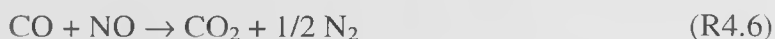
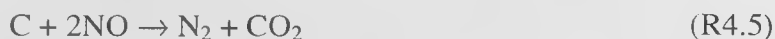
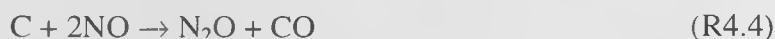
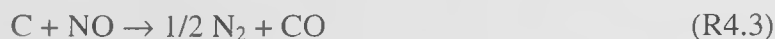
The trends featured in Figs. 4.16 - 4.22, where lower values of R<sub>ff</sub> lead to a higher NO reduction efficiency for a fixed SR<sub>2</sub>, are the result of the proportional increase in the flow of oxygen in the reburn zone as R<sub>ff</sub> is increased. The net result is the enhancement of reactions that forms NO rather than reduce NO, either by forming more NO from the increased fuel-nitrogen input into the reburn zone, or by consuming the NO reducing agents produced by the reburning coal.

This contradicts previous work by Liu *et al.* (1995a, 1995b) where NO emission decreased almost linearly with increase in R<sub>ff</sub> from 8-22%. Smart and Morgan

(1994) also reported an improvement in reduction with increasing  $R_{ff}$  in the range 10-25%. However, in both these earlier studies the reburn zone stoichiometry was not kept constant as the  $R_{ff}$  was varied and as such the results are not surprising because as  $R_{ff}$  is increased the concentration of NO-reducing agents (from the coal) in the reburn zone is also increased while  $SR_2$  is decreased. The combined effect of both favour the NO reduction paths (as illustrated in Fig. 2.12).

#### 4.3.4 Residence Time in the Reburn Zone

The main reason behind the trends in Fig. 4.23 lie in the fact that the volatile part of the coal is more efficient at destroying NO than the char part of the coal (Greene *et al.*, 1986; Kircherer *et al.*, 1994; Liu *et al.*, 1995a). After the release and combustion of the volatiles in the reburning coal, the residual char part of the reburning coal will gradually burn-out. It is during these residual char burnout stages that NO could be reduced through the following reaction paths (Wang *et al.* 1994):



However, since NO is also formed by the heterogeneous oxidation of char-N ( $Char-N + 1/2 O_2 \rightarrow NO$ ), the amount of NO produced would be the balance of its production and reduction. This together with any unconsumed volatile nitrogenous

fragments which could be oxidised to form NO in the burnout zone, account for the relative increase in NO concentration at the furnace exit compared to the value reached at the exit of the reburn zone (Figs. 4.3 - 4.7). In this study the effect char on NO reduction amounted for only 10% of the total NO reduction. This supports earlier work by Levy *et al.* (1981).

#### 4.3.5 Carrier Gas Oxygen Concentration

Figures 4.24 - 4.26 demonstrate the influence that coal transport medium or SR<sub>r</sub> has on reburning efficiency. The decrease in NO reduction efficiencies at 21% O<sub>2</sub> are mainly due to the increase in SR<sub>r</sub> which effectively means that the coal jets are more premixed with oxygen resulting in higher conversion of fuel nitrogen to NO and rapid oxidation of hydrocarbon radicals. This would hence decrease the availability of hydrocarbon radicals thus hindering the destruction of primary NO. Although the changes in SR<sub>r</sub> were accompanied by small changes in SR<sub>2</sub>, the increase in emission is believed to be mainly due to increases in oxygen concentrations in the transport medium since increase in emissions is characteristic of systems which utilise premixed burners (McCarthy *et al.* 1988).

The influence of the carrier gas stoichiometry is further highlighted in Fig. 4.12 where the O<sub>2</sub> concentration in the reburn zone (from both primary and carrier-gas air) remained constant, yet at lower values of SR<sub>r</sub> better NO reduction were achieved. This confirms the carrier-gas oxygen concentration to the reburn zone to be the dominant impact variable when reburning with coal, and as such in practical systems it is desirable to have an inert transport medium such as nitrogen or flue gas recirculation (FGR).

#### 4.3.6 Temperature

Thermal history has a substantial impact on the speciation of TFN since devolatilisation and nitrogen partitioning between the volatiles and char are known to be a function of temperature and particle heating rate (Wendt, 1980). An increase in temperature should therefore produce more gas-phase nitrogen compounds and thus affect the NO<sub>x</sub> yield. However, the pyrolysis results of Song *et al.* (1982) for a Montana sub-bituminous coal indicate that fuel-NO yields were essentially the same for furnace temperatures of 1203 K and 1503 K but decreased by 20-25% when furnace temperature was raised to 1753 K. Also, Haussmann and Kruger (1990) demonstrated with a bituminous and a sub-bituminous coals that fuel nitrogen loss increased with gas temperature in the range 1323-1523 K, but had little change when the temperature was increased from 1523 K to 1653 K. The NO yield showed similar trends to the results of Song *et al.* (1982). Even though the results presented in Figs. 4.21 - 4.24 are 120 K higher than the upper limit of Haussmann and Kruger's experiment, from the established trend it is hardly possible for the yield of volatile nitrogenous species to be significantly higher at 1773 K than at 1573 K. Thus, the difference observed in NO reduction Figs. 4.27 - 4.30 cannot be explained by the evolution processes of coal fuel nitrogen.

It can be explained, however, by considering NO + CH<sub>i</sub> and NO + NH<sub>i</sub> reactions which are one of the main routes to NO destruction in the fuel rich reburn zone (Fig. 2.12). The temperature dependence of the kinetic rate coefficients of these reactions (Glarborg *et al.*, 1986; Miller and Bowman, 1989) show that NO destruction by CH<sub>i</sub> species is favoured at higher temperatures, whereas, NO destruction by NH<sub>i</sub> species

is favoured at lower temperatures. Previous work with bituminous coals has indicated that they produce large amount of  $\text{NH}_3$  under fuel rich conditions and very little hydrocarbon (Chen *et al.* 1982), and it is a well known fact that gaseous fuels have the greatest potential for CHI production. Consequently in coal reburning,  $\text{NO} + \text{NH}_i$  reactions may dominate the destruction of NO in the reburn zone, while  $\text{NO} + \text{CHI}$  reactions dominate NO destruction in gaseous fuel reburning. This explains the contrasting effect of temperature which was observed by Chen *et al.* (1986) when reburning with propane and coal, and supports the coal reburning results of Knill and Morgan (1989) who used a model based solely on  $\text{NO} + \text{NH}_i$  reactions to describe the NO decay in the reburn zone. Also, if the reburn zone is close to the fuel lean side, low concentrations of HCN would be present and higher temperatures promote the destruction of hydrocarbon species to form neutral products, mainly due to reaction with O radical (Glargborg *et al.*, 1986). Consequently, less hydrocarbon species are available at higher temperatures and less NO destruction by  $\text{NO} + \text{CHI}$  reactions.

The overall NO formation and reductions rates for reactions occurring in the fuel rich reburn zone can be written as (De Soete, 1975):

$$\frac{d[X_{NO}]}{dt} = A_1 X_{HCN} X_{O_2} \exp\left(\frac{-67,000}{RT}\right) + A_2 X_{NH_3} X_{O_2} \exp\left(\frac{-32,000}{RT}\right) \quad (4.13)$$

$$\frac{d[X_{N_2}]}{dt} = A_3 X_{HCN} X_{NO} \exp\left(\frac{-60,000}{RT}\right) + A_4 X_{NH_3} X_{NO} \exp\left(\frac{-27,000}{RT}\right) \quad (4.14)$$

where  $A_i$  is the pre-exponential factor and  $X_i$  is a mole fraction. They show that the NO forming reactions and the NO reducing reactions both compete for HCN and  $\text{NH}_3$ , which are the major volatile nitrogenous species produced by the reburning coal. The NO formation rate (4.13), however, has higher activation energies than the NO reduction rate (4.14) and thus the NO forming processes are more temperature sensitive. As the temperature is increased, the balance of the competition for HCN and  $\text{NH}_3$  will shift towards the NO forming reactions and thus more NO is formed than reduced resulting in a higher NO emission (or a lower NO reduction by reburning). However, as  $\text{SR}_2$  is reduced the NO formation rate diminishes due to the reduced oxygen concentration in the reburn zone and the impact of temperature becomes secondary, as shown in Figs 4.29 and 4.30.

#### 4.3.7 Mixing in the Reburn Zone

Mixing of the reburning fuel with the primary effluent is an important factor that affects the overall destruction of NO in reburning. Poor mixing conditions can limit reburning effectiveness by delaying the contact of the primary NO with hydrocarbon radicals that are generated from the reburning fuel. Thus, improved mixing conditions may enhance reburning effectiveness, as is suggested in previous works (Chen *et al.*, 1986; Miyamae *et al.*, 1986; Overmoe *et al.*, 1986; Lafond and Chen, 1987; Kolb *et al.*, 1988). At the reburn fuel injection point, oxygen and NO compete for hydrocarbon radicals, and enhanced reburning effectiveness would be expected if NO contact with hydrocarbon radicals can be improved.

The trends featured in Figs. 4.33 and 4.34 where the single nozzle was most efficient at destroying NO for the range of stoichiometries ( $\text{SR}_2$ ) between 0.925 and 0.99

might be due to the presence of local fuel rich pockets within which NO destruction is a significant proportion of the overall NO reduction. The relatively low NO reduction efficiencies achieved by the two and four nozzle systems for the same range of  $SR_2$  can be attributed to high dispersion rates of the reburning coal achieved by the nozzle systems, resulting in the rapid oxidation of the reburning fuel which in turn increases the conversion of reburning fuel nitrogen to NO. While the increase in NO emissions in Fig. 4.33 of 2% and 5% for the two and four nozzles respectively is mainly due to the relatively high oxygen concentration in the reburn zone ( $SR_2=0.99$ ) which promotes the oxidation of hydrocarbons to produce CO, CO<sub>2</sub> or H<sub>2</sub>O leaving a lower than normal concentration of hydrocarbon radical. This together with the high fuel-N conversion rate shifted the balance towards NO forming reactions resulting in an increase in NO concentration.

However, when a mixture of air and nitrogen (12%O<sub>2</sub>) is used as carrier gas for the range of  $SR_2$  between 0.86 and 0.91 (Fig. 4.34), the four nozzle configuration dominated with respect to NO reduction; with the two and one nozzle systems being progressively less effective. This result demonstrates that the use of a mixture of nitrogen and air as carrier gas helped decrease the conversion of fuel nitrogen by limiting the amount of oxygen in the contact with the reburning coal while maintaining the rapid dispersion of the coal thus achieving considerable reduction in NO emission at the exit.

The above results indicate that rapid dispersion of the reburning coal is important in terms of NO reduction, however, its effectiveness is governed by the stoichiometric ratio in the reburn zone: high dispersion rates at relatively high oxygen concentration

( $SR_2 = 0.925 - 0.99$ ) would result in a reduced NO reduction, and in some cases (where the reburning coal contains significant nitrogen) an increase in NO emission, while high dispersion rates at relatively low oxygen concentration ( $SR_2 = 0.86 - 0.91$ ) would achieve considerable NO reduction. Low reburning jet mixing rates can also achieve significant NO reduction, since poorer mixing of coal and combustion products may form fuel rich pockets in the reburn zone which can therefore improve NO reduction and prevent oxidation of nitrogen in the reburn fuel to NO.

The data in Fig. 4.35 demonstrate the improved and rapid mixing conditions created by the four and two nozzle systems at high  $R_{ff}$  (or low  $SR_2$  value). However, if the reburn zone is operated fuel-lean or near fuel-lean ( $R_{ff} = 13\% - 18\%$  corresponding to  $SR_2 = 1.03 - 0.98$ ) improved mixing conditions have a two fold effect: reducing the existence of the fuel rich regions thus limiting NO reduction, and improving the contact between the reburning fuel and oxygen (especially carrier gas oxygen) which maximises the conversion of reburning fuel nitrogen. The net effect of which is the decrease in NO reduction efficiency which deteriorates under fuel-lean condition ( $R_{ff} = 13\%$ ,  $SR_2 = 1.03$ ) as shown in Fig. 4.35. Also, the data point ( $R_{ff} = 18\%$ ,  $SR_2 = 0.98$ ) taken for the one nozzle system confirms earlier results in Fig. 4.33 where local fuel rich pockets were beneficial in destroying NO. Similar results were obtained by Greene *et al.* (1986).

However, when a mixture of nitrogen and air (12%  $O_2$ ) is used as carrier gas (Fig. 4.36) for the same setup as in Fig. 4.35, all three nozzle systems showed a considerable improvement in NO reduction efficiency compared to Fig. 4.35, achieving a massive 75% reduction in NO emission for the four nozzle



configuration. The combined effect of the improved and rapid mixing conditions coupled with the relatively low oxygen concentration in the vicinity of the reburning coal are responsible for the trends in Fig. 4.36. The trends in Fig. 4.36 also indicate that at high  $R_{ff}$  the difference between the two and four nozzles systems decreases. This is quite the opposite of the results in Fig. 4.35 when air was used as carrier gas, and the difference between the two systems seems to be increasing. From the trends in Fig. 4.36 it is clear that although the optimum NO reduction was beyond the range of this experiment, the level of reduction was starting to flatten indicating near optimum conditions. However, the rapid rise in the level of NO reduction shown in Fig. 4.35 suggests that the optimum occurs at  $R_{ff}$  well beyond 35% which is both unpractical uneconomical for most industrial applications. Thus an oxygen deficient carrier gas (such as FGR) is of critical importance to reburning effectiveness, especially if good mixing is employed in the reburn zone, to limit the oxidation of the reburning fuel nitrogen and reduce the amount of reburning fuel required to produce the desired stoichiometry in the reburn zone.

#### **4.4 Sensitivity Analysis and Correlation of Experimental Data**

As a result of the large number of variables associated with the reburning process it is clear that it is a complex process and the interdependence of many of these variables, makes it difficult to examine the effect of each variable separately. The process is even more complicated when the influence of reburning coal properties (such as volatile matter, particle size, rank, ash, fuel-N and S content) are considered. Thus, in order to investigate the effect of coal properties and type on reburn performance, a statistical method was employed. Using a statistical Package,

MINITAB Version 11 (Ryan *et al.*, 1985), for eight coals only (South Brandon coal not included) and 257 experimental points corresponding to a fixed reburn zone temperature of 1573 K and a reburn zone residence time of 400 ms, it was possible to carry out a relativity analysis of experimental results with reburn coal properties from Table 3.2.

A multivariate correlation analysis was also carried out to determine the most important experimental parameters which affect the NO reduction efficiency during coal reburning. Two approaches were used: one where a statistical Package (MINITAB) was used and all the experimental data was inputted and then correlated. This approach required a large number of data, and the main experimental variables for which there was sufficient data for a valid statistical analysis included the primary zone stoichiometry, the reburning zone stoichiometry, the reburn fuel fraction, the reburning coal volatile matter content and the carbon burnout efficiency. In the second approach statistically designed experiments were used to derive empirical correlation relating reburning effectiveness to operating parameters. This approach was complemented by detailed tests in which one variable was varied at a time. This combination can yield greater insight into understanding the reburning process.

The correlation of experimental data is an efficient method, since it provides an estimate of system performance with a reasonable accuracy in the absence of sophisticated theoretical models. Combustion engineers can use this information as a practical alternative starting point from which predictions can be made for similar

but larger-scale furnaces with comparable operating temperatures and residence times.

#### 4.4.1 Sensitivity Analysis

The extent of the association between NO reduction efficiency and reburn coal properties, namely, volatile matter content (VM, dry ash free basis), carbon content (C), hydrogen content (H), oxygen content (O), nitrogen content (N), and sulphur content (S) was undertaken in order to evaluate the effect of each factor independently without the interaction with other factors. This was achieved by correlating the observed NO reduction against coal properties for the different coals at the same operating conditions. Thus individual effects were estimated independently and a relativity value (which is a measure of the sum of the squares of the difference between the measured response and the predicted response) calculated for each of the rank-related coal properties. The relativity is a dimensionless number lying between 0 and 1 and is a measure of how well each property agrees with the initial assumption that NO reduction is linearly dependent on that property. The closer the relativity value is to 1 the better the correlation, and the closer it is to zero the poorer the relationship between the variables (Yang *et al.*, 1997).

The result of the relativity analysis of experimental data with reburn coal properties is illustrated in Fig. 4.40. It is clear from Fig. 4.40 that the volatile matter content (as characterised by the proximate analysis test) is the most influential coal characteristic. This is consistent with earlier work by Liu (1995c) using a large number of coal types with a much wider rank than considered here. Hydrogen content is also very prominent in Fig. 4.40, but this is not unexpected since, like the

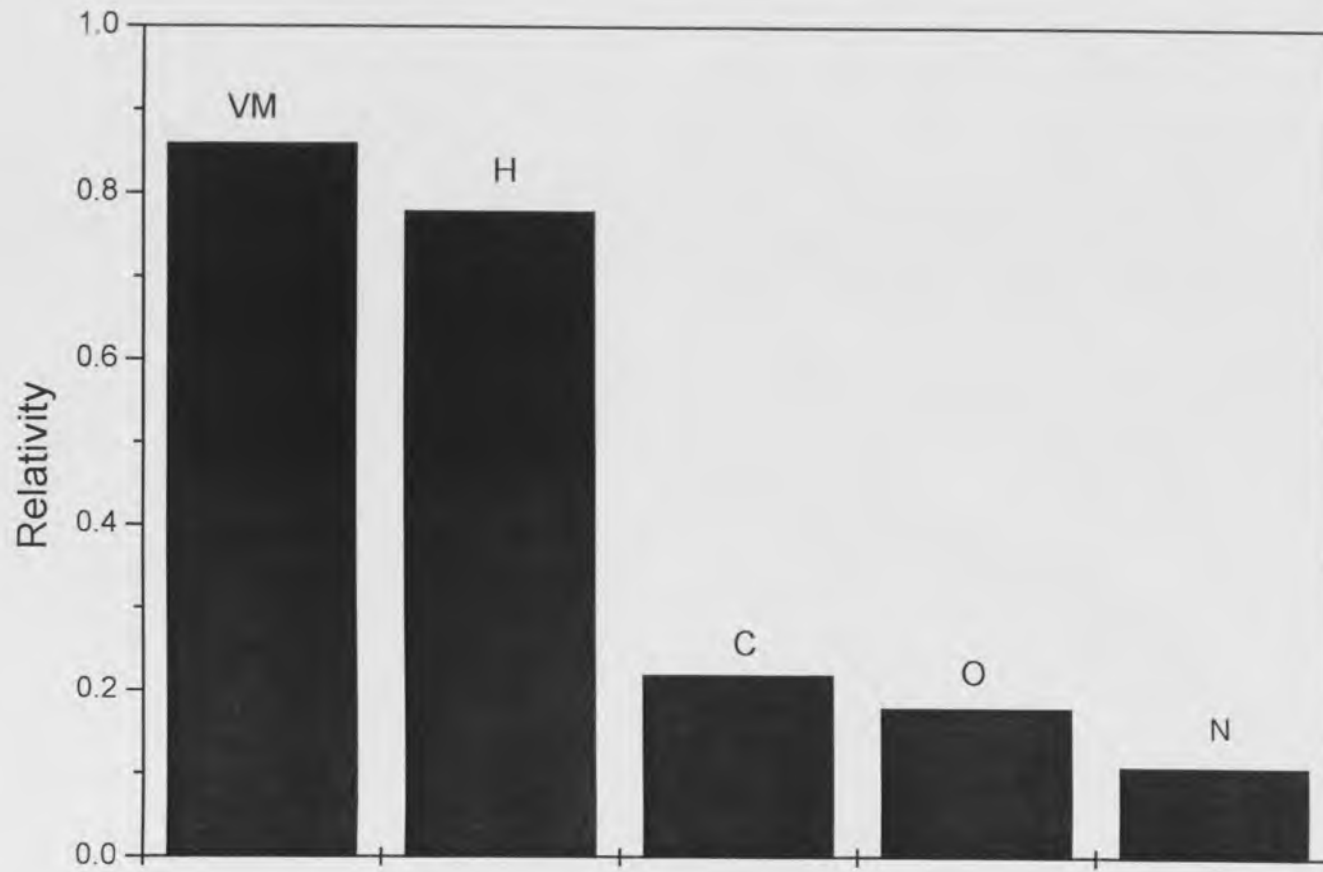


Figure 4.40 Relative sensitivity of volatile matter and elemental H, C, O, N content of coals towards NO reduction

proximate volatile matter, it is a strong indicator of rank and the two are inter-related. The carbon content influence was relatively small and possible contribution could be through enhancing CO or CHi species formation during combustion. The oxygen content had a negative effect on NO reduction as expected since higher coal oxygen content could increase the possibility of direct NO formation during coal combustion. The results, however, did not show as strong a dependency on fuel-N content as might be expected from consideration of the mechanisms for NO reduction by nitrogenous intermediates. A possible explanation can be given on the assumption of a uniform distribution of fuel nitrogen between volatile and char (Levy *et al.*, 1981), so that the reduction of NO by volatile-N species (HCN or NH<sub>3</sub>) in the reburn zone is largely offset by any char-N remaining, which is released as NO in the burnout zone, so the net effect of coal-N is small. This effect can also be clearly seen in the axial concentration profile for NO shown earlier in Figs. 4.34 - 4.38, and will depend on operating conditions and coal type. Earlier work by Liu *et al.* (1995a) and Hampartsoumian *et al.* (1995) found that increasing the rate of fuel-N input into the reburn zone was more effective under fuel rich reburning zone conditions. However, the measurements were conducted in an experimental system that did not include a burnout zone, as in the present reactor. Sulphur content was found to have no influence on NO reduction.

As hydrocarbons are the dominant product of devolatilisation, the sensitivity of the results to volatile matter suggest that hydrocarbons must play an important role in reducing NO to N<sub>2</sub>, along with HCN and NH<sub>3</sub> (Smart and Morgan, 1994). Thus, higher volatile content coals will be more efficient at reducing NO as shown by

Asfordby, which has the highest proximate VM content (37.7%, dry basis) among the tested coals, in Fig. 4.15. Moreover, the high temperature and high heating rate conditions experienced in a real furnace will surely increase the volatile yield of the coal particles well beyond the value determined using standard proximate volatile tests (BS 1016) (Howard, 1981; Saxena, 1990; Gibbins *et al.*, 1993). Furnace temperature and heating rate will also affect the relative distribution of fuel-N between the volatiles and char and their subsequent contribution to NO emission (Rudiger *et al.*, 1997). The effect of all these factors could explain the variability in the extent of NO reduction for the nine coals shown in Fig. 4.15, which are of the same rank.

#### 4.4.2 Correlation of Experimental Data

##### A) Using MINITAB Statistical Package

The method used to measure the response or association between two variables is referred to as Pearson product moment correlation coefficient, or correlation coefficient in short (Ryan *et al.*, 1985). This method was employed here to determine the extent of interaction between the NO reduction efficiency and the different operational variables namely primary zone stoichiometry ( $SR_1$ ), reburn zone stoichiometry ( $SR_2$ ), reburn fuel fraction ( $R_{ff}$ ), carrier gas oxygen concentration ( $O^*$ ), carbon conversion efficiency ( $\eta_c$ ), and volatile matter (VM). The main objectives are: to identify the significant variables which affect reburning effectiveness, to examine their individual contribution based on their empirical correlation, and to determine the linear regression equation. Using the data from eight coals, a total of 257 experimental points corresponding to a fixed reburn zone

temperature of 1573 K and a reburn zone residence time of 400 ms were correlation analysed. Table 4.1 presents the correlation coefficients between NO reduction efficiency and the different variables.

**Table 4.1** Correlation Results

Variable	SR <sub>1</sub>	SR <sub>2</sub>	R <sub>ff</sub>	O*	η <sub>c</sub>	VM
Correlation Coefficient <sup>1</sup>	-0.608	-0.855	0.489	-0.658	0.307	0.825

<sup>1</sup>The correlation coefficient is always between -1 and +1. The correlation coefficient is positive if the NO reduction efficiency tends to increase as the factor increases. Conversely, the correlation coefficient is negative if the NO reduction tends to decrease as the factor increases.

The important variables are identified in the following order of significance: stoichiometry in the reburn zone (SR<sub>2</sub>), volatile matter content of the coal (VM, daf), carrier gas oxygen concentration (O\*) and stoichiometry in the primary zone (SR<sub>1</sub>). The other variables, namely, the reburn fuel fraction (R<sub>ff</sub>) and carbon conversion efficiency (η<sub>c</sub>) were of minor significance in the experimental range that was covered. Furthermore, the magnitude of each coefficient is an indication of the significance of the corresponding effect.

Correlation shows how much association there is between two variables and the correlation coefficient estimates the significance of the relationship, whereas, regression gives an equation that uses one variable to help explain the variation in another and the regression coefficient estimates the relationship between the two variables. Thus fitting a correlation equation to the experimental data using multiple

regression procedure helps predict the effect of the various independent variables on the single dependent variable, in this case NO reduction efficiency.

A correlation was fitted to the 257 data points using multiple regression procedure (MINITAB Version 11) to determine the regression equation for NO reduction efficiency versus other variables, namely, stoichiometry in the reburn zone ( $SR_2$ ), volatile matter content of the coal (VM, daf), carrier gas oxygen concentration ( $O^*$ ), stoichiometry in the primary zone ( $SR_1$ ), the reburn fuel fraction ( $R_{ff}$ ) and carbon conversion efficiency ( $\eta_c$ ).

Table 4.2 shows the results of the multi-variant analysis using the Stepwise method. This method evaluates the contribution of each term at each and every step of the regression to see if they are still worth including in the regression. The exclusion of a certain contribution by the regression is based on an evaluation of the t-ratio, which is a measure of the variation in the predicted response due to contribution of certain term, relative to the variation of the residual. The residual is defined as the algebraic difference between the measured response and the predicted response obtained by substitution in the fitted regression equation. There is one residual for each of the original measured values, and the regression coefficients in Table 4.2 are estimated by minimising the sum of the squares of these residuals. The t-ratio is also a measure of the significance levels of the different variables i.e. the degree of contribution of each variable to the variation of the response. The p value in Table 4.2 measures the probability of a certain contribution having a slope of zero. A p value of 0.000 for all the variables indicates that it is almost certain that all the variables contribute significantly to the variation of the correlation and that none has a slope of zero.



**Table 4.2** Multiple Regression Results

Dependent Variable: NO reduction efficiency ( $\eta_{NO}$ )

Predictors in the Equation:

Predictors	Coefficient	Stdev	t-ratio	p
Constant	2.8142	0.1532	18.36	0.000
SR <sub>2</sub>	-4.5721	0.2291	-19.96	0.000
SR <sub>1</sub>	1.5162	0.1929	7.86	0.000
$\eta_C$	0.19128	0.04602	4.16	0.000
VM	1.2484	0.1110	11.24	0.000
Rff	-1.3232	0.2335	-5.67	0.000
O*	-0.6880	0.1205	-5.71	0.000

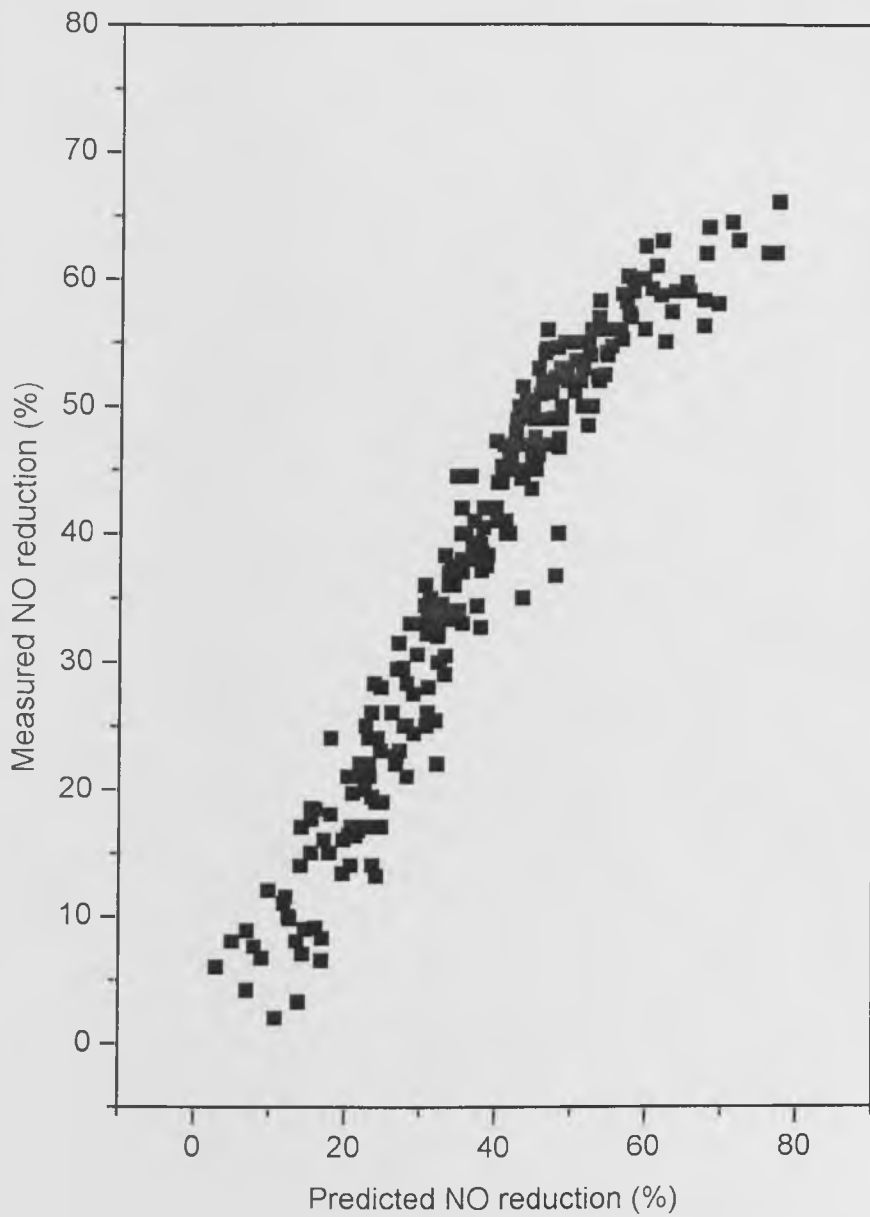
s = 0.04995

R Square = 90.5%

R Square (adj.) = 90.3

The regression equation is

$$\eta_{NO} = 2.81 - 4.57 \text{ SR}_2 + 1.52 \text{ SR}_1 + 0.191 \mu_C + 1.25 \text{ VM} - 1.32 \text{ R}_{ff} - 0.688 \text{ O}^*$$



**Figure 4.41** Comparison of measured and predicted NO reduction using the correlation equation derived from Minitab package (relativity = 0.905, standard deviation = 5.0)

The coefficients of the different variables of the system ( $SR_1$ ,  $SR_2$ ,  $O^*$ ,  $VM$ ,  $R_{ff}$ , and  $\eta_c$ ) are calculated by the regression, as seen in Table 4.2. The different variables are represented in the regression equation and 90.5% of the variation among the 257 data points is accounted for by the variation of the different variables. However, since the derived correlation is linear with respect to all variables including reburn zone stoichiometry, no optimum reburn zone stoichiometry would be predicted by the correlation.

The comparison between the correlation predictions of  $\eta_{NO}$  using the regression equation in Table 4.2 and the experimental measured NO reductions is shown in Fig. 4.41. As can be seen, the agreement with the experimental data is very good with a relativity of 0.905 and a standard deviation of 5% of the maximum NO reduction efficiency achieved.

#### B) Using Statistical Design of Experiments

In this approach a statistical method was used to design experiments in which various factors were varied over an experimental range of interest. The outcome of the experiment was determined by the values of the different variables of the process. A variable is a parameter that can be changed from one level to another such as  $SR_1$ , or a fixed parameter which varies with the variation of coal type such as  $VM$ . In this statistical design, the outcome or NO reduction efficiency and several measurable variables were linked by an empirical correlation based on experiments involving a small number of runs, and expressed as a function of the controlled variables (Yang *et al.*, 1997).

The trends of the experimental data have highlighted the importance of several controlled variables, namely, the operating stoichiometries ( $SR_1$  and  $SR_2$ ), the reburn fuel fraction ( $R_{ff}$ ), the primary NO concentration, and the carrier gas oxygen concentration.

Figure 4.15 highlighted the importance of reburn zone stoichiometry, with the measured NO reduction being almost linearly dependent on  $SR_2$ . On the basis of this relationship, a correlation between NO reduction efficiency and  $SR_2$  may take the following form:

$$\eta_{NO}^* = A - B (SR_2 - SR_2^*) \quad (4.15)$$

where  $\eta_{NO}^*$  is the NO reduction efficiency at 600 ppm baseline NO emissions;  $SR_2^*$  is the lower physical limit of reburn zone stoichiometric ratio, corresponding to when the oxygen input to the reburn zone is zero, so that  $(SR_2 - SR_2^*)$  would be proportional to the oxygen concentration in the reburn zone. The parameter, A, is the maximum possible theoretical NO reduction which would be achieved for a coal for each of the conditions investigated in this work. The coefficient, B, represents the effectiveness of the oxygen in the reburn zone to prevent NO reduction reactions by consuming the major reductants (CO, CH<sub>i</sub>, HCN and NH<sub>3</sub>).

From a statistical correlation of experimentally measured NO reduction data (shown in Figs. 4.9, 4.10, 4.15, 4.16 - 4.22 & 4.32) and coal analysis in Table 3.2, the following relationships were derived:

$$A = 1.172 \text{ VM} - 4.36 \text{ N} + 0.16 \text{ C} + 0.147 \text{ F} - 0.011 \quad (4.16)$$

$$B = 20.8 (1 - \text{VM}) \text{ F}^{0.333} + 17.6 \text{ O} - 4.75 - 12.1 (\text{R}_{\text{ff}}/(1 + \text{R}_{\text{ff}})) \quad (4.17)$$

and

$$\text{SR}_2^* = 0.6514 - 0.482(\text{R}_{\text{ff}}/(1+\text{R}_{\text{ff}})) + 0.33 \text{ SR}_1 \quad (4.18)$$

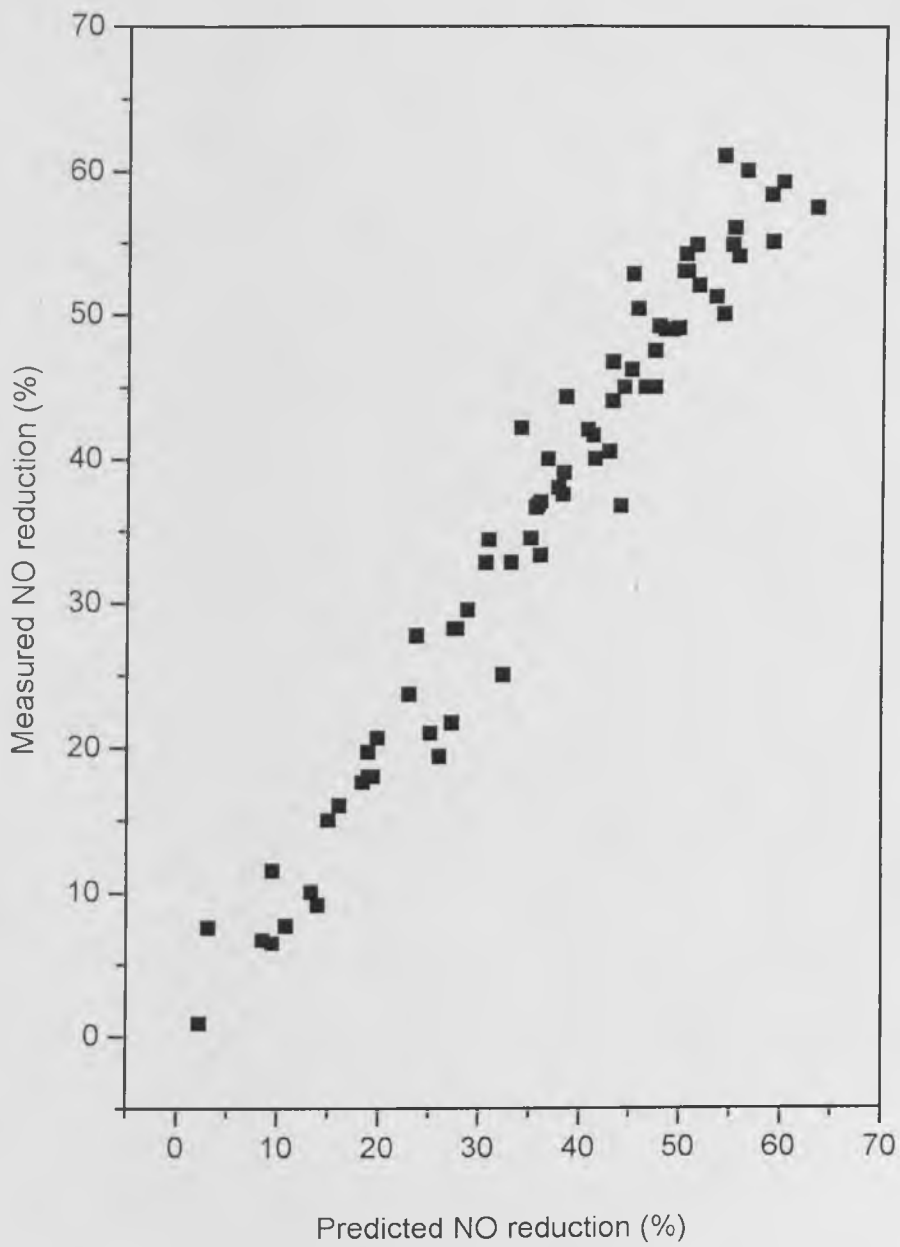
where N, C, O and VM represents the fraction of nitrogen, carbon, oxygen and volatile matter respectively in the reburn coal on a dry, ash free basis, F is the weight fraction of coal particles under 63  $\mu\text{m}$  and  $\text{R}_{\text{ff}}$  is the reburn fuel fraction as previously defined.

From Fig. 4.8, a relationship between the NO concentration at the start of the reburn zone,  $\text{NO}_{\text{pr}}$ , and the total NO reduction efficiency ( $\eta_{\text{NO}}$ ) can be determined to account for the effect of varying inlet NO concentration as follows:

$$\eta_{\text{NO}} = 1.2 \eta_{\text{NO}}^* (1.0 - 117/\text{NO}_{\text{pr}}) \quad (4.19)$$

where  $\text{NO}_{\text{pr}}$  is in ppm.

The comparison between the correlation predictions for  $\eta_{\text{NO}}$  using equations (4.15 - 4.19) and the experimental measured reductions from Fig. 4.15 is shown in Fig. 4.42. The agreement is very good with 98% of the variation among the 80 data points accounted for by the correlation, and giving an average deviation of  $\pm 3.2\%$  of experimentally determined NO reduction efficiency from the predicted efficiency.



**Figure 4.42** Comparison of measured and predicted NO reduction using empirical correlation

An indication of the variability associated with the range of coals investigated is shown in Table 4.3 which compares the measured and predicted NO reduction efficiencies for the coals with the lowest and highest volatile content.

**Table 4.3** Comparison of measured and predicted NO reduction efficiency ( $\eta_{NO}$ ) for a range of coals ( $SR_1= 1.03$ ,  $SR_2= 0.93$ ,  $R_{fl}= 19\%$ )

Coal	Asfordby	Thoresby	Pittsburgh #8	Koonfonteine
VM % daf	42.6	38.4	35.6	32.2
N % daf	1.57	1.94	1.64	2.07
$\eta_{NO}$ predicted	57	50	47	40
$\eta_{NO}$ measured	59	50	43	40

It must be emphasised that the above correlations only apply to bituminous coals and have not been tested for coals of other rank. Residence time and temperature have not been included as specific parameters so that application should be limited to systems operating at comparable temperatures with reburn zone residence times not less than 400 ms. Thus the above conclusions might not hold outside the experimental range of this study.

#### 4.4.3 Evaluation of the Two Statistical Approaches

The use of a statistical design proved to be a more efficient method than conventional means, capable of estimating the performance of the system with reasonable accuracy. In contrast to the MINITAB package, this approach required a minimal number of tests and included several more variables than the former.

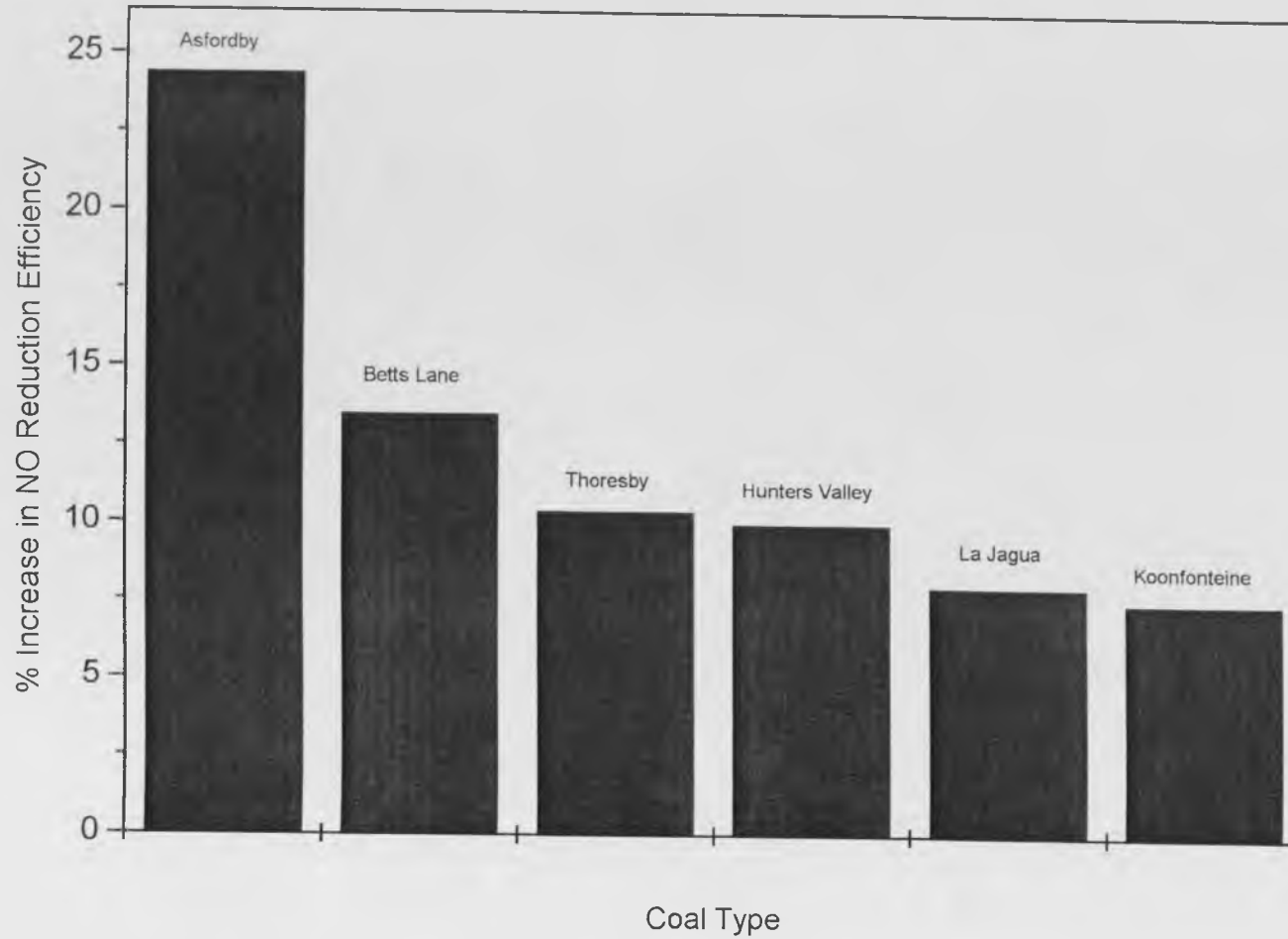
However, in both cases the empirical correlations did not predict the optimum reburn zone stoichiometry. Nevertheless, the correlation equations could be used to quantitatively predict the effect of each variable on NO reduction efficiency as well as the reburning performance of any non-tested reburning coals under the same experimental conditions. It must also be noted that the above correlations do not predict an optimum configuration for reburning and as such their use should be restricted to a qualitative, rather than a quantitative, examination of reburning.

#### **4.5 Effect of Coal Type**

The sensitivity analysis in Fig. 4.40 highlighted the importance of the proximate volatile matter content as the most dominant coal characteristic influencing reburn performance. However, since the proximate volatile matter content is not representative of the actual volatile yield, and does not predict the devolatilisation behaviour of the different reburn coal types under typical reburning conditions investigated in this study, it cannot be used to fully explain the variation in some of the data.

The results presented in Figs. 4.29 and 4.30 show that lower temperature is beneficial to NO reduction efficiency, especially at high  $SR_2$  values. However, the degree of effectiveness varies with coal type. Figure 4.43 demonstrates the relative increase in NO reduction efficiency for each of the coals, the order of which is not in line with their respective proximate volatile content. In fact, Betts lane which has the lowest proximate volatile content (26.8 %, dry basis), achieved the second highest increase in NO reduction efficiency (13.5%), and La Jagua which is second only to Asfordby in volatile matter content (36.1%, dry basis), achieved an 8% increase in

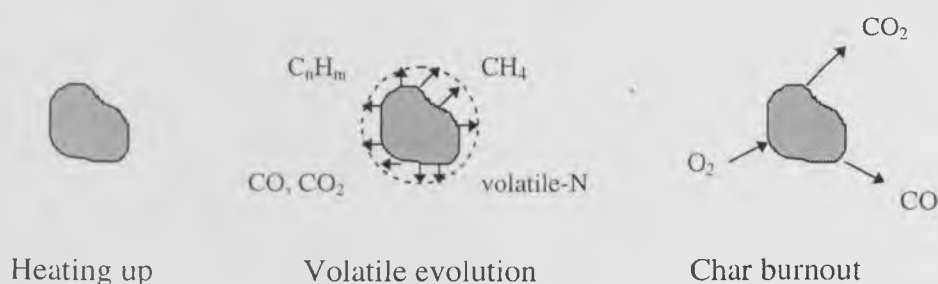




**Figure 4.43** Increase in NO reduction efficiency for different coal types due to a change in temperature from  $T_{pr} = 1773$  K to  $T_{pr} = 1573$  K (SR1= 1.03, SR2= 0.97, Rff= 19%)

NO reduction and came second to last. These trends could be explained in terms of coal devolatilisation behaviour (i.e. quantity and composition of evolved volatiles) which is strongly dependent on temperature, heating rate, coal rank, reactor pressure and particle size (Bengtsson, 1986; Hindmarch *et al.*, 1995; Howard, 1981; Saxena, 1990; Niska *et al.*, 1982; Suuberg *et al.*, 1979). Thus, the relatively high increase in NO reduction efficiency attained by Betts Lane coal, despite having the lowest volatile content, could be due to the fact that 74.5% by weight of the coal has a particle size distribution of less than 63  $\mu\text{m}$ , and smaller particle size is known to increase volatile yield (Niska *et al.*, 1982; Suuberg *et al.*, 1979).

The devolatilisation behaviour of the reburning coals strongly influences the combustion process by affecting both the rate of volatile evolution and volatile yield which in turn influences ignition, rate and form of nitrogenous species evolution and most importantly the mechanism governing NO reduction. The classic model of coal combustion assumes the following sequence of effects (Wendt, 1980):



In reburning, it is important that the nitrogen in the coal is devolatilised and does not remain in the carbonaceous residue. The fate of volatile nitrogen is then determined by the local oxygen environment in which it is found immediately upon leaving the particle surface. This is determined by the overall mass evolution rate, the speciation

of the mass evolved and the manner in which evolution takes place. Thus the variability in NO reduction efficiency shown in Fig. 4.15 for the different coals (which are of the same rank) is a measure of all these parameters, and although they could not be quantified in this study, they have a significant bearing on the overall effectiveness of the reburning process and could also affect the design and operating conditions of other coal combustion systems.

#### 4.6 Summary

The results presented in this chapter demonstrate the effectiveness of nine bituminous reburn coals in reducing NO emission in a typical reburning configuration. A reduction efficiency of over 70% was achieved by optimising operating parameters. The most influential operating parameter controlling NO reduction efficiency was the reburn zone stoichiometric ratio, giving greater reductions in fuel rich operation. The effect of varying the primary zone stoichiometry on reburn performance was of minor significance, and only exerted its influence through indirectly affecting other parameters, mainly  $SR_2$  and to a lesser degree temperature and residence time. The optimum reburn zone residence time was around 450 ms, beyond which only marginal gains in NO reduction were obtained. The NO reduction efficiency increased with increasing primary NO concentration up to around 600 - 700 ppmv, after which the trend levels off, however, at low primary NO (<200 ppmv) it was difficult to obtain a positive NO reduction efficiency. The amount of reburn fuel or  $R_{ff}$  required to generate the hydrocarbon radicals necessary for effective NO control was not conclusively quantified, however, from the results obtained the optimum amount of reburn fuel

was in the region of 20-25% of the primary fuel input. Lower inlet gas temperature in the reburn zone generally enhanced NO reduction, however, this effect diminished under sufficiently fuel rich conditions. Furthermore, the effect of temperature in the reburn zone was dependent on residence time, with high temperature (1773 K) and long residence time (>500 ms) achieving higher reduction. Improved mixing conditions in the reburn zone enhanced reburning effectiveness, however, in fuel lean operations poorer mixing was found to improve NO reduction through local fuel rich pockets. Finer particle size distribution of the reburning coal gave rise to better NO reduction and higher burnout efficiency. Burnout efficiency was also improved by higher gas temperature, however, under fuel rich conditions ( $SR_2=0.85$ ) burnout efficiency could be hampered by low oxygen concentration. Finally, the results of the multi-variate analysis undertaken to determine the importance of some of the above operational parameters on NO reduction as well as the influence of reburn coal properties such as fuel nitrogen content and volatile matter, confirmed the importance of  $SR_2$  as the dominant variable in coal reburning. The volatile matter content was the most influential characteristic of the reburn fuel affecting reburn performance, while fuel nitrogen content was not as influential a parameter for the range of operating conditions and coals studied.

# CHAPTER FIVE

## Conclusions and Proposals for Future Work

Experiments were conducted on a 200 kW pilot-scale furnace to investigate various aspects of the reburning process as a combustion modification technique to reduce NO. The focus was on coal reburning, with propane gas doped with ammonia being used as the primary flame. The influence of individual parameters for each zone of the process was determined and the following conclusions were derived.

### 5.1 Conclusions

1. The reburn zone stoichiometry was the most influential operational parameter, with higher reductions generally achieved under fuel rich operation. However, for the range studied (0.85 - 1.03) no optimum reburn zone stoichiometry was obtained.
2. The NO reduction process was mostly completed in the reburn zone, with a slight increase in NO reduction in the burnout zone due to NO formation from char-nitrogen and any unconsumed volatile nitrogenous species.
3. The primary zone stoichiometry also affected NO reduction efficiency, but only through its influence on other reburning parameters, mainly  $SR_2$  and to a lesser extent temperature and residence time.

4. The NO reduction efficiency increased with increasing primary NO concentration up to around 600 - 700 ppmv, after which the trend levels off, however, at low primary NO (<200 ppmv) it was difficult to obtain a positive NO reduction efficiency because of the NO<sub>x</sub> contribution from the Fuel-N in the reburn fuel.
5. The optimum reburn zone residence time was around 450 ms and only marginal gains were achieved beyond this point. The carbon conversion efficiency, however, dropped as the reburn zone residence time increased.
6. The amount of reburn fuel or  $R_{ff}$  required to generate the hydrocarbon radicals necessary for effective NO control was not conclusively quantified, however, from the results obtained the optimum amount of reburn fuel was in the region of 20-25% of the primary fuel input.
7. Lower inlet gas temperature (1573 K) in the reburn zone generally enhanced NO reduction, however, this effect diminished under sufficiently fuel rich conditions.
8. The effect of temperature in the reburn zone was dependent on the residence time, with higher temperature (1773 K) and longer residence time (>500 ms) achieving higher reduction.
9. Improved mixing conditions in the reburn zone enhanced reburning effectiveness, however, in fuel lean operations poorer mixing was found to improve NO reduction through local fuel rich pockets.

10. Finer particle size distribution of the reburning coal gave rise to better NO reduction and higher burnout efficiency.
11. The carbon burnout efficiency was around 85% - 95%, and higher gas temperature improved carbon burnout efficiency, however, under fuel rich conditions ( $SR_2=0.85$ ) burnout efficiency was hampered by the low oxygen concentration.
12. From the sensitivity analysis, the most important coal property was the content of the proximate volatile matter, while fuel nitrogen content was not as influential a parameter for the range of operating conditions and coals studied.
13. The examination of reburning using statistical methods failed to predict optimum configuration. However, these tests confirmed the importance of the reburn zone stoichiometry as the dominant variable affecting reburn performance.
14. The parametric study, based on statistical experimental design, was an efficient method for a qualitative, rather than quantitative, examination of the reburning process. The regression equation obtained by linking NO reduction efficiency with other variables, was in good agreement with experimental values, with 98% of the variation being accounted for by the correlation.

## **5.2 Proposals For Future Work**

Finally, the following recommendations are made for future work:

1. The use of propane gas flames laden with ammonia in this study allowed for a straight forward assessment of each coal without the complexity and problems

associated with pulverised coal firing on a smaller scale. However, in coal-fired applications, coal flames form the primary combustion zone. Thus, there is a need to study the effect of coal reburning on a coal-fired primary flame which is normally longer than that of a gas primary flame and could overlap the reburn zone. The extent of interference by large quantities of residual char particles which continue to burn and react needs to be quantified. The effect of reburning in a premixed primary flame mode relative to an axial diffusion primary flame mode can also be investigated.

2. Time resolved nitrogenous species (HCN and  $\text{NH}_3$ ) profiles in the reburn zone were not measured in this study and thus the total fixed nitrogen speciation was not known. The analysis of HCN and  $\text{NH}_3$  formed in coal reburning could be included in future work.
3. In this study, the mixing effect proved to be a limiting factor in the optimisation of the reburning process and thus needs to be quantified. A theoretical mixing model, coupled with a kinetic model, would provide a valuable tool in the design of combustion modification configurations for low NO emissions.
4. Lower temperatures and poor mixing conditions, in this study, enhanced the overall destruction of NO when the reburn zone was operated near fuel lean. Thus the application of reburning under fuel lean conditions in the reburn zone can be useful in achieving moderate reduction in NO emissions without the need for the hostile reducing conditions that cause severe problems and increase maintenance costs. Further investigation is thus required.



5. The use of nitrogen as carrier gas proved to be an influential factor in ensuring optimum reburn performance. However, the use of nitrogen gas as a transport medium on a large scale boiler would not prove to be very economical, therefore, it would be more desirable to use flue gas recirculation to transport the reburning coal. Experiments to that effect should be carried out.

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# APPENDIX A

## LBC 2000 Loss-In-Weight Feeder

The principal aim of the LBC 2000 is to weigh and control the coal feed rate thus regulating the quantity of coal according to the requirement of the operator. The system consists of 5 main parts:

- A) 100 litre Hopper
- B) Rotary valve
- C) 30 litre hopper (the feeder or liquids vessel)
- D) weigh platform
- E) operator panel
- F) power panel

### **A) 100 Litre Hopper :**

This is used as a storage vessel ready for use when required. Mounted on the outside of the hopper is a vibratory engine that stops the coal from bridging inside the hopper.

### **B) Rotary Valve :**

This is an automatic filling valve which allows the 30 litre hopper to be filled up to a preset level. Once the coal reaches the preset high weight, set by the operator, the

valve will close. The valve will re-open and engage refill procedure when the coal level in the hopper falls below a preset low weight.

### **C) 30 Litre Hopper :**

This is where the coal is temporarily stored before entering the conditioning chamber ready for feeding.

### **D) The Weigh Platform :**

This holds the metering screw feeder which consists of a conditioning chamber within which is a slowly turning agitator to de-aerate and densify the pulverised coal and keep it sticky free thus preventing it from 'bridging'. Below the conditioning chamber are two variable speed archimedean screws which run completely and evenly full of material. The speed of the screws is modulated to keep the output weight of the loss-in-weight system constant and accurate.

The weighing unit itself consists of a rigid support frame on which three load cells are mounted. The 30 litre hopper is fixed directly to the load cells which are mounted equispaced around the frame and supports the weigh platform using a unique self-centering location method. This allows the weigh platform to effectively float with good weighing and protection characteristics but still retain good positional location.

The weigh platform measures the net weight of the coal in the hopper every few milli-seconds, this is then averaged and stored in the microprocessor as a falling weight per unit time (kg/hr). This weight per unit time is compared to a weight per



unit time already pre-set by the operator on the microprocessor key pad and stored in the memory. Any difference in the actual slope of the falling weight per unit time and the slope of the pre-set weight per unit time, is fed to a process controller and used to speed up or slow down the product feed in order to make the two slopes identical.

#### **E) The Operator panel :**

This is where all the information is entered by the operator. It consists of a microprocessor board, a keyboard an LCD and an LED numerical display. All operator inputs take place on this unit by means of a touch sensitive key pad. Also included is a digital LED indicator for the display of an operator set parameter and an 8 line LCD display for entry and display of machine operating parameters.

#### **F) Power Panel :**

This houses a second microprocessor system in a dust protecting enclosure. It also contains the electrical controls for powering and operating the feeder as well as controls for manual operation.

The general principle of operation of the Rospen loss-in-weight feeding system is as follows:

1. The loss-in-weight hopper is rapidly filled via the automatic filling valve. At a hopper-full weight, preset within the microprocessor, the rotary valve will close.
2. The metering feeder starts feeding the coal into the vibrating tray (at a rate set by the operator); thus the weight in the hopper gradually falls.

3. The net weight is measured every few milli-seconds, averaged and stored by the microprocessor as a falling weight per unit time (kg/hr). This weight per unit time is compared to the weight per unit time already preset by the operator on the microprocessor key pad and stored in the memory.
4. Any difference in the actual slope of the falling weight per unit time and the slope of the pre-set weight per unit time, is fed to a process controller and used to speed up or slow down the coal feed rate in order to make the two slopes identical.
5. The cycle will repeat with the microprocessor going through a continuous learning curve which will become more accurate with each cycle.

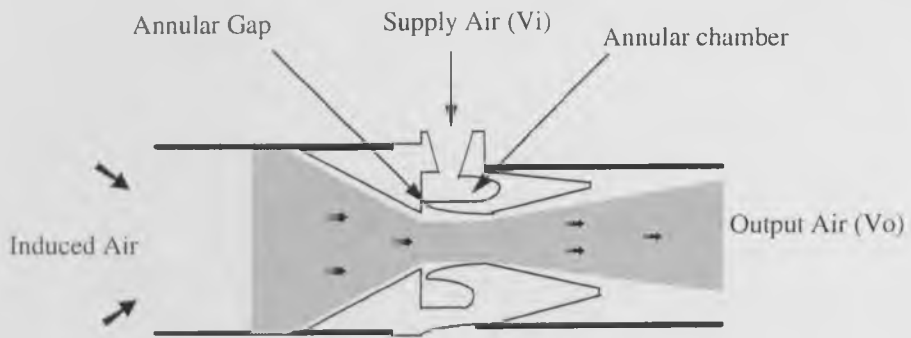
# APPENDIX B

## Brauer Airmover

### B.1 General Description and Principle of Operation

The airmover used in this study was a stainless steel type SS20 Brauer airmover. A schematic diagram of the airmover is shown in Fig. B1. The airmover was connected to the compressed air supply via the supply inlet which directed the air flow into an annular chamber where the air was throttled by an annular gap. The resultant thin layer of high velocity air adhered to the profile which turned the flow through 90° to pass down the bore. The action of the high velocity supply air flowing over the profile caused a pressure drop in the device which induced large volumes of ambient air. The induced flow was augmented, and gained velocity by contact with the supply air flow through the bore of the unit. The volume output from the air mover was therefore the sum of the supply air plus the induced air.

The amount of induced air was estimated by calibrating the airmover. This was done by connecting the output duct to a flowmeter as well as measuring the volume of supply air. For a fixed air supply flow rate, the total output flow and the resulting pressure drop were measured. This was repeated for a range of air supply flow rates. Thus the volume of induced air could be accurately estimated. Figure B2 shows the calibration plot for the reburn coal carrier gas flow rate as a function of the pressure drop reading across the airmover.



$$\text{Volume Output (} V_o \text{)} = V_i + \text{Induced Air}$$

**Figure B1** Schematic of the SS20 Brauer Airmover

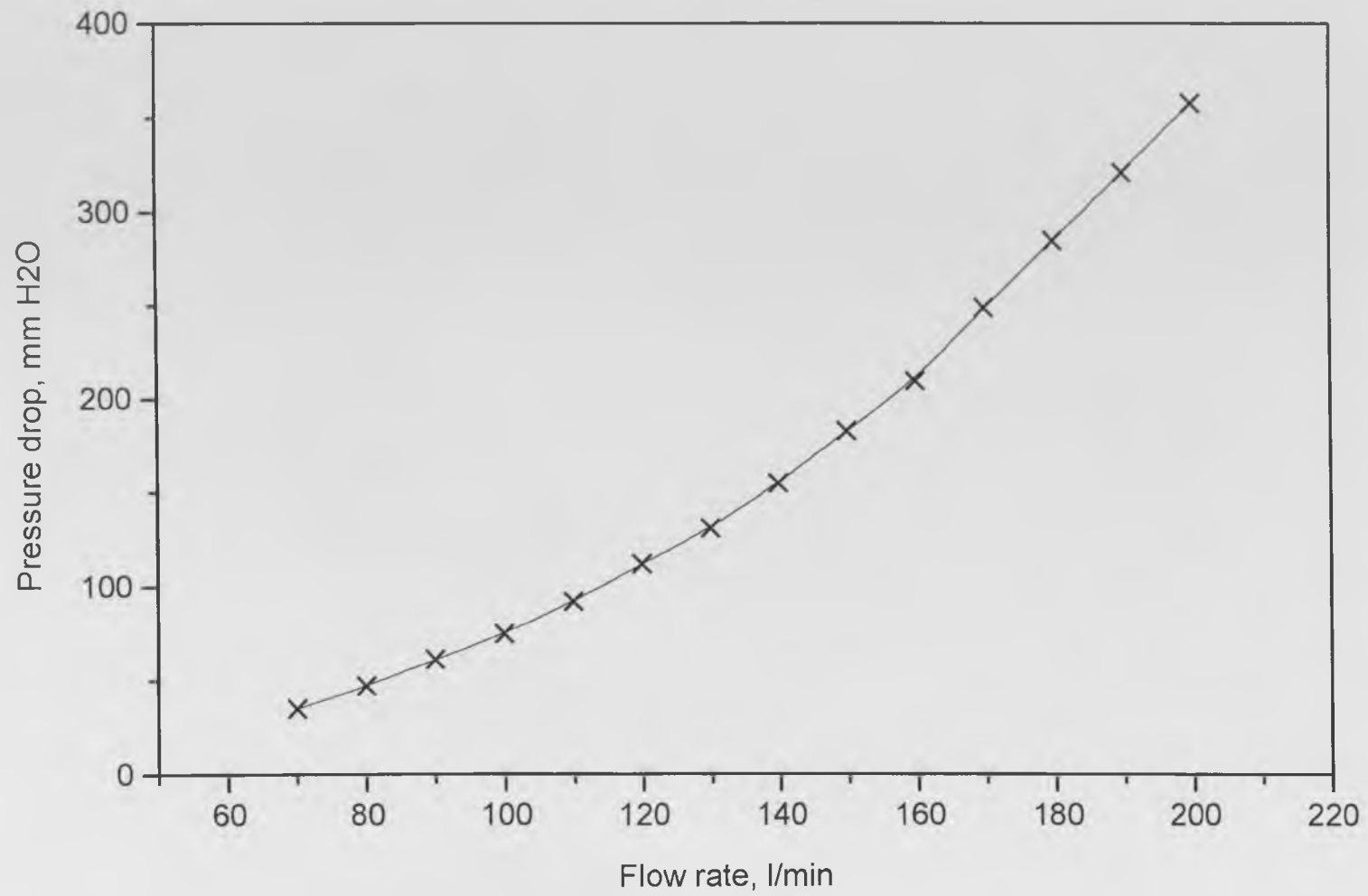


Figure B2 Calibration of the carrier gas flow rate as a function of pressure drop

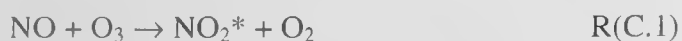
# APPENDIX C

## Gas Analysis Instrumentation

The following instruments were used for continuously monitoring the gas composition within the furnace enclosure and the flue gas area.

### C.1 Chemiluminescent NO-NO<sub>x</sub> Analyser

A Signal series 440 Chemiluminescent NO<sub>x</sub> analyser was used to measure NO and NO<sub>2</sub> concentrations. It is based upon the chemiluminescence reaction of NO and O<sub>3</sub> to give an electronically excited NO<sub>2</sub> which emits light in the 600-3000 nm region with a maximum intensity near 1200 nm. In a NO<sub>x</sub> analyser, NO from the polluted sample is exposed to excess O<sub>3</sub> in a chamber and the resultant rapid reaction produces electronically excited nitrogen dioxide and oxygen.



The excited NO<sub>2</sub>\* molecules then revert to ground state and lose their energy by emitting light which is monitored through an optical filter by a high sensitivity photomultiplier positioned at one end of the reaction chamber. The ozone generator is a silent discharge device and only about 2% conversion of the oxygen supply is necessary for the chemiluminescent reaction. The filter/photomultiplier combination responds to light in a narrow wavelength unique to the above reactions (hence little

interference) and the output of the photomultiplier is linearly proportional to the NO concentration in the chamber.

The analyser is only sensitive to NO molecules and NO<sub>x</sub> must first be converted to NO. This conversion is accomplished by passing the gas through an electrically heated coil constructed from 6 feet of 1/8 inch diameter 316 stainless steel tubing provided in the analyser. The recommended operating temperature of the converter is 600 °C to 650 °C and the conversion efficiency is between 95% to 100% within this temperature range. The stainless steel acts as a catalyst accelerating the already favoured NO state at high reaction temperatures of the NO/NO<sub>2</sub> system. The chemiluminescent response in the chamber to the converter effluent is linearly proportional to the NO concentration entering the converter.

Prior to each run, the analyser was set to read zero by drawing sample from a nitrogen cylinder containing zero ppm NO, then it was calibrated using a calibration gas containing 500 ppmv NO.

## **C.2 Non-Dispersive Infra-Red Analyser**

Carbon monoxide measurements were taken using an Analytical Development Company (ADC) non-dispersive infra-red gas analyser (range 0-2%). The sample gas to be measured is passed through an optical cell, located between an infra-red radiation source and the detector. Some radiation is absorbed by the CO in the gas sample leading to a reduction of energy level reaching the detector. This energy is compared with the output of a cell containing a pure sample and the difference in energy is then amplified to give the analyser output signal.

The analyser was carefully calibrated using a 100 ppmv CO calibration gas and the gas sample was thoroughly dried using a water trap to remove the majority of the moisture and a manganese perchlorate drying agent before entering the measuring cell. A particulate filter removed any solid matter from the stream.

The linearity of the analyser when operated according to the specifications as stated by the manufacturer is within 99% in full scale reading.

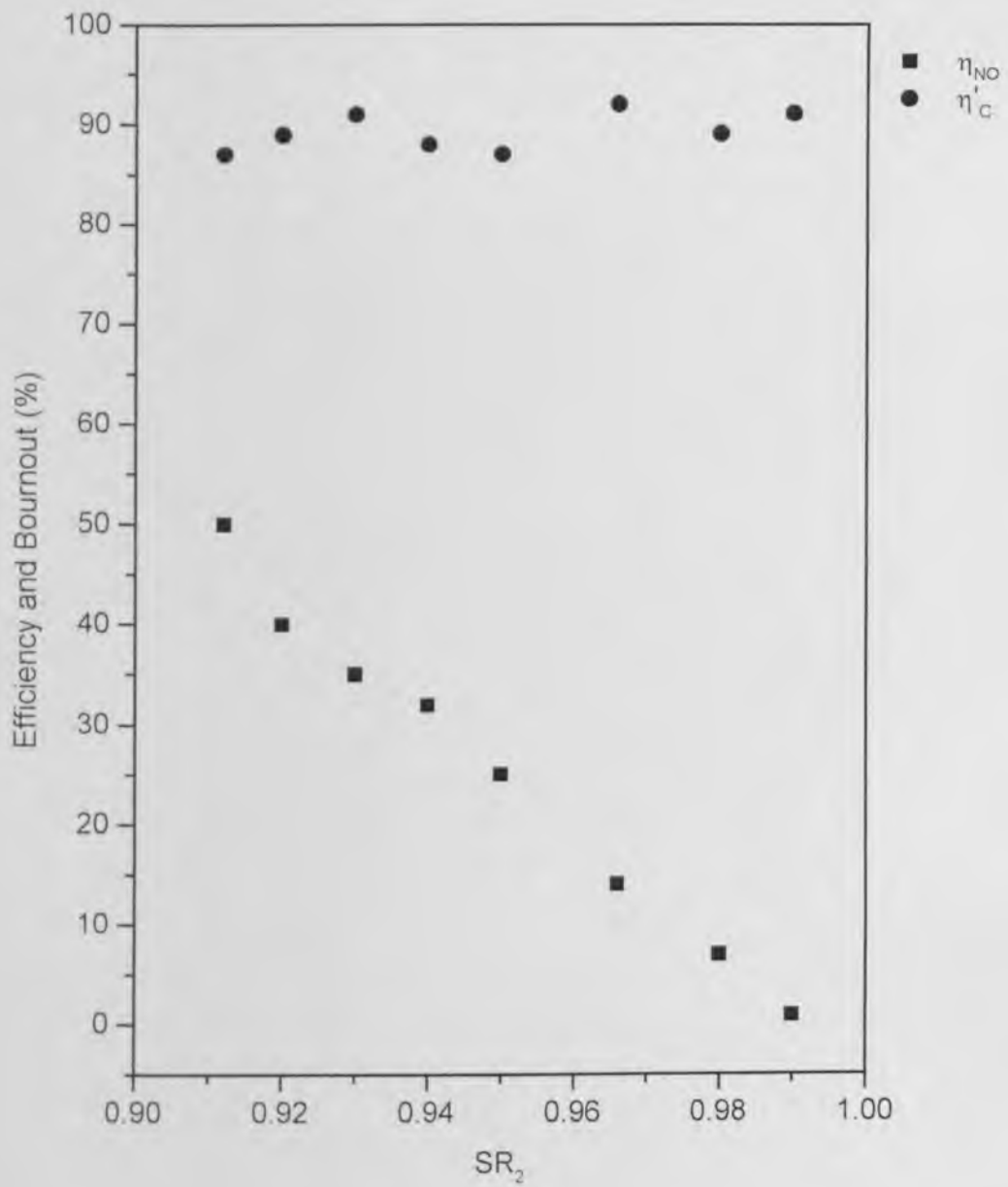
### **C.3 Paramagnetic Oxygen Analyser**

The oxygen concentration in the sample gas was measured using a Taylor-Servomex OA 570 paramagnetic oxygen analyser. The analyser measures the paramagnetic susceptibility of the sample gas by means of a magneto-dynamic type measuring cell. Oxygen molecules are attracted much more by a magnetic field in comparison to other common species such as N<sub>2</sub> due to their greater paramagnetic susceptibility. The analyser works on the principle of measuring the force developed by a strong non-uniform magnetic field on a suspended diamagnetic test body surrounded by the sample.

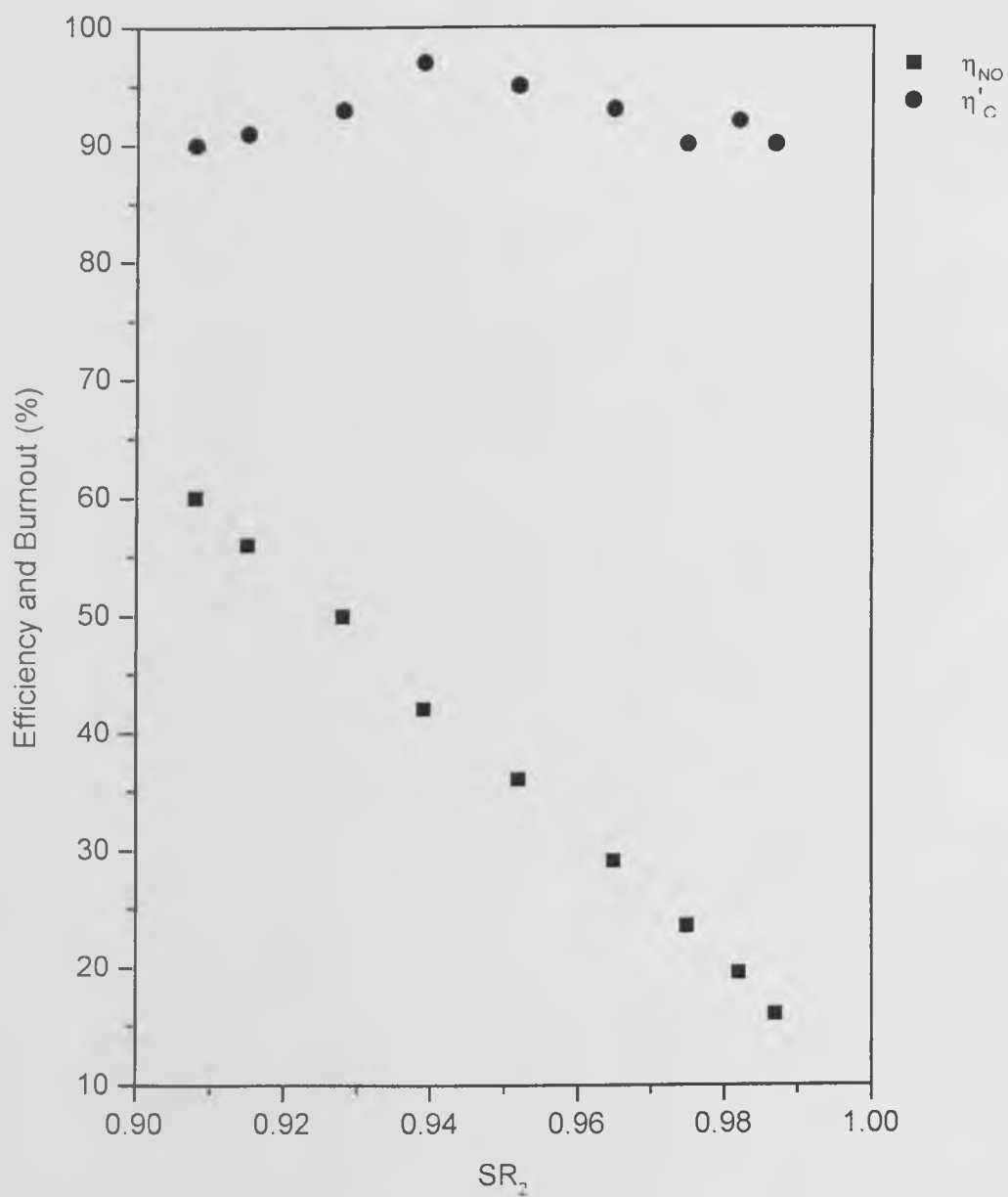


# APPENDIX D

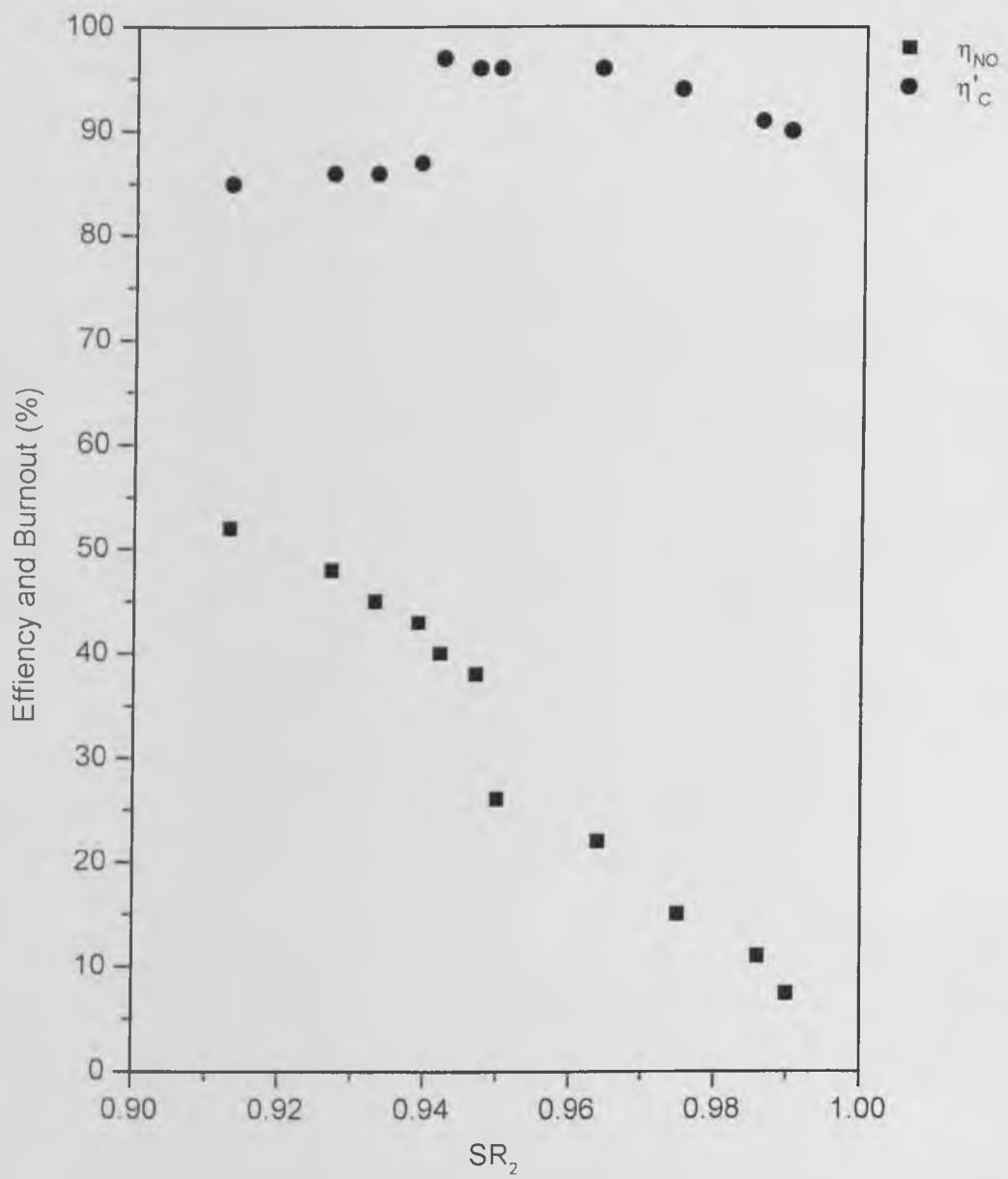
Figures D1 - D9



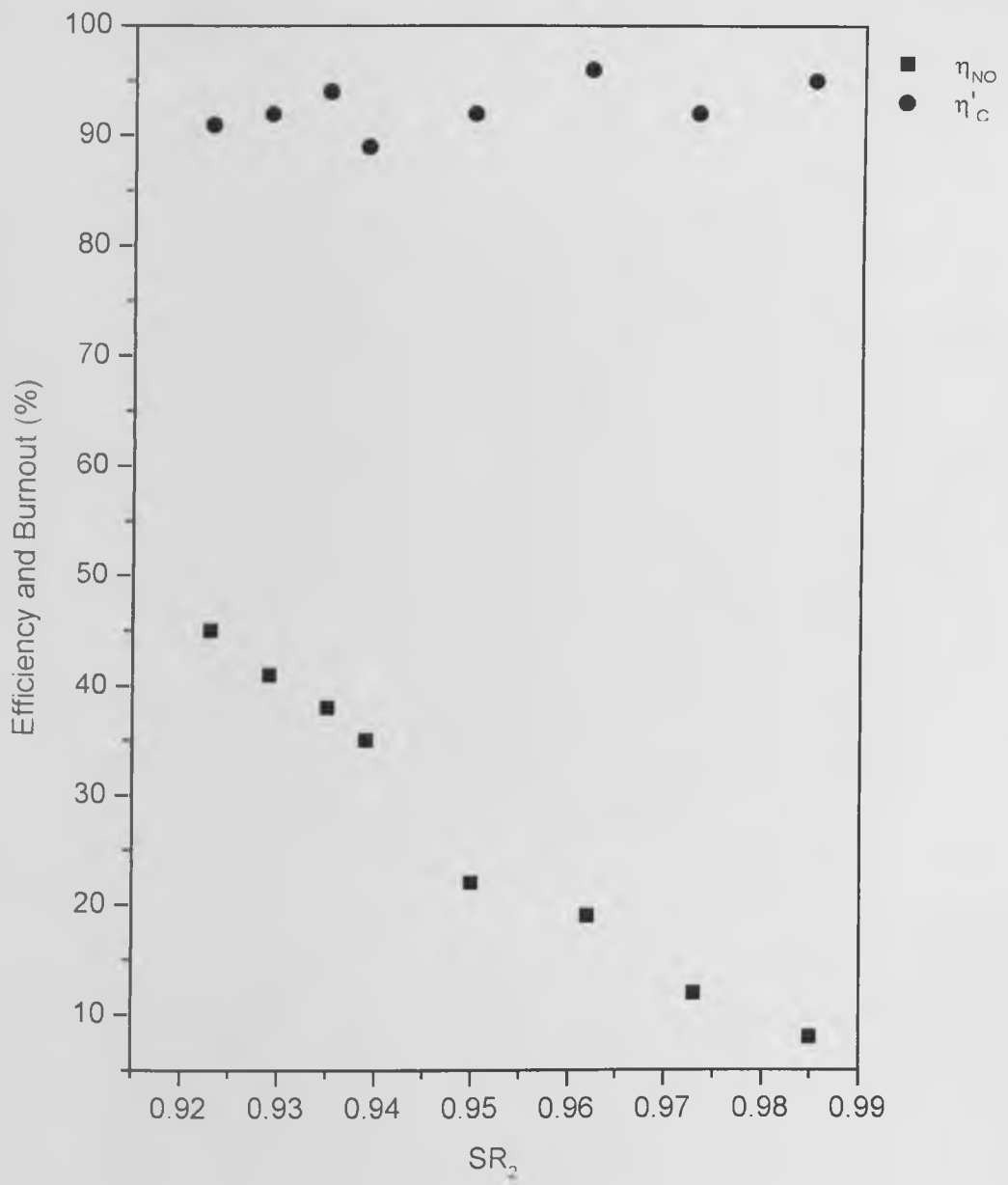
**Figure D1** NO reduction and carbon burnout efficiencies  
 Pittsburgh No 8.,  $R_{ff}=19\%$ ,  $SR_1=1.03$ ,  $SR_3=1.065$ ,  $T_p=1573$  K



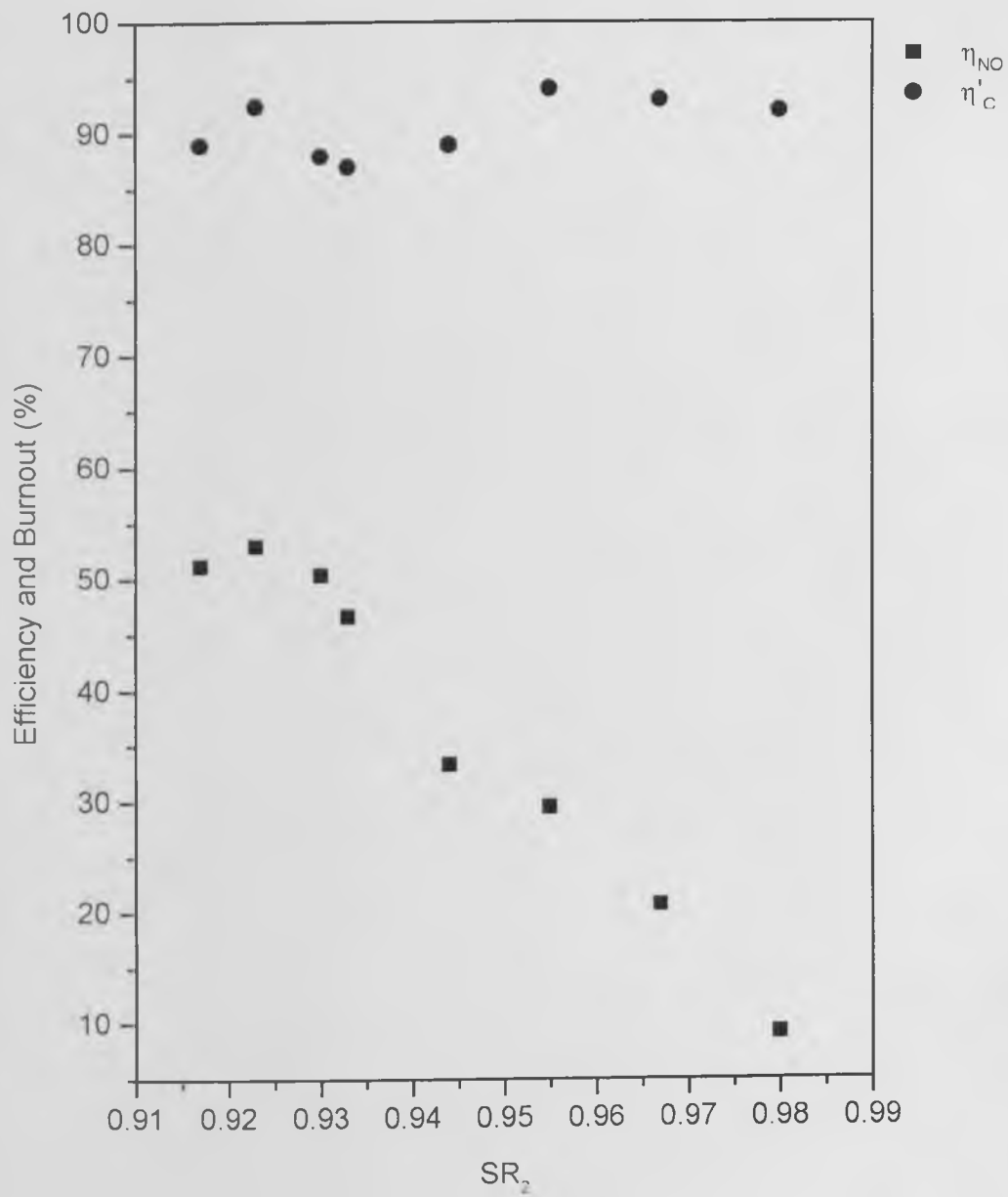
**Figure D2** NO reduction and carbon burnout efficiencies  
 Thoresby, Rff=19%, SR1=1.03, SR3=1.065, T<sub>pr</sub>=1573 K



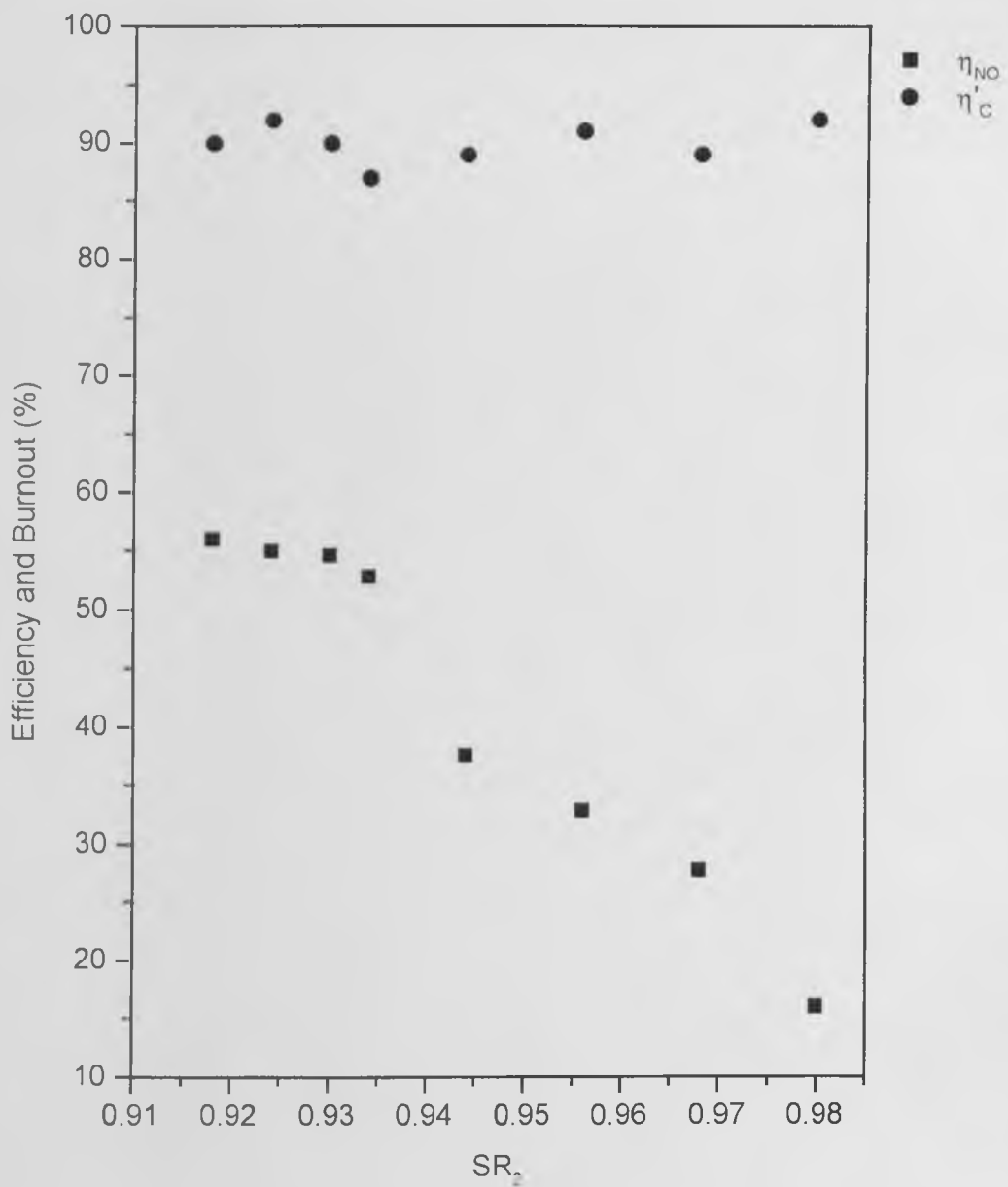
**Figure D3** NO reduction and burnout efficiencies  
 Gascoigne Wood, Rff=19%, SR1=1.03, SR3=1.06, T<sub>pr</sub>=1573 K



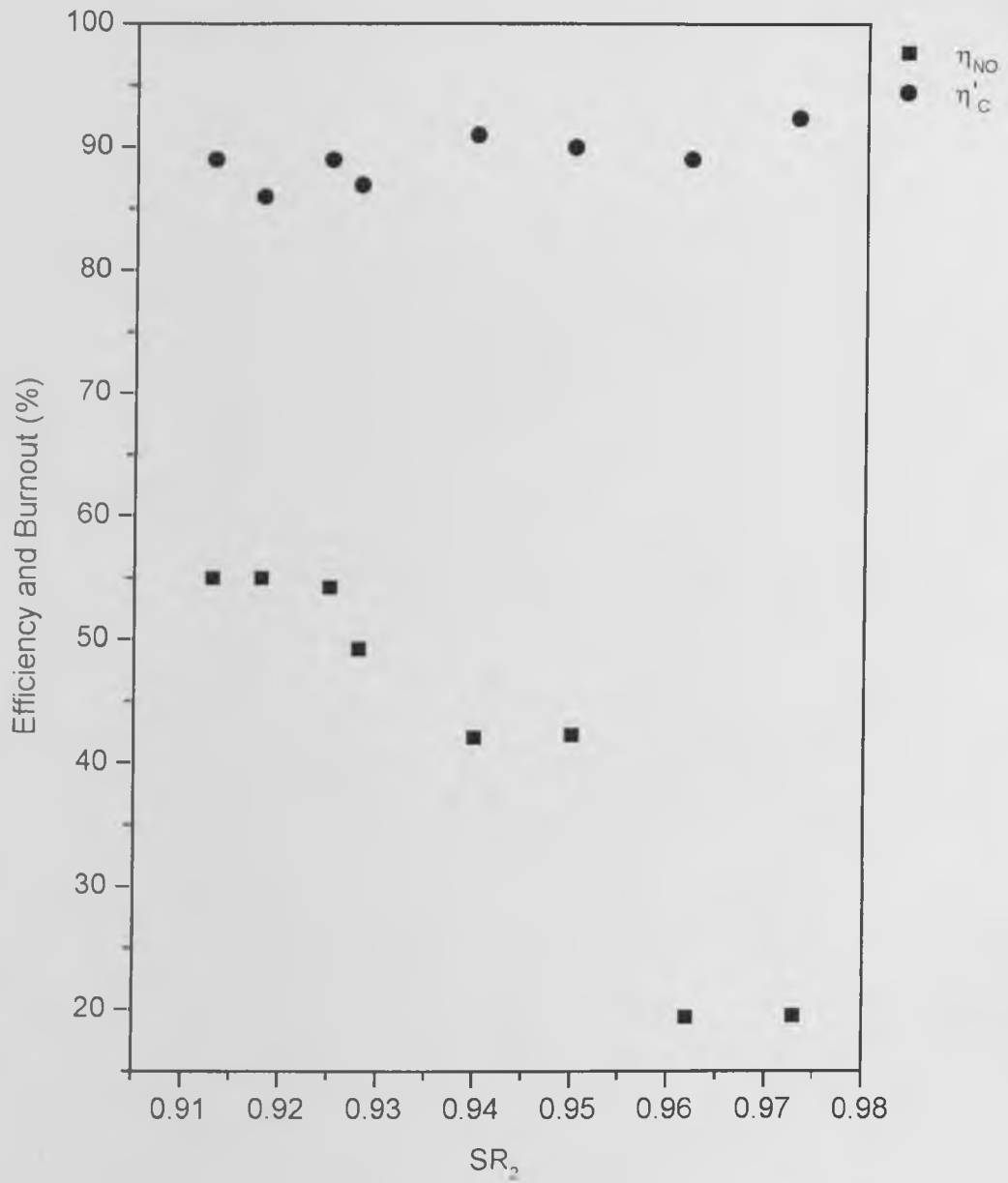
**Figure D4** NO reduction and carbon burnout efficiencies  
 Koonfonteine, Rff=19%, SR1=1.03, SR3=1.10,  $T_{pr} = 1573$  K



**Figure D5** NO reduction and carbon burnout efficiencies  
 Hunters Valley, Rff=19%, SR1=1.03, SR3=1.09, T<sub>pr</sub>=1573 K



**Figure D6** NO reduction and carbon burnout efficiencies  
 La Jagua, Rff=19%,  $SR_1=1.03$ ,  $SR_3=1.075$ ,  $T_{pr}=1573$  K



**Figure D7** NO reduction and carbon burnout efficiencies  
 Betts Lane, Rff=19%, SR1=1.03, SR3=1.07,  $T_{pr}=1573$  K



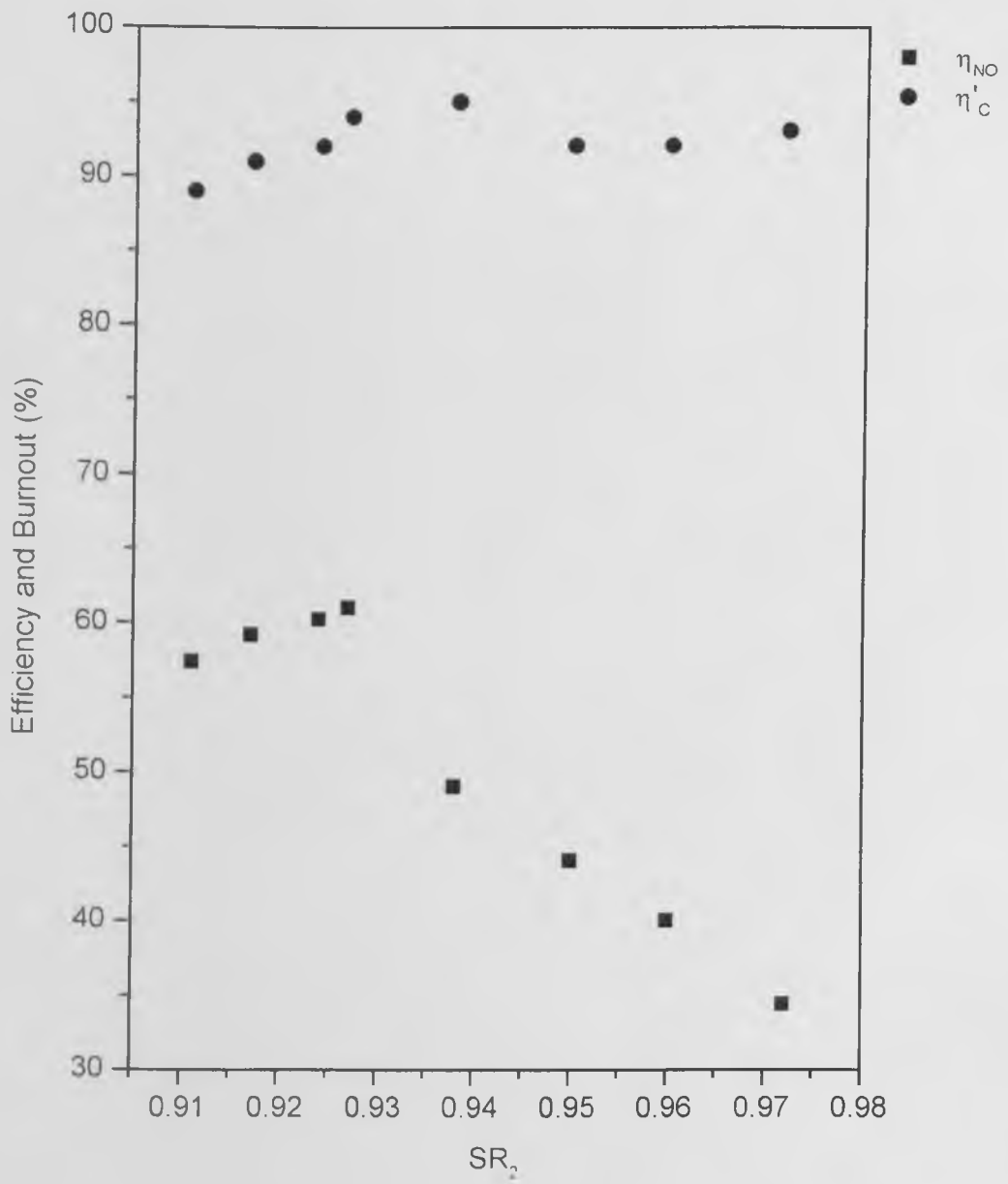
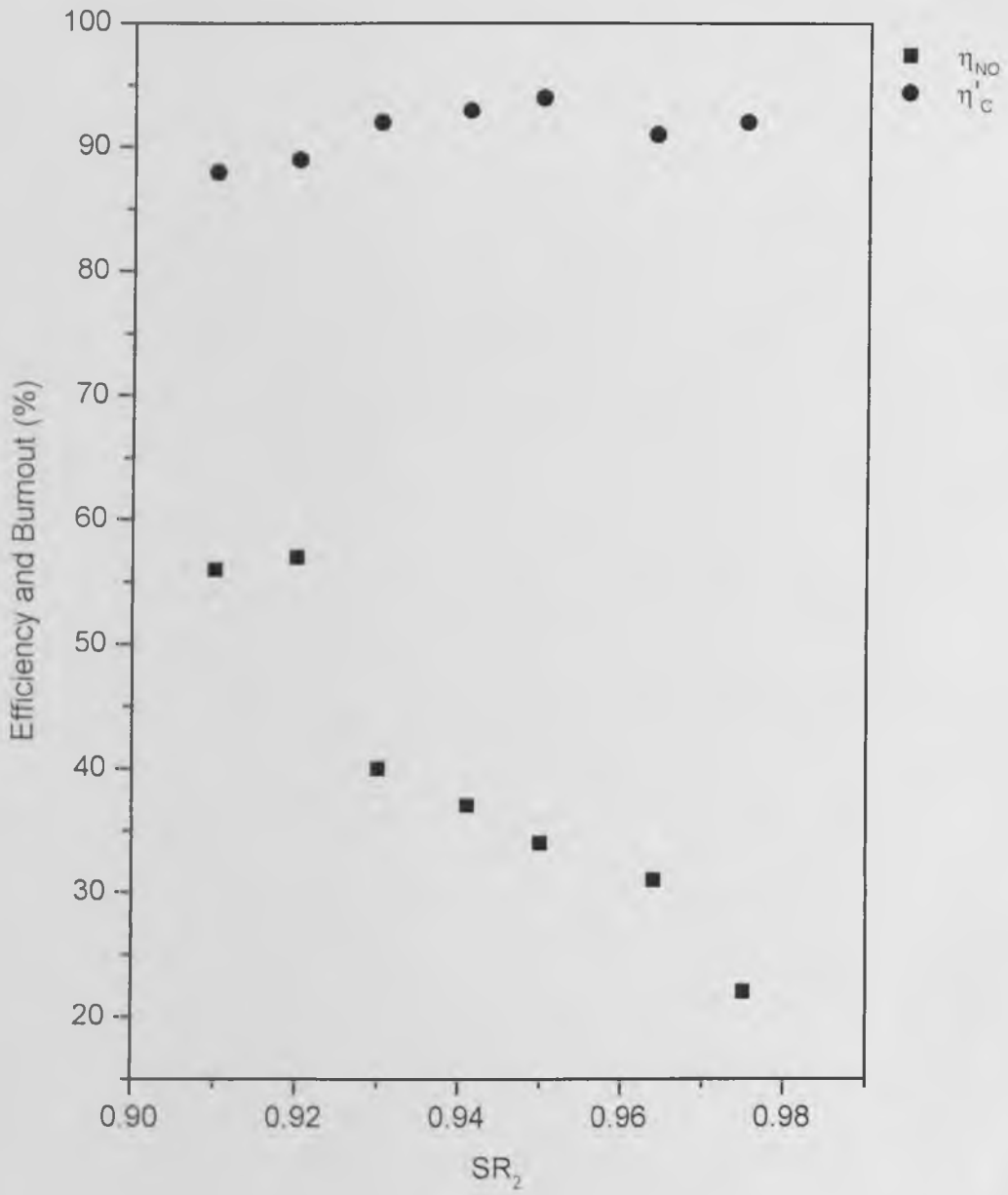


Figure D8 NO reduction and carbon burnout efficiencies  
 Asfordby, Rff=19%, SR1=1.03, SR3=1.07,  $T_p=1573$  K



**Figure D9** NO reduction and carbon burnout efficiencies  
 South Brandon Blend, Rff=19%, SR1=1.03, SR3=1.09,  $T_{pr} = 1573$  K

# APPENDIX E

## Sources and Estimation of Error

### E.1 Coal Feeding System

Initially the coal feeding system presented a lot of difficulties in stabilising the coal feed rate which was fluctuating in the order of  $\pm 20\%$  for a typical feeding period. This was mainly due to the incorrect configuring of both the hardware and software factors of the system. The problem was later rectified and the coal feed rate could be controlled to within  $\pm 0.25-1\%$  of the set value. Proper calibration of the feeding system with coal type was also essential in maintaining constant feed rates.

### E.2 Rotameters

Based on manufacturers specification the variable area flowmeters used in this study had a typical accuracy of 2.5% of their full scale range. Fluctuations in air, nitrogen and propane supplies were very rare and seldom went un-noticed.

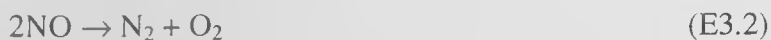
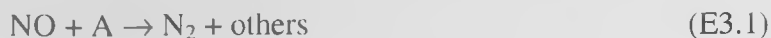
### E.3 Gas Analysis Instrumentation and NO Sampling

The measurements of NO, CO and O<sub>2</sub> were taken using standard instrumentation and gaseous concentrations recorded on a data logger where reading were averaged over a typical feeding period. The NO reading was estimated to the nearest 1 ppmv while the CO and O<sub>2</sub> measurements were averaged to the nearest 0.005% and 0.01% respectively. However, in order to achieve satisfactory analysis of the flue gases it is important to collect a representative sample and transfer it to the instrument without

reaction or any change in composition. This is normally done with the aid of a probe; in this case a water cooled stainless steel probe with rapid quenching effect. As the sample enters the probe the quenching process begins. Ideally, quenching should instantaneously arrest chemical reaction thus preserving the initial composition of the sample. Actually this process requires a finite time during which the sample may change from its initial composition. The slower the cooling the greater the alteration, provided the gas is capable of chemical reaction, and in the case of NO sampling the following problems may result in loss of sample concentration (Hampartsoumian, 1982):

i- Chemical Reactions in the Probe:

NO could be reduced or decomposed during sampling by the following reactions



where A may be CO, H<sub>2</sub>, hydrocarbons or nitrogenous volatile fragments. The above reactions can be controlled by a rapid reduction in gas temperature of the order of  $2 \times 10^6$  K/sec which are easily obtained by using water cooled probes (Heitor and Moriera, 1993).

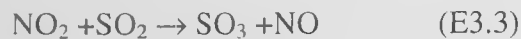
ii- Interaction with Solid Surfaces

Sample changes can also take place if the probe surface in contact with the gas has any catalytic effect. This action is particularly noticeable when sampling nitric oxide with stainless steel probe since the hot metal surface acts as a catalyst for NO

reduction (Hampartsoumian, 1982). NO can also be reduced in neutral atmosphere by hot carbon particles.

Catalytic surfaces can also influence the NO<sub>x</sub> measurements by their ability to convert NO<sub>2</sub> to NO. Since NO<sub>2</sub> is not stable at high temperature catalytic surfaces such as stainless steel can, at sufficiently high temperatures, accelerate the conversion of NO<sub>2</sub> to NO. The above process being the main mechanism by which NO<sub>2</sub> to NO converters operate.

When SO<sub>2</sub> is present from the combustion of sulphur-bearing fuels, it can react with NO<sub>2</sub> to form SO<sub>3</sub> and NO (Driscoll, 1975):



The kinetics of this reaction are rapid, but the reduction of NO<sub>2</sub> in flue gas sample by this reaction is slow since the concentrations of NO<sub>2</sub> and SO<sub>2</sub> are small. However, the rate of formation of NO by this reaction may well be faster than its rate of oxidation by O<sub>2</sub>.

### iii- Oxidation of NO to NO<sub>2</sub>

NO<sub>2</sub> can be formed in the sampling probe through the oxidation of NO by mainly HO<sub>2</sub> radicals during the rapid cooling process (Hori, 1986; Johnson *et al.*, 1972). The main root of NO<sub>2</sub> formation in the probe is



With increasing cooling rate of the sample,  $\text{NO}_2$  increases due to high  $\text{HO}_2$  concentration formed during the rapid cooling process. Oxygen present in the sample line can also oxidise NO. The longer residence time in probes also favours  $\text{NO}_2$  formation. This can be minimised by using short sample lines and ensuring that the sample spends as little time as possible travelling from the combustor to the analyser.

The oxidation of NO is very temperature sensitive and the kinetics of this reaction have been subjected to many studies (Baulch et al., 1973). The pooled experimental data from these studies suggested that it is a third order reaction with respect to NO although agreement has not been achieved concerning the data obtained:

$$-\frac{d(\text{NO})}{dt} = 2k[\text{NO}]^2[\text{O}_2] \quad (\text{E3.5})$$

where  $[\text{NO}]$  is the concentration of NO at any instant and  $[\text{O}_2]$  is the oxygen concentration. In the temperature range of 273 K to 650 K, the value of  $k$  is, according to the correlation  $k = 1.2 \times 10^{10} \exp(530/T)$  ( $\text{cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ ). Hampartsoumian (1982) used this information to estimate the extent of NO oxidation taking place during sampling. With these calculations the conversion of NO to  $\text{NO}_2$  was found to be almost negligible at 12% oxygen and 500 ppm NO which was the worst possible condition, the experimental residence time was determined as 20 - 40 seconds depending on sample gas flow rate.

#### E.4 Temperature Measurements

All the temperatures presented refer to uncorrected, sheathed, R-type thermocouples digital outputs. However, the temperature recorded by the thermocouple will not be the true temperature due to aerodynamics and thermal disturbances caused by the thermocouple when inserted into a combusting gas stream (Heitor and Moreira, 1993). This normally results in a false temperature reading.

The aerodynamic disturbances caused by the physical presence of the thermocouple can be minimised by using small diameter wires with small beaded construction. In this study, the thermocouples used were very small in diameter and thus offered very little disturbance to the aerodynamics of the gas. The predominant source of error, therefore, in thin thermometry was due to thermal losses; more specifically radiation and convection losses caused by the thermocouple acting as a heat sink and they are a function of the temperature difference between the stream and the device. To determine the degree of error an expression derived by Kaskan (1956) based on cylindrical geometry was used.

$$\Delta T_{\text{rad}} = \frac{1.25\epsilon\sigma D^{0.75}}{\lambda} \left[ \frac{\eta}{\rho v} \right]^{0.25} \quad (\text{E4.1})$$

where  $\epsilon$  is the bead emissivity,  $\sigma$  is the Stefan Boltzmann constant,  $D$  is the bead diameter,  $\lambda$  is the thermal conductivity,  $\eta$  is the viscosity at the wire temperature and  $\rho v$  is the mass flow. In this work  $D$  was taken as the diameter of the thermocouple wire. By using the aforementioned equation in a simple computer program, the

# APPENDIX F

## Particle Size Distribution of Reburn Coals

Size Analysis - % on sample by weight

Pittsburgh No. 8

Particle Diameter Range (mm)	Percentage by Weight (%)
+0.300	0.42
+0.212	0.34
+0.150	2.48
+0.090	21.20
+0.075	7.49
+0.063	6.08
- 0.063	61.95

Thoresby

Particle Diameter Range (mm)	Percentage by Weight (%)
+0.300	1.04
+0.212	1.09
+0.150	11.43
+0.125	8.55
+0.090	12.26
+0.075	0.15
+0.063	8.08
- 0.063	51.35

Koonfonteine

Particle Diameter Range (mm)	Percentage by Weight (%)
+0.300	0.56
+0.212	1.0
+0.150	6.3
+0.125	6.8
+0.090	12.2
+0.075	6.5
+0.063	7.3
- 0.063	59.2



La Jagua

Particle Diameter Range (mm)	Percentage by Weight (%)
+0.300	0.68
+0.212	1.07
+0.150	3.39
+0.125	3.68
+0.090	13.68
+0.075	6.69
+0.063	8.43
- 0.063	62.21

Hunters Valley

Particle Diameter Range (mm)	Percentage by Weight (%)
+0.300	1.4
+0.212	1.2
+0.150	4.6
+0.125	5.9
+0.090	11.5
+0.075	6.0
+0.063	6.8
- 0.063	62.7

Betts Lane

Particle Diameter Range (mm)	Percentage by Weight (%)
+0.300	0.7
+0.212	1.1
+0.150	3.0
+0.125	3.3
+0.090	7.0
+0.075	4.5
+0.063	5.8
- 0.063	74.5

Asfordby

Particle Diameter Range (mm)	Percentage by Weight (%)
+0.300	0.1
+0.212	1.6
+0.150	7.0
+0.125	6.5
+0.090	10.7
+0.075	6.6
+0.063	7.6
- 0.063	59.9

Gascoigne Wood

Particle Diameter Range (mm)	Percentage by Weight (%)
+0.300	0.05
+0.250	0.23
+0.212	0.86
+0.150	4.92
+0.106	12.03
+0.075	15.89
+0.038	27.14
- 0.038	38.89

South Brandon

Dry Sieving

Particle Diameter Range (mm)	% Passing Through
0.300	98.6
0.150	91.8
0.750	73.1

Wet Sieving

Particle Diameter Range (mm)	% Passing Through
0.075	78.4

## Papers Published During this Study

Optimisation of Operating Parameters for NO Reduction by Coal Reburning in a 0.2 MWt Furnace. Yang Y.B., Naja T.A., Gibbs B.M. and Hampartsoumian E. Journal of the Institute of Energy, March 1997.

An Investigation of NO Reduction by Coal Reburning in an Experimental Furnace. Yang Y.B., Naja T.A., Gibbs B.M. and Hampartsoumian E. The 4th European Conference on Industrial Furnaces and Boilers, April 1997.