Abstract

This report discusses the development of modelling and prediction methods for estimating and minimising the level of NOx production during the combustion of pulverised coal. Current approaches include the use of computational fluid dynamics (CFD), kinetic and chemical engineering models, quantitative and empirical relationships and artificial intelligence methods. Applications of the CFD-based modelling approaches for designing new plants or modifying existing ones as well as for the simulation of pilot-scale burners and full-scale boilers are detailed. The current capabilities and limitations of CFD for accurately predicting levels of NOx production during coal combustion are also discussed.
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Legislation to control emissions from coal-fired plants is in place in many parts of the world. The 1990 US Clean Air Act Amendments (CAA) and similar legislations imposed by the EC, such as the 1988 Large Combustion Plant Directive (LCPD), have created a market of opportunity for commercially viable technologies for reducing pollutant emissions especially nitrogen oxides (NOx) and sulphur dioxide (SO2). NOx and SO2 lead to the formation of acid rain by reacting with water vapour in the atmosphere to produce nitric acid and sulphuric acid compounds. NOx also contributes to the formation of tropospheric (that is ground level) ozone. Ozone and acidic deposition have been blamed for photochemical smog formation, damage to the aquatic ecosystems, forests, structural materials, visibility and health. NOx legislation varies from country to country. For example, in the UK emission standards lie in the range of 200 mg/m3 (98 ppm) and 650 mg/m3 (317 ppm) for utility plants (>50 MWt) in operation after 1995 and those in operation before 1987 respectively. On the other hand, in the US emission standards lie in the range of 185 mg/m3 (90 ppm) and 220 mg/m3 (107 ppm) for utility plants (>73 MWt) reconstructed or modified since 1997 and those which were constructed in 1997 respectively. The emission standard for a typical >29 MWt utility plant constructed after 1997 is 246 g/m3 (120 ppm). More details for the emission standards of other countries may be obtained from an earlier report by Soud and Fukasawa (1996) and from the Clean Coal Compendium website (http://www.iea-coal.org.uk).

In chemical terms, NOx should constitute all the possible oxides of nitrogen, including nitric oxide (NO), nitrogen dioxide (NO2) and nitrous oxide (N2O). However NOx as conventionally described by the United States National Ambient Air Quality Standards is generally defined as NO and NO2 (Davidson, 1994). NO is the main contributor of NOx during pulverised coal combustion whilst NO2 is of secondary importance. In this report only NO and NO2 are considered.

In order to understand and hence control emissions from coal combustion plants it is necessary to be able to model carbon monoxide (CO), unburnt hydrocarbons (UHCs), sulphur oxides (SOx), nitrogen oxides (NOx) and particulates. The most difficult one to model is NOx. There are three different reaction mechanisms for NOx formation. NOx formation is also influenced by a number of parameters, such as coal quality, boiler type, temperature amongst others. These will be discussed in Chapter 3.

Most computational fluid dynamics (CFD) modelling work of pulverised coal combustion is concerned with the prediction of NOx. CFD is the method by which fluid flows and other coupled equations are mathematically solved. CFD is founded on fundamental physical principles, and can thus predict fluid flow (for gases, liquids and entrained solids such as coal particles) and heat transfer properties within boilers under virtually any conditions. The mathematical equations governing fluid flows and turbulence will be described in Chapter 4. CFD has been developed to such an extent that numerical models can be used to examine the flows in any part of a power plant. The most powerful of the modelling methods are those based on 3-D CFD. According to King and others (1996), the application of CFD to power generation systems has the capability of tackling a wide range of technical and economic issues within a power plant. Furthermore, numerical modelling may be used to assess the impact of alternative design and operating conditions on boiler performance and efficiency.

With the addition of turbulence and combustion in the submodels, these methods also provide a full representation of chemically reacting flows throughout the furnace. Hence, the combustion air, burner, fuel handling, heat exchanger and flue gas cleaning systems can be all analysed in greater depths. Mathematical models of flames and furnaces have proved to be very useful in understanding the complex correlations between flame characteristics and pollutant formation pathways (Schnell and others, 1993). Applications of CFD modelling for plant designs and as a predictive tool for pollutant emissions will be discussed in Chapter 5.

More recently, neural networks and artificial intelligence have been used for NOx predictions, but also for plant optimisation and emission control. However, this will not be covered in this report. Details on the use of artificial intelligence and neural networks have been recently reported by Soud (1999).
2 NOx formation and control

NOx is a by-product of coal combustion and originates both from the coal-bound nitrogen and the nitrogen from the air, used in the firing process. According to Fiveland and Wessel (1991), reduced emissions of NOx can be accomplished most economically by control of their formation and reduction processes in the combustion system, instead of removal from the stack gases, such as in the case of SOx. In this chapter, NOx formation and control technologies are discussed.

There are three formation mechanisms of NOx which can be described as follows:

- **Thermal NOx** – reaction between oxygen and nitrogen in the combustion air at temperatures >1300°C in oxidising atmospheres; dependent on flame temperature and residence time at high temperatures; predominantly formed in the flame envelope;
- **Fuel NOx** – oxidation of coal-bound nitrogen compounds at temperatures >750°C; dependent on nitrogen content of coal, the amount of nitrogen evolved at high temperatures during devolatilisation and burner design. The burner design affects the rate of mixing between combustion air and the volatile nitrogen. This in turn affects the degree of conversion of volatile nitrogen to NOx;
- **Prompt NOx** – fixation of atmospheric (molecular) nitrogen by hydrocarbon fragments in reducing atmospheres; formed in the early part of all coal flames, in the ignition region.

These mechanisms have been discussed in greater detail in an earlier report by Mitchell (1998) and will be briefly discussed in Section 2.1. Fuel-bound nitrogen often accounts for over 75% and sometimes as much as 95% of the total NOx emitted during pulverised coal combustion, depending on whether primary NOx reduction technologies are implemented as well as on the properties of the coal used. The contribution of fuel and thermal NOx to the total NOx emission can be in the order of 80% fuel and 20% thermal for a bituminous coal with high nitrogen content. It has been claimed that prompt and thermal mechanisms account for the remaining 5–25% with prompt responsible for no more than 5% of the total NOx generated (Hesselmann, 1997).

**Fuel NOx** can be further classified into two groups: volatile and char nitrogen. Volatile nitrogen is given off during devolatilisation of the coal particles and char nitrogen is the residual nitrogen remaining in the char-mineral matter matrix following devolatilisation.

Overall, NOx is formed via two pathways:

- conversion of HCN in the gaseous phase;
- heterogeneous conversion of nitrogen in char and soot.

The reaction chemistry of NOx formation and the effects of coal properties, furnace designs and combustion conditions will be briefly discussed in this chapter. Further details on the effects of coal quality on NOx formation have been recently reported by Davidson (2000).

2.1 Reaction chemistry of NOx formation and reduction

The reactions leading to the formation of thermal, fuel and prompt NOx will be discussed in the following sections. As a result of the complexity of nitrogen chemistry some of these reactions lead to the destruction of NOx and are thus important in practical NOx reduction techniques such as staged burners and reburn.

2.1.1 Formation of thermal NOx

Thermal NOx is produced via a series of oxidation reactions, known as the ‘Zeldovich mechanism’. This is shown in equations 1 and 2. Although most literature still raise doubts on the temperature at which this oxidation takes place, the oxidation proceeds almost exponentially with increase in peak flame temperature. All power generation boiler flames from whatever burner system operating at the required combustion conditions and efficiency may be deemed to achieve peak temperatures at or above the base required for the nitrogen and oxygen to react (that is, thermal NOx production).

\[
\begin{align*}
N_2 + O & \rightarrow NO + N \quad (1) \\
O_2 + N & \rightarrow NO + O \quad (2)
\end{align*}
\]

In a fuel-rich environment, the reactions change slightly as follows:

\[
N + OH \rightarrow NO + H \quad (3)
\]

2.1.2 Formation of fuel NOx

A number of investigators have proposed various pathways and mechanisms for the formation of fuel-NOx. Nelson and others (1992) and Kambara and others (1993) have identified HCN as the primary volatile nitrogen component from coal devolatilisation above 1300 K. Niksa and Cho (1996), for instance, have suggested that fuel nitrogen is first liberated during the primary devolatilisation as tars (consisting of heavy aromatic hydrocarbons) in the primary coal flames. Additional fuel nitrogen is released from the char as HCN and sometimes as NH₃, on time scales that are considerably longer than those for tar formation. At the same time, the volatiles undergo secondary reactions in the hot, fuel-rich gaseous phase which converts the nitrogen contained in the tar into HCN. Some of the tar is consequently converted into soot. The char and soot formed are then oxidised and hence liberate additional nitrogen by chemical conversion to NO or by thermal dissociation induced at higher temperatures associated with char combustion.

The situation with fuel NOx formation remains less clear.
than its thermal counterpart. Numerous chemical reaction routes have been proposed which postulate that a series of intermediates such as CN, CNO and NH radicals and compounds are produced from fuel nitrogen which can then form gaseous nitrogen or NOx depending on the availability of oxygen. The structure of the fuel nitrogen is of particular importance (Visona and Stanmore, 1999b), since it governs the way in which the fuel nitrogen molecular bonds break and form volatile nitrogen radicals. Once the nitrogen species are in the gaseous phase, homogeneous reactions govern the net reaction rate of NOx formation.

De Soete mechanism

The De Soete (1975) reaction has often been used as the key reaction for NOx formation. De Soete used a flat premixed hydrocarbon/cyanogen (C2N2)/oxygen/argon or helium flame to determine the global overall formation rates of NO and N2 by adding small amounts of nitrogen compounds, such as NH3 or NO. Samples of the HCN, NO, NO2 formed were taken along the axial centre line of the burner. By adding cyanogen to ethylene/oxygen/argon flames, rate equations were obtained for the formation of NO and N2 via HCN. Further experiments were carried out with methane/oxygen/helium flame and the global reaction rates of the NH3/NO/O2 system were determined. An expression for determining the concentration of prompt NOx was obtained from the ethylene mixture. The author claimed that 90% of prompt NO was produced via HCN. Oxidation of HCN would then produce NO. A typical reaction route proposed by De Soete may be seen in the following reaction:

\[
\text{HCN} + \text{O}_2 \rightarrow \text{NO} + \ldots
\]  

Moreover, it was claimed that atomic N played an important part in the formation of NOx (De Soete, 1975). Nevertheless, the formation of atomic N was very difficult to determine at the time. Another alternative route for the formation of NO and eventually N2, was via the hypothetical intermediate ‘XN’, if the latter ever existed at all.

Visona Stanmore NOx model

The reaction scheme in Figure 1(a) known as the Visona Stanmore NOx model, (Visona and Stanmore, 1995) also describes the formation of thermal NOx. This model has been used for the modelling of various furnaces such as drop tube furnaces, pilot-scale furnaces and full-scale furnaces (Visona, 1997). According to Visona, computed exit NOx values were within 15% of the measured value.

This model was run for three levels of gas-phase nitrogen chemistry: a base-line study in which the effect of ammonia and hydrocarbons were neglected (De Soete mechanism), a study in which ammonia was added and correlations relating the ratio of HCN to NH3 (Kambara and others, 1993) from the functional forms of nitrogen in the coal and finally a study which includes the effect of hydrocarbon reburn.

It should be noted that a simplified De Soete reaction mechanism for the formation of NOx and HCN works as well as the model proposed by Visona, for higher rank coals. However, the De Soete mechanism is inadequate for lower rank coals, during which NH3 release is more significant (Chen and others, 1982b).

Schnell model

Schnell and others (1991) proposed a fuel-NOx reaction model during which the fuel-bound nitrogen is released in two separate stages, as seen in Figure 1(b). Experimental evidence showed that it was safe to assume that a relatively high portion was devolatilised as HCN, with a rate proportional to the release of volatiles. According to Schnell the fate of the HCN and the intermediate nitrogenous species is dependent on flame conditions, particularly on stoichiometry and temperature.

The model proposed by Schnell and others (1991) was later elaborated by Förtsch and others (1997, 1998) to a more advanced NOx model for staged combustion of pulverised coal, as shown in Figure 1(c). The model includes primary pyrolysis and secondary reactions of tars formed during primary pyrolysis. This model accounts for the different pathways of coal nitrogen release during primary and secondary pyrolysis, as well as the combustion of char and soot. The subsequent conversions of nitrogen-containing species include the formation of fuel and thermal NO, as well as the reduction of NO by hydrocarbon and NH radicals, char and soot. According to the authors, modelling of coal combustion can be based on the assumption that the conversion of coal can be divided into three steps: pyrolysis of the raw coal, combustion of volatiles and char burnout. Pyrolysis on the other hand, may be regarded as a two-stage process: during primary pyrolysis volatiles are released during coal decomposition. These volatiles subsequently undergo secondary pyrolysis.

Simplified NOx formation routes

Figure 1(d) shows a simplified reaction route for the formation of NO, as suggested by Chui and Hughes (1996), based on the findings of Miller and others (1984) and Wendt (1993), with some modifications. According to Chui and Hughes (1996), this pathway has been considerably simplified and is meant to provide an approximation of the NOx chemistry in coal flames.

Reaction paths 1 to 8 represents the major steps of the conversion of coal bound N to NO.

NO formation from char-bound nitrogen

According to Visona and Stanmore (1997, 1999b), the NO formed in the first step can undergo chemisorption of fuel nitrogen on the char surface and subsequently be reduced to N2. Therefore, char N to NO conversions tend to have efficiencies below 100% and typically 40% in a full-scale boiler. This is particularly relevant for the design of low NOx burners (LNBs), which are effective in the reduction of volatile nitrogen species but not for char nitrogen. The char nitrogen tends to be released outside the fuel-rich zones of the flames and thus outside the NOx reducing atmosphere of the burner.

Wang and others (1994) have suggested that the nitrogen in the coal is partitioned between the volatiles and char such that its concentration in volatiles is identical to that in the dry.
ash-free parent coal. The volatile nitrogen is lost as either HCN or NH₃, which may be secondary products from the pyrolysis of primary tar. These products enter homogeneous gas phase reactions as follows:

\[ \text{HCN} + \text{O}_2 \rightarrow \text{NO} + \text{O} \quad (\text{De Soete, 1975}) \quad (5) \]

Alternatively the following may also take place. The NH radical formed is representative of ammonia:

\[ \text{HCN} + \text{O}_2 \rightarrow \text{NO} + \text{O} + \text{H} \quad (\text{De Soete, 1975}) \]

Figure 1  Comparison of reaction schemes of full NOx formation and destruction
2.1.3 Formation of prompt NOx

This form of NOx occurs in fuel-rich environments, whereby, hydrocarbon radicals (mostly CH) react with atmospheric nitrogen. This is common in natural gas combustion, in which large concentrations of CH radicals are present. However, the formation of large concentrations of CH radicals is less likely in coal flames, and their formation may be more concentrated in 'hot spots'. This might explain the low concentrations of prompt NOx in pulverised coal combustion. Prompt NOx is inferred rather than determined. The CH radicals are more likely to be quenched before they leave the vicinity of the coal particles.

\[
\text{CH} + \text{N}_2 \leftrightarrow \text{HCN} + \text{N} \quad (9)
\]

\[
\text{HCN} + \text{O} \leftrightarrow \text{NH} + \text{CO} \quad (10)
\]

\[
\text{NH} + \text{O} \leftrightarrow \text{NO} + \text{H} \quad (11)
\]

According to De Soete (1975), HCN seems to play a more important role in the formation mechanism of prompt NOx. This was shown, according to De Soete, by comparing the experimental values of total prompt NO concentrations with values calculated by numerical integration of a mathematical expression, in which all NO formation is through HCN as intermediate.

However, prompt NOx may be negligible during pulverised coal combustion, and its formation is probably localised at ‘hot spots’ in the boiler. A quoted value of 5% is, most probably, more relevant to natural gas combustion, during which no fuel NOx occurs. Hydrocarbon (HC) radical interception of atmospheric N\(_2\) at elevated temperatures is less likely in coal flames, because HC radicals in these tend to be more dispersed.

2.1.4 NOx reduction: reaction chemistry of reburning mechanisms

Typical reburn fuels include natural gas and pulverised coal. Advanced reburning technology makes use of natural gas injection followed by coal or a combination of these (Xu and others, 1998). Pilot-scale experiments with lignites or medium volatiles coals as reburn fuel have shown similar NO reductions to that obtained during gas reburn. Hesselmann and Chakraborty (1998) proposed that, despite the high effectiveness of natural gas as reburn fuel, the use of coal as reburn fuel is more economical. This is due to the fact that it would be necessary to install a dedicated gas supply pipeline. This could add considerably to the cost of the reburn retrofit in a pulverised coal utility plant. Figure 2 shows a schematic diagram of the coal over coal reburn process. Moreover, biomass or sewage sludge (Storm and others, 1999) as well
as the use of non-hydrocarbon fuels such as CO or H₂ (Glarborg and others, 1999) may be used as reburn fuel for NOx reduction, although the latter case was studied predominantly for biomass fuels.

The reburning-NO mechanism is important in an atmosphere rich in hydrocarbon radicals. Coal combustion normally occurs in diffused flames where combustion gases are released from coal and then mix with the oxygen in the bulk stream. In regions rich in hydrocarbon radicals, the reburning-NO mechanism becomes significant.

### Chemical pathways

During hydrocarbon reburning, the NO formed is reduced to HCN as will be seen in reactions 12 to 13 (Bartok and Sarofim, 1991):

\[
\begin{align*}
\text{CH} + \text{NO} & \rightarrow \text{HCN} + \text{O} \quad (12) \\
\text{CH}_3 + \text{NO} & \rightarrow \text{HCN} + \text{H}_2\text{O} \quad (13)
\end{align*}
\]

Moreover, Xu and others (1999a) undertook the modelling of NOx emissions during staged combustion. The key reactions for NO formation and reduction used for this study were as follows:

**NO formation:**

\[
\text{HCN} + \text{O} \rightarrow \text{NCO} + \text{H} \quad (14)
\]

**NO destruction:**

\[
\begin{align*}
\text{CH}_2 + \text{NO} & \rightarrow \text{HCNO} + \text{H} \quad (15) \\
\text{HCNO} + \text{H} & \rightarrow \text{HCN} + \text{OH} \quad (16)
\end{align*}
\]

NO formation is hindered as seen from reaction 14, owing to the lack of oxygen. An excess of fuel promotes the formation of CH radicals, which thus reduces NO to HCN. Hence NO concentration will decrease significantly, if the concentrations of CH₂ and HCNO increase.

### NOx destruction via coal over coal reburn

In general, bituminous coals are expected to be effective reburn fuels (Hampartsoumian and others, 1995). High volatile and reactive coals have been found to be the most effective reburn fuels for high NO reduction. Low-reactive coals, such as anthracite and semi-anthracite, needed higher reburning zone temperatures as well as longer residence times. Moyeda and others (1995) suggested that low-rank coals had higher NOx reduction performance, which was influenced by the nitrogen and volatile matter content, whereas these parameters did not seem to affect the performance of high-rank coals. Fuel-N content of the reburn fuel is not necessarily an important parameter for maximising NO reduction in the reburn zone (Yang and others, 1997). Therefore coals with high nitrogen content may not necessarily lead to poor NO reduction efficiency. In fact NO might be formed in the burnout zone, if these coals produce high N-char.

The most promising combinations for reburning systems are low or high volatile coal as the primary fuel, and a high volatile, highly reactive coal as the reburn fuel. However, the quality of the primary coal has the greatest impact on the overall NOx (Azvedo and others, 1999). The results obtained by Yang and others (1998) also suggested that high volatile yields as well as high rates of devolatilisation increased the overall NO reduction during coal reburn. Faster devolatilisation entails the earlier release of volatile gases into the surrounding primary NO-laden stream provided that the reburn stoichiometry is sufficiently oxygen lean to deter the early oxidation of volatile gases (Yang and others, 1998). Typical quantities of >10 % reburn fuel fractions were required for effective NOx reduction in combination with a primary zone stoichiometry of ≈0.9 (Morgan and others, 1998) in a semi-industrial scale furnace. NOx reductions of >77% were achieved.

### NOx reduction on char surfaces

The heterogeneous reaction of NO and coal char has the potential of being a reburning and post combustion clean-up process to reduce NOx emissions during pulverised coal combustion. This reaction is also important in understanding the formation and reduction of NO during combustion (Guo and Hecker, 1998). The kinetics of NO reduction by chars were studied from five US standard research coals, ranging from lignites to low-volatile bituminous, as well as graphite and coconut chars. The reduction of NO by char was seen to be first order with respect to NO partial pressure for all chars studied. All chars were also shown to cause a shift in the activation energies for NO reduction. However, this shift was seen to increase with increasing coal rank. Thus the low-rank coals were considerably more reactive than the high rank ones; graphite was the least reactive. Similar observations were made by Moyeda and others (1995), who also suggested that char reactivity depended both on char surface area as well as mineral matter content (that is, CaO content).

However, heterogeneous NOx reduction mechanisms by char for pulverised coal flames may not be as effective as the gas phase reduction mechanisms (Visona and Stanmore, 1999b).

#### 2.1.5 Chemical kinetics

Detailed chemical kinetics of NOx formation and destruction have been studied by various investigators such as Miller and Bowman (1989) as well as Peck and others (1991). In computer modelling, however, it would be impractical to include all these elementary chemical kinetic schemes, together with turbulent fluid dynamics, heat transfer and chemical reactions due to computational constraints. Moreover, the formation and destruction rates of NOx are of the same magnitude as turbulent mixing rates, and thus the equilibrium assumption is not adequate in the calculation of NOx concentrations (Chen and others, 1996b). The rate of formation is the sum of the rates of the NOx formation/destruction (reversible) reactions. However, it is assumed that N₂ and O₂ are in equilibrium concentrations, the N atom concentration is at steady state and the O atom concentration is at partial equilibrium. For instance the rate of thermal NO formation is as follows (Visona and Stanmore, 1998a):

\[
\frac{d[NO]}{dt} = \frac{2[O](k_1k_2[O_2][N_2] - k_1k_2[NO]^2)}{k_2[O] + k_1[NO]} \quad (17)
\]
2.2 NOx abatement and control technologies

Over the years pressure has been increased on plant operators to improve thermal efficiency, reduce costs (for example by burning cheaper imported coals), reduce pollutant emissions (especially with increasingly stringent environmental legislation), whilst maintaining safe operating conditions. Hence, the application of one (or more) of a range of NOx reduction technologies appropriate to the legislative requirements of the different countries has become a necessity. However the relationships between all these conditions are complicated, as follows:

- using hot flue gases to pre-heat the combustion air increases thermal efficiency but the hotter flame may also increase NOx emissions;
- firing with lower excess air increases the efficiency and reduces NOx emission levels, but increases unburnt carbon levels and carbon in ash. Furthermore, reducing excess air levels may cause the flame to become unstable and thus could entail severe safety hazards;
- burning cheaper fuels has a direct impact on reducing costs and improving plant economics, but may increase pollutant emission levels.

Thus in view of:

- increasing need to alter and improve plant design, for example, the capital intensive retrofitting of low-NOx burners and flue gas clean-up; and
- new designs having to guarantee to meet increasingly stringent requirements;

more and more investments are being made in the development, application and validation of mathematical modelling. Although these investments can be costly, and often require the help of software experts, the costs are relatively small compared to full-scale plant trials. Furthermore, results can be obtained in a relatively shorter time.

Developers and manufactures of computer modelling software aim to demonstrate the capabilities of modelling and thereby convince industry that these methods are reliable and accurate for problem solving, plant designing and evaluating retrofits. NOx control and abatement technologies have been extensively discussed in an earlier report by Soud and Fukasawa (1996). There are two categories of NOx reduction technologies: combustion modifications and post combustion processes, which are briefly described as follows:

**Combustion modifications**

**Low-NOx burners (LNBs)** – designed to control the mixing of fuel and air, to achieve staged combustion. This lowers the maximum flame temperature and reduces oxygen concentration, thereby lowering thermal and fuel NOx.

**Overfire air (OFA)** – process during which air is injected above the normal combustion zone, to ensure complete combustion, during air-staging, where lower air to fuel ratios are used to ensure low-NOx formation.

**Reburn** – process whereby natural gas or pulverised coal is injected in the coal flame to produce a reducing environment.

It is a well established technique, based on laboratory-scale studies in the early 1970s by Wendt and Strenling of Shell Development Company, which is widely used in pilot-scale and in full-scale furnaces (Østberg and others, 1998). There are typically three zones in the furnace in reburn:

- a combustion zone with lower air to fuel ratios;
- a reburn zone;
- OFA, which is injected above the reburn zone to ensure complete combustion.

**Flue Gas Recirculation (FGR)** – during which part of the flue gas is recirculated in the furnace to modify conditions in the combustion zone, by lowering the temperature and reducing oxygen concentration, to achieve low NOx emissions. The FGR may also be used as a carrier to inject fuel into the reburn zone, thus promoting thorough mixing.

**Burner Out of Service (BOOS)** – this is achieved if the burners firing coal are starved of air. If the air is subsequently supplied through adjacent non-firing burners, then the boiler effectively becomes air-staged. However, although this technology is attractive from a capital point of view, there is a potential penalty arising from the tendency for the level of unburnt carbon (UBC) in the fly ash to increase. This could lead to efficiency loss and since there is a carbon in ash limit for certain uses of fly ash, this could have detrimental effects on ash sales to the construction industry, for instance.

**Post-combustion processes**

Other NOx control methods include selective catalytic reduction (SCR) or selective non catalytic reduction (SNCR). In SCR, a catalyst vessel is installed downstream of the furnace. A reducing agent, ammonia, is injected into the flue gas before it passes over the fixed-bed catalyst, which promotes the reaction between ammonia and NOx, producing N2 and H2O. The capital costs for SCR range over $36–140/kW (Soud and Fukasawa, 1996).

In SNCR the reducing agent (typically ammonia) is injected into the furnace above the combustion zone, where it reacts with NOx to form N2 and water vapour, as in SCR. The capital costs for SNCR range over $8–22/kWe (Soud and Fukasawa, 1996). SCR, however, involves high capital in comparison to other NOx reducing techniques, such as fuel reburning which involve capital costs of $30–35/kW (Soud and Fukasawa, 1996). Moreover, gas stratification and uneven temperature distribution in large boilers (>250 MWe) significantly reduce the viability of SNCR as a NOx control option (Baimbridge and others, 1999). A hybrid technique may also be used in which SCR and SNCR are used in conjunction with each other. Moreover, both processes may be used with LNBs or with other combustion modifications.
3 Factors affecting NOx formation

The reaction chemistry of NOx formation and the effects of coal properties, furnace designs and combustion conditions will be briefly discussed in this chapter. More details on the effects of coal properties on NOx formation have recently been reported by Davidson (2000).

3.1 Effects of coal properties

Unlike SOx emissions which predominantly depend on sulphur content of the coal, NOx formation depends not only on the nitrogen content of the coal, but on a number of other parameters, which in turn control the combustion properties of coal. Such properties may cause major uncertainties in the furnace predictions, since these vary with coal types, but also because there are various methods of measuring and analysing coal combustion-rate data (Fiveland and Wessel, 1991). Coal properties affecting the formation of NOx pollutants include volatile content and coal nitrogen content as well as coal-particle size distribution, devolatilisation rate, char oxidation rate and volatile combustion rate. It is generally agreed that more than 80% of NO is formed from the nitrogen in the coal and it is to be expected therefore, that NO emissions will be related to nitrogen content. It is also recognised that the high temperature volatile release in a low-NOx combustion system is an important coal property. Thus the higher the proportion of volatile nitrogen released during devolatilisation, the lower the NO formation by the subsequent oxidation of char nitrogen.

The differences in NOx emissions from various coals may be due to the inherent differences in the nitrogen associations in the coals, as well as external factors such as temperature and residence time. The nitrogen in bituminous coals is released as CN⁻, while the lower-rank coals release most of the nitrogen as NH₃, according to studies by Chen and others (1982b). Furthermore the distribution of nitrogen between the volatiles and the fixed carbon also varies significantly amongst coal ranks. Investigations carried out by Chen and others (1982b) suggested that the HCN yield was greater than NH₃ for all bituminous coals. On the other hand the concentration of HCN was less than that of NH₃ for all bituminous coals. On the other hand the others (1982b) suggested that the HCN yield was greater than amongst coal ranks. Investigations carried out by Chen and (1982b). Furthermore the distribution of nitrogen between the volatiles and the fixed carbon also varies significantly amongst coal ranks. Investigations carried out by Chen and others (1982b) suggested that the HCN yield was greater than NH₃ for all bituminous coals. On the other hand the concentration of HCN was less than that of NH₃ for all bituminous coals. On the other hand the others (1982b) suggested that the HCN yield was greater than amongst coal ranks. Investigations carried out by Chen and others (1982b) suggested that the HCN yield was greater than NH₃ for all bituminous coals. On the other hand the concentration of HCN was less than that of NH₃ for all bituminous coals. On the other hand the others (1982b) suggested that the HCN yield was greater than amongst coal ranks. Investigations carried out by Chen and others (1982b) suggested that the HCN yield was greater than NH₃ for all bituminous coals. On the other hand the concentration of HCN was less than that of NH₃ for all bituminous coals. On the other hand the others (1982b) suggested that the HCN yield was greater than amongst coal ranks. Investigations carried out by Chen and others (1982b) suggested that the HCN yield was greater than NH₃ for all bituminous coals. On the other hand the concentration of HCN was less than that of NH₃ for all bituminous coals.

3.1.1 Functionality of nitrogen in coal

Due to the highly heterogeneous nature of coal structure, problems are encountered during the characterisation of a coal for combustion purposes. The heterogeneity may be classified in macroscopic and microscopic terms. In the former case, coals may have a banded structure, whilst at the microscopic level, coals are described in terms of macerals. These macerals may be separately characterised in for instance, carbon, volatile matter and nitrogen. The heterogeneity aspect of coal is a very important parameter, more especially for the small particles used in pulverised coal combustion. Depending on the coal used, the pulverised coal may be regarded to consist solely of maceral concentrates. On the other hand when considering the type of nitrogen, functionality is important. For instance, the nitrogen contained in the coal may be described as pyrrolic (5 carbon ring), pyridinic (6 carbon ring) or quartenary nitrogen (Visona and Stanmore, 1998b).

Pyrrolic nitrogen tends to decrease with increasing coal rank (Davidson, 1994; Visona and Stanmore, 1998b), whereas the pyridinic form tends to increase with coal rank. On the other hand, the reverse was observed by Kambara and others (1993), who claimed that pyrrolic nitrogen increased considerably with coal rank, whilst the pyridinic form decreased with increasing coal rank. However, a clear trend has not been found, and according to van der Lans and others (1997), more information is required to confirm the relation between nitrogen functionality and the nitrogenous species released.

3.1.2 Effects of volatile matter and coal nitrogen content

One of the most important parameters is the volatile content of the coal. In earlier work, Gupta and Wall (1994) used a plug flow model for the burning of low volatile coals. Their treatment of NO chemistry was based on the findings of Mitchell and Tarbell (1982) as follows:

- NOx concentration was proportional to coal-nitrogen;
- volatile matter had little influence on NOx during air-staged combustion, but with excess air there was a slight increase in NOx emissions with volatile content;
- NOx increased with excess air; and
- under reducing conditions the finer coal particles caused lower predicted NOx. It was then concluded that more measurements of the evolution of nitrogenous species during pyrolysis were required to fully utilise the model.

More recently, a number of investigators, including Mereb (1996, 1999) and O’Connor (1999) confirmed that for LNBs higher volatile coals produced lower NOx emissions than low-volatile ones, irrespective of the nitrogen content of the coal. However, within the same coal group, NOx emissions increased with the nitrogen content of the coal.

3.1.3 Effects of fuel ratio

Fuel ratio (the ratio of fixed carbon to volatile matter) is
generally used to account for the effects of both coal rank and volatile content. Studies of Mereb and Douglas (1997) suggest that both coal rank and volatile content are significant coal properties affecting NOx emissions, but the two effects are not independent. In general fuel ratio is one of the main properties of coal that accounts for most of the variations of NOx with coal type (Mereb, 1999). The fuel ratio is an indication of the fuel nitrogen split between volatile products and char during combustion, which affects NOx formation. This decreases with decreasing coal rank with values of 4 for low-volatile bituminous, 1.2–1.5 for high-volatile bituminous, and 1 for subbituminous coals. Figure 3 shows the variation of NOx with fuel ratio, at different % excess O2 (Mereb, 1999) for a low NOx 70 kW combustor. It may be seen that NOx levels increase with increasing coal rank, and hence increasing fuel ratio. NOx levels decrease with decreasing fuel ratio due to the higher volatile matter content in lower rank coals, thus resulting in greater volatile release in the near burner zone. Consequently NOx emissions are inhibited because of:

- release of fuel nitrogen in a reducing environment would promote its conversion to N2 as opposed to NOx; and
- less retention of fuel nitrogen in char would inhibit formation of NOx from char oxidation.

A non-linear variation of NOx with fuel ratio is observed. In this study the lignite and subbituminous coals had similar fuel ratios (0.9–1.0), and thus produced similar NOx emissions. A similar trend was observed with the 0.5 MW combustor, also used during this investigation.

### 3.1.5 Char nitrogen content

Gibbins and others (1994) suggested that the nitrogen content of the char and the amount of volatile nitrogen preceding coal combustion are good indicators of NOx emissions. Experiments were carried out in a high temperature Wire Mesh Reactor, in which a small coal sample is heated at $10^4$ K/s by an electric current passing through a wire mesh which holds the sample (heating rates in full-scale burners are $10^6$ K/s). Char remaining in the wire mesh and the volatile matter can be collected for measurement or analysis. Thus this apparatus allows the determination of volatile yield rates at conditions nearer to those of pulsed combustion coals than those obtained by proximate analysis but are not fully representative.

### 3.2 Effects of combustion conditions and furnace designs on NOx

NOx emissions do not solely depend on the coal properties but also on the furnace configuration, the burner type, the number of burners, the load, etc. Table 1 summarises the various parameters which influence NOx emissions.

Operational characteristics of two boilers can never be the same on the same coal (O’Connor, 1999; Tilley and others, 1998). Some of the differences are due to changes in plant condition and differences in plant construction. More specifically, the distribution of fuel between individual burners could have significant impacts on unburnt carbon and NOx emissions. In comparing plant and rig data, it is important to consider the differences between a large power plant boiler and a relatively small rig. The most important

### Table 1 Summary of parameters which influence NOx emissions

<table>
<thead>
<tr>
<th>Boiler design</th>
<th>Boiler operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiler type (wall-fired or tangential)</td>
<td>Load</td>
</tr>
<tr>
<td>Boiler capacity</td>
<td>Mills in operation</td>
</tr>
<tr>
<td>Burner type (conventional boiler, low NOx burners)</td>
<td>Excess air</td>
</tr>
<tr>
<td>Number and capacity of burners</td>
<td>Burner tilt</td>
</tr>
<tr>
<td>Burner zone heat release rate</td>
<td>Burner operation</td>
</tr>
</tbody>
</table>

Studies conducted by Williamson and others (1998) and O’Connor (1999) show that coal nitrogen content, devolatilisation rates and the rate at which nitrogen is released are important factors affecting NOx emissions. Coals with fast devolatilisation and nitrogen release rates are expected to be good coals in LNBs. On the other hand, coals in which nitrogen is slowly released are more likely to produce higher NOx since more nitrogen would remain in the char. Less NOx is produced from coal with lower nitrogen and higher volatile contents. Moreover, the rate of release of volatiles may also affect NOx emissions. For instance Asfordsby coal (% N daf: 1.55; fuel ratio: 1.39) produces higher NOx emissions than expected despite its high volatile matter content, due to the slow release of nitrogen in the flame. This slow release has been attributed to the porous structure of Asfordsby coal as determined by Brunauer, Emmet and Teller (BET) measurements (O’Connor, 1999).
differences are the coal and air distribution and temperature. The comparison of data obtained between a full-scale furnace and the laboratory-scale was discussed in greater detail by O’Connor (1999). The experimental results showed that the sensitivity of NOx to excess oxygen was greatly reduced under air staging conditions (NRTF rig). The CTF data indicated that with sufficient residence time and temperature in the burnout zone, the application of air staging does not necessarily give rise to an increase in unburnt carbon loss. Furthermore, coal quality was shown to influence both NOx emissions and carbon burnout under air-staging conditions.

Low NOx technologies

The effects of coal properties on NOx emissions in low NOx combustion systems were investigated by Conn and others (1995). These properties influence NOx emissions as well as unburnt carbon levels, slagging and fouling tendencies. In the course of that study, a 265 MW boiler retrofitted with a Flame Attachment Nozzle (FAN) burner was discussed in terms of the basic coal properties. During this investigation a Drop Tube Furnace (DTF) was used to simulate the two kinetically dissimilar stages of low NOx combustion, namely the rapid devolatilisation in an oxygen-lean atmosphere and the much slower burn-out of the char under oxidising conditions. The DTF is capable of establishing the extent to which the fuel nitrogen can be evolved under simulated low-NOx combustion conditions, that is close to the burner. The DTF gas outlet is monitored to establish the NOx concentration. This information can thus be used to provide a ranking order for different coals under realistic and identical conditions, and the data correlated with results from full-scale tests.

According to van der Lans and others (1997), coal properties influence the effect of NO reduction from staged combustion by the partitioning of nitrogen between the char and the volatiles, since mainly volatile nitrogen is sensitive to the stoichiometric conditions in the flame. Under unstaged conditions that is 0% overfire air (OFA), the conversion of volatile nitrogen to NO is more efficient than the conversion of char nitrogen to NO. Hence, increasing the amount of volatile nitrogen or burning a lower rank coal gives rise to higher NOx emissions at unstaged conditions (Smart and Nakamura 1993). On the other hand, during staged combustion the volatile nitrogen released from the coal is reduced. Moreover, the degree of reduction is governed by the volatile content of the coal; the higher the volatile content, the more reduction takes place, thus reducing NO formation. In a conventional boiler (with no low-NOx facility), lower levels of NOx would be emitted from a low volatile coal than from a high volatile coal. For modern boilers equipped with low-NOx however, burning higher volatile coals minimises NOx emissions. This is because for staged combustion conditions, precursors for NOx formation can easily be converted to molecular nitrogen (N₂) due to the reducing conditions in the zone where the volatiles burn.

A very rough relation between the nitrogen content of a coal and the NO produced can be found; the higher the % fuel-N, the higher the NO emissions, as seen from Figure 4 (van der Lans, 1997 based on data reported from Chen and others, 1982a,b). However, less scatter is observed under staged conditions and correlations are more difficult under unstaged conditions.

A similar trend was observed by Gibb and others (1995) during which full-scale experiments were conducted using seven high volatile bituminous coals. Less scatter can be observed under staged conditions, especially at higher levels of OFA (for instance at 25% OFA). On the other hand, considerably more scattering can be observed for unstaged combustion (0% OFA) as seen in Figure 5.
nitrogen to the higher NO levels under less staged combustion conditions (Gibb and others, 1995).

On the other hand, Morgan (1990) observed the opposite effect, that is, correlations were more difficult under staged conditions in a 2.5 MW furnace. The author suggested that secondary factors such as gas composition, temperature and residence time changed when coal type changed.

### 3.3 Effects of combustion conditions

There are many factors concerned with boiler design and operation, which potentially influence the formation of NOx in pulverised coal combustion. However, once the burner has been optimised and the boiler tuned, there are several factors that govern NOx production as follows:

- particle size distribution;
- swirling;
- stoichiometry;
- residence time;
- temperature;
- excess air.

#### 3.3.1 Particle size distribution

Investigations by Afonso and others (1993) suggested that particle size distribution had no significant effect on NOx emission levels, in a tangentially-fired boiler. Similar observations were made by Schnell and others (1993), using a 500 kW test rig as well as by Azvedo and others (1999). However, large particle size (>75 µm) entailed poor burnout levels (Schnell and others, 1993; Azvedo and others, 1999). In swirl burners, however, a decrease in particle size resulted in an increase in NOx emission for conventional burners and a decrease in NOx emission for low-NOx burners (Afonso and others, 1993). The increase in NOx emissions with smaller particles is believed to be due to a weaker penetration in the internal recirculation zone (IRZ) of the flame. This weak penetration should lead to a shorter residence time in the oxygen deficient zone in the IRZ, hence promoting NOx formation (Visona and Stanmore, 1997).

Fiveland and Wessel (1991) on the other hand, demonstrated that coal particles had a large effect on NOx emissions for a standard cell burner, whereby NOx emissions decreased with increasing particle size distribution. Similarly, results obtained by Mereb (1996) suggest that particle size distribution had an important influence on the overall performance of a boiler. According to Baimbridge and others (1999), improving mill product fineness allows operation (of full-scale boilers) at reduced excess air levels whilst maintaining ‘acceptable’ quantities of carbon in ash, thus reducing NOx emissions, and potentially increasing boiler efficiency. Visona and Stanmore (1997) observed a significant reduction in NOx emissions, by up to 10%, when finer particles were made finer (≈100 µm), despite the general belief that small particles contribute to higher NOx. A possible explanation for the lower NOx emissions from smaller particle size may be due to the high volatile content of the coal used. Smaller particles have higher heating rates than larger ones, which would then drive off a greater proportion of the volatile fuel nitrogen as NOx precursors, such as HCN (or NH3). The excess HCN (or NH3) produced would then reduce NO, rather than react with O2 to produce NO. Similarly, Mereb (1996) observed that finer particles of a high volatile coal produced less NOx than finer grinds of a low volatile coal, since finer coals enhance both volatile combustion, which inhibits NOx and also char combustion which promotes NOx. Hence, the effects on NOx emissions depend on which property dominates. The study conducted by van der Lans and others (1997) suggests that the effects of particle size are unclear: some investigators have observed a trend in NO emission with particle size, whilst others have not.

#### 3.3.2 Swirling

Work carried out by Schnell and others (1993) on a 500 kW test rig showed that low NOx emissions are achieved by having swirled primary and secondary air and unswirled core air. A large recirculation zone is normally created when the secondary air is unswirled whilst the core air is swirled, which would then cause fast heating of air and fuel, via the recirculation of hot flue gases, which would hence produce higher NOx emissions. When the secondary air is swirled, a pressure drop is caused in a small area of the unswirled core air. Thus almost no hot flue gases can be recirculated to heat up the incoming air and coal, causing low NOx emissions. Overall low swirl numbers lead to low NOx emissions, at the expense of poor burnout, as a result of poor mixing between coal particles and the air. High swirl numbers on the other hand, typically generate very high NOx, due to high turbulence and better mixing. Similar observations were made by Weber and others, (1995) in Type-2 (high NOx) flames.

Contrary to Schnell’s observations, Nazeer and others (1999) concluded that 0 swirl produced the highest level of NO (740 ppm) due to coal devolatilisation taking place in the vicinity of an oxygen rich environment, in a 0.2 MWth reactor. On the other hand, increasing the swirl number to 1.5 caused a significant drop in NO emissions, due to devolatilisation taking place in the recirculated product gases which contain less oxygen. This type of flame behaviour can be extremely useful in designing LNBs where coal devolatilisation is initiated in an oxygen poor environment, and additional air is supplied around the outer fringes of the flame to complete combustion. Laser Doppler Anemometer (LDA) measurements were also made to determine axial and tangential velocity information in the 0.2 MWth pulverised coal flame (Pickett and others, 1999), at different swirl settings. It was concluded that swirl numbers as well as the interaction of burner velocity profiles and NOx were important boundary conditions for combustion modelling (Pickett and others, 1999). However, no modelling studies have been reported by Nazeer or Pickett. Breussin and others (1997a) and Visona and Stanmore (1998a) simulated the effects of swirling as will be seen later in Chapter 5.

#### 3.3.3 Stoichiometry

The effects of stoichiometry on NOx emissions were studied...
by Chen and others (1982a, b). Their findings suggested that varying the primary zone stoichiometry whilst maintaining an excess oxygen of 5% minimised the NO emissions, using a coal stoichiometry of 0.7, at a residence time of 1 s. With air staging, the combustion process is separated into a fuel-rich and oxygen-deficient stage, as well as a burnout stage, that operates in excess air. More air enhances the production of NO, whereas less air promotes the formation of gaseous nitrogen, which eventually oxidises to NO in the burnout region. The optimum stoichiometry (air:fuel ratio) in the fuel-rich combustion zone was found to be \( \approx 0.7 \), according to van der Lans and others (1997). On the other hand, Hesselmann (1977) and Hesselmann and others (1997a) found that the optimum primary zone stoichiometry was 0.9, with excess oxygen maintained at 3 vol%. However, the level of NOx measured was dependent on the distance of the flame end to the overfire ports, that is, increasing the distance to the overfire air port caused a drop in NOx emission.

### 3.3.4 Residence time

Investigations carried out by Spliethoff and others (1996) inferred that increasing residence time in a primary combustion zone favoured the decomposition of gaseous nitrogenous species (NO, HCN, NH\(_3\) ), thus resulting in a significant reduction in NOx emissions. Typically around 75 to 400 ms are necessary for HCN to convert to \( \mathrm{N}_2 \), depending on the reaction temperature (Hesselmann and others, 1997b), whilst Yang and others (1997) suggested that the optimum residence time lay between 450 ms and 500 ms.

### 3.3.5 Temperature

Thermal NOx formation is highly dependent on temperature, whereby higher temperatures promote NOx formation but fuel NOx might not be as dependent according to Pohl and Sarofim (1976). However temperature dependence during staged combustion conditions is a function of the stoichiometry of the primary combustion zone, especially at higher air ratios (Kremer and others, 1987). Spliethoff and others (1996) suggested that NOx emissions increased in an oxygen rich environment, at higher temperatures, whereas in a fuel-rich environment (as in air-staged combustion), less NOx was produced. This was thought to be due to the acceleration in the release of volatile nitrogen or decomposition of gaseous nitrogen species, under such reducing environments. Overall, increasing the average reburn zone temperature results in poorer NO reduction efficiencies as a consequence of more rapid production and consumption of hydrocarbon volatile gases before they can actually mix and react effectively with primary NO (Yang and others, 1998).

### 3.3.6 Excess air

The level of excess air has a considerable effect on NOx emissions, regardless of the boiler configuration or type of firing system. In general a lower level of air results in lower NOx emissions. However, low air levels may lead to incomplete coal combustion, thus resulting in an increase in carbon in ash. The effects of excess air on NOx emissions were investigated by Mereb (1996), using low volatile and high volatile coals. Results of this investigation showed that an increase in the level of excess air led to an increase in the production of NOx. Moreover staging tests showed that NOx sensitivity to excess oxygen (O’Connor, 1999) and to coal quality (Jones and others, 1996) was greatly reduced as the degree of air-staging increased.

### 3.4 Comments

In order to model and predict NOx emissions during pulverised coal combustion, it is important to develop detailed chemical pathways for NOx formation and destruction. Moreover, the factors affecting NOx such as coal types and furnace designs should be taken into consideration in order to produce accurate predictions of NOx emissions. Various investigators have proposed different NOx formation pathway routes. Although these are more elaborate than the De Soete model, none of them account for every nitrogenous species that could contribute to NOx. Further understanding of the NOx formation mechanism is imperative in order to develop accurate predictive models; to date the mechanisms of NOx formation are not fully understood.
4 Overview of computational fluid dynamics

In this chapter a brief description of CFD modelling as well as the mathematical equations governing two-phase combustion and NOx formation will be shown. The objective of NOx modelling is to obtain a prediction of the NO field within the calculation, assuming that the predominant contribution to NOx emanates from NO. All transport processes in practical geometries are represented by an average, convective transport equation.

Mathematical models are now widely used in many industrial applications, for instance for stress analysis, thermal conduction and in aerodynamics. On the other hand, modelling of combustion plants is not so well developed because of the complexity of the underlying physical and chemical processes that occur during combustion. Combustion plants are designed to heat a variety of materials such as metals in reheating furnaces (during the manufacture of stainless steel), fluids in fired heaters among others as well as to raise steam in boilers in power plants. Hence, plant designs vary according to their functions as well as their scales and capacities. Thus, in order to produce accurate simulations and predictions, these factors need to be accounted for in the mathematical modelling of the particular combustion process.

Experimental measurements from semi-industrial scale furnaces and single burner test rigs provide invaluable information of the combustion process, and may be accurately obtained using non-intrusive laser techniques (Pourkashanian and others, 1998). This information is important for validating the mathematical models. However, complications arise during scale up of these burners. For instance, most industrial plants consist of several burners rather than a single burner, for which a mathematical model would be valid. However, in some modellers’ opinions, combustion plants are inaccessible, hence it is difficult as well as expensive to obtain plant performance data.

Nevertheless, mathematical modelling has become a quick and invaluable tool for validating plant design changes, for a wide range of plant operating conditions without involving costly full-scale plant trials. Computational modelling may be used for:

- problem solving;
- assessing changes to plant operating conditions;
- predictions and control of pollutant and ash formation;
- predicting the influence of furnace conditions on NOx emissions and of coal quality in existing combustion boilers (particularly important for the purchase of coal by the power generating industry);
- characterisation of fuels for use in novel combustion systems;
- assessing coal quality impacts on pollutant (such as NOx) emissions;
- evaluating retrofits;
- designing new plants and optimising existing ones.

However, in order to accurately predict NOx emissions from furnaces, a knowledge of the fate of coal nitrogen during the combustion process is imperative.

4.1 Types of mathematical modelling

There are two different numerical methods commonly used to model combustion plants. The first method, suggested by Lobo and Evans (1939) calculates Heat Balances taking the heat released by the combustion of the fuel into consideration. This method, however, is limited to radiative heat transfer and thus does not attempt to calculate convective heat transfer (Pourkashanian and others, 1998). The other method, computational fluid dynamics (CFD), was developed by Spalding at Imperial College of Science, Technology and Medicine. This method starts with the basic equations for flow, enthalpy, etc, and introduces approximations to take turbulence into account. The resulting equations are subsequently discretised on a suitable grid solved numerically. Quantitative determinations of gas velocities, temperature and concentrations of the major species may be obtained from the nodes of the grid. Coal fired boilers differ considerably in their design. For instance, they may be front or opposed wall-fired, tangentially-fired or down-shot fired. These parameters need to be taken into account in the CFD modelling. However, despite the fact that CFD is a very powerful tool, uncertainties may arise from approximations made during modelling. These two modelling methods have been used in different applications. The Heat Balance method has been used for fired process heaters, reformers and reheating furnaces while the CFD method has been applied to model burners and power station boilers and combustion processes.

CFD may be used to simulate entire multiburner furnaces, heat transfer modelling combined with chemical kinetics and simplified fluid dynamics of the entire system. However, it is important to realise that in complex systems, such as a power plant boiler, a variety of techniques should be employed, as one technique in isolation can provide only part of the answer (Smart, 1997). The reason for the growing interest in CFD models lies in their flexibility in being able to describe a range of furnaces and conditions. Sensitivity studies may be carried out to determine the main variables and their influence on NOx emissions. Changes in coal feed composition or particle size distribution can be trialed.

Modelling could provide a link between laboratory-scale and full-size plants, and also for design and optimisation of burners and combustion systems as well as fuel selection. A further benefit of modelling is the ability to understand what is happening inside the furnace, thus helping the development of reaction kinetics. In the longer term, this approach could lead to NOx abatement through greater understanding of the fundamental coal nitrogen chemistry. Since the cost of evaluating various NOx abatement techniques in full-scale...
experiments can be prohibitive, operators of combustion boilers are increasingly resorting to CFD modelling in order to determine the appropriate emission control techniques for their specific units. It is also important to be able to use predictive tools such as computational modelling to understand the behaviour of coals during combustion thus allowing the effective use of emission control techniques. Furthermore the use of computational modelling is more cost effective and less time consuming than undertaking combustion experiments in pilot plants. However, it is important to first establish the confidence limits of the chosen NOx model prior to using CFD-based predictive methods to assess NOx production in industrial coal flames.

4.2 Methodology of CFD

CFD calculations require a number of inputs or parameters pertaining to the coal and furnace:

- coal properties such as ash content, moisture content, elementary analysis, particle size;
- fuel type such as fossil fuels, wastes, biomass and a mixture of these;
- the oxidant (normally air);
- chemical reactions between the fuels and the air and product species;
- convective and radiative heat transfer;
- formation of pollutants;
- slagging, fouling and erosion of furnace walls;
- turbulence and two-phase flow modelling (solid and gas);
- firing configuration (whether furnaces are tangentially-fired, front or wall-opposed);
- combustion kinetics – that is volatile release and char combustion;
- burner type – such as conventional swirl, low NOx, etc;
- the operating conditions – temperature, air/coal stoichiometric ratios.

Figure 6 shows a schematic diagram of the major mechanisms occurring during pulverised coal combustion (Eaton and others, 1999).

During the modelling of pulverised coal combustion by CFD, solutions for mass, energy and momentum conservation are solved. Other submodels are further coupled with this framework to account for gaseous species mixing and chemical reactions, coal particle devolatilisation, char oxidation and heat transfer by radiation. From this computation, the temperature distribution and aerodynamic properties of the gaseous phase may be obtained. A number of predictions may be obtained, namely, ash deposition, NOx emissions, temperature distributions, gas composition, particle velocity and trajectories, etc. These predictions are usually carried out using a post-processor once the CFD conservation equations are fully converged.

Despite the fact that the major reaction mechanisms of NOx formation have been identified, as previously seen in Chapter 2, NOx modelling is far from being a straightforward exercise. The reaction mechanisms leading to the formation of NOx, for instance, consist of many intermediate steps

(Miller and Bowman, 1989). Many judicious assumptions are made to simplify the modelling process. Moreover, NOx formation in coal flames is closely intertwined with flame chemistry, turbulence effects, heat transfer characteristics, coal particle heat-up, pyrolysis and char combustion. Unless these processes are properly simulated, realistic NO predictions cannot be expected. Due to these assumptions, there is a degree of uncertainty in the available NOx prediction methods (Chui and Hughes, 1996; Weber and others, 1995). Reliable NOx modelling can only be obtainable in very special circumstances where the predictions have been rigorously verified using in-flame measurements (Weber and others, 1995; Poinsot and others, 1995, Eaton and others, 1999).

The processes leading to the formation of NO are very complex, involving the design of the burner, coal composition and firing conditions, which hence make it difficult to estimate NOx emissions. Moreover, coal with similar amounts of fuel-N contents can produce very different levels of NOx emissions when combusted using the same burners and furnace. The key to an understanding of this complex heterogeneous system is an accurate prediction of the properties of the coal flame, especially the flame
temperature. The NOx chemistry also needs to be superimposed on the model at all stages, namely devolatilisation and char burn-out.

The following section describes the steps that need to be followed during modelling.

### 4.2.1 Grid generation

The first stage of CFD modelling requires the generation of a grid which needs to cover or fit the burner system under investigation. Finite element or finite volume CFD techniques are generally used. Finite elements are generated by subdividing the solution domain into smaller regions (elements) with the vertices of the elements (also known as nodes) being the location of the unknown variables. The solution is obtained at these nodes. By determining the element property (stiffness) matrix, an element by element assembly procedure will enable the evaluation of the global system matrix. A similar technique is used for a finite volume solution except that the solution domain is divided into a number of non-overlapping control volumes. There is one control volume surrounding each grid point. The differential equations are integrated over each control volume. The final solution (using either approach) may be determined by then applying boundary conditions and using one of the known methods of linear equation solving.

The finer the grid, the more accurate the predictions (Wirtz and others, 1995). Moreover, the grids should be fine enough to produce grid independent solutions. In order to assess grid independence, Breussin and others (1996) tested several numerical grids during the modelling of a 2 MWth furnace. A 2-D grid containing 10,000 and 40,000 nodes was tested. It was seen that increasing the number of grid nodes by a factor of four did not alter the results by more than 2%.

Moreover, if the grid spacings were too large in proportion to furnace volumes, they would become too large to resolve any concentration gradients caused by devolatilisation or mixing layers and internal recirculation zones found in full-scale furnaces. This problem can be overcome by breaking down the computational grids into separate zones in the near burner zones. This is known as domain decomposition procedure and is used to resolve the burner simulations into independent calculations that are tied to furnace simulations. The advantage of domain decomposition techniques is the possibility to introduce refined sub-grids, providing a better resolution of regions where high gradients occur (for example, high velocity and temperature gradient near the burners).

In the simulation, a number of particles is injected individually into the furnace through the coal burner and tracked cell by cell through the furnace. These particles undergo reactions by devolatilisation and combustion, are subjected to heat exchange by convection and radiation and are buffeted by random turbulent eddies.

Figure 7 shows the computational grid (58 x 17 x 17 cells) for simulating a pilot-scale ash deposition furnace (Schnell and others, 1995).

### 4.2.2 Fluid flows

The next step in CFD modelling is the determination of fluid flows. These are mathematically described by the continuity and Navier Stokes equations, which can be seen in Section 4.3. A description of flow through the furnace also involves a turbulence model such as the k-ε model (where k represents turbulent kinetic energy and ε represents dissipation energy). This will be described in more detail in Section 4.3. The flow conditions are calculated from the flow rates and feed and air temperatures. The turbulent diffusion behaviour is obtained from the intensity of turbulence, which is determined from the k-ε model.

### 4.2.3 Physical modelling

Physical modelling is concerned with the construction and operation of experimental rigs which simulate full-scale coal-fired units. As far as possible, this is based on the
'similarity' between the test rig and the plant (Pourkashanian and others, 1998). Since mathematical modelling has limitations, validation against experimental measurements is much needed especially on a large scale. However, large-scale experiments are costly and difficult to conduct. Thus, laboratory- or pilot-scale experiments (physical modelling) are often required to simulate the larger furnaces, for model validation, and at lower costs. However, problems arise during the scaling-up tests from, for instance, a 1 MWth rig to a 50 MWth rig, since this is often not well understood. Moreover, combustion plants tend to be made up of multiple rather than single burner units, and thus complications arise from burner to burner interactions.

4.2.4 Modelling turbulence

Turbulence, according to Niksa (1996) remains a problem: the modelling of turbulence presents difficulties that no simulator overcomes without unreasonable simplifications. Moreover, the velocity of turbulent flows in pipes and channels cannot be easily calculated, since this varies logarithmically near the walls. Thus such a rapid variation cannot be easily calculated according to Pourkashanian and others (1998), unless an approximate near-wall treatment is used instead. Thus a special low Reynolds number could be used instead of the k-ε. Moreover, in an isothermal flow, it is relatively easier to model turbulence, since the flow field consists of a single characteristic. On the other hand, this is not the case with non-isothermal flows as in coal flames. Changes in flow characteristic in this case are far too numerous and complex for a single-number flow characterisation.

According to Bender and others (1993), flow is highly turbulent in any entering jet, with Reynolds numbers typically in the region of 10⁶. However, downstream from the main jet-entry and mixing region, the flow field may be close to laminar, especially in smaller furnaces. Furthermore, turbulence also entails turbulent particle dispersion (Coimbra and others, 1994). However, the calculation of turbulent particle dispersion in a large-scale pulsed flame can be very difficult and ignoring it could produce unrealistic coal flame behaviour. The chemical species mass fractions are strongly influenced by this, and their distribution in space as well as the reaction locations require good agreement between the actual particle motion and the model.

The use of the k-ε model has proved to be successful in the modelling of turbulence. However, certain flaws do occur especially for the determination of the location of the eye and the strength of the recirculation zone. Hence it would be very unwise to depend solely on the k-ε model without any experimental validation. In turbulent flows, the particle motions are not only influenced by the mean motion of the gaseous phase, but also by turbulent interaction of eddies and particles. These fluctuational velocities are thus modelled using more advanced turbulence models such as Reynolds Stress Model (RSM) and Algebraic Stress Model (ASM). The RSM turbulence model was used by Schnell and others (1991) and more recently by Breussin and others (1996) and Richter and others (1998) to improve overall accuracy of predictions. Breussin and others suggested that the RSM is superior for predicting Type-1, that is low NOx flames. Type-2 flames are high NOx flames for which the Renormalisation group (RNG-k-ε) and k-ε model failed to predict jet penetration. Moreover, the flame length and volume, the temperatures of the near-burner-zone and oxygen concentrations were directly affected by jet penetration. The NOx predictions, were also strongly dependent on jet penetration. According to the authors, the failures in predicting properties of the fuel-rich zone while using either the k-ε or the RNG-k-ε model result in the over-prediction of NO flue concentrations. More recently though, Fan and others (1999) claimed more accurate results using a RNG-k-ε model to model turbulence.

However, despite all its limitation the k-ε turbulence model remains the most popular.

Turbulent combustion may be modelled by various methods, which are briefly summarised as follows.

Eddy Break Up (EBU)
Mixing rates are normally determined by the EBU (Spalding, 1971; Magnussen and Hjertager, 1977) model, which assumes fast chemistry. This has recently been used by Liang and others (1999), to model the equilibrium gas-phase chemistry and the coupled turbulent flow field with chemical reactions in a W-shaped boiler furnace under different conditions. Results of this work suggest that the predicted and measured gas-phase velocity fields, concentrations of the gaseous species, temperature distribution and particle trajectories were in good agreement. Peters and Weber (1991) also used the concept instead of chemical kinetics to handle chemical reactions in turbulent flames. However, the model tended to overpredict NO formation. The EBU approach is an engineering treatment which accounts for the interaction of turbulence and chemistry in flames, in which it is assumed that the reaction rate is controlled by the dissipation rate of the eddies. However, according to Niksa (1996), EBU models are accurate only after their parameters have been tuned for a specific flow structure – the simpler the flow, the better the performance.

Presumed Probability Density Function (PDF)
Turbulent reactive flows may be described as an ensemble of random flow fields. Each of these fields, however, satisfies the thermochemical equation with a particular set of initial and boundary equations. To satisfy these fields it is important to know the statistical information, such as mean values, variances, covariance and if possible, the PDF. A knowledge of the PDF is important in determining the scalar mean (average) values. In turbulent flows, the combination of PDF and scalar value is an important quantity to determine average values.

Similar to the EBU model, very fast chemical reactions are assumed to take place. These fast reactions may help to reduce the complexity of turbulent diffusion flames. In such situations, detailed knowledge of chemical reactions is not required. This simplification is based on a group of assumptions known as Shavab-Zeldovich formulation. The governing equations of PDF have been extensively described...
by Pope (1981, 1985). Briefly, a transport equation, which also includes convection and turbulent diffusion effects is first solved for a point PDF at each location in the flow field.

Reaction rates in turbulent flows are dependent on the fluctuations of the local flame conditions if the reaction time constants are of a similar order of magnitude or smaller than those of the mixing time constants. This situation is typical of the reactions of pollutant formation that have high activation energies. In large coal flames, it may be assumed that the concentration fluctuations are not strongly correlated with temperature fluctuations, in which radiation is the dominant mechanism of heat transfer. Hence, a simplified PDF approach with a model instantaneous temperature fluctuation was used by Schnell and others (1991) to model HCN reactions in turbulent flows. However, the PDF method has generally been used in gas combustion modelling rather than in pulverised coal combustion modelling.

The investigations undertaken by Chui and Hughes (1996) attempted to validate the accuracy of simplified NOx modelling for engineering estimates, by making in-flame measurements, using an assumed PDF and eddy dissipation concepts (EDC). Eddy dissipation concept is usually used to model the interaction between turbulence and chemistry, for gaseous reactions (Magel and others, 1995; Schnell and others, 1995). The purpose of Chui and Hughes’ study was to establish confidence in a NOx modelling approach before it is applied to industrial-scale boilers, in order to help with NOx abatement strategies in industry.

Although various mathematical methods have been used to model turbulence, turbulence related effects are still not understood enough, according to Niksa (1996), to describe in defined mathematical terms. Yet they need to be defined, in order to close the mathematical equations. In nearly all coal combustors, however, a drastic assumption is made: all chemical reaction rates in the gaseous phase are fast enough to achieve thermochemical equilibrium at the pace of the mixing rates. This assumption may be plausible for a near-stoichiometric reaction (for instance the oxidation of hydrocarbons), but not for NOx formation.

Conditional moment closures (CMC)

Turbulent combustion may also be modelled by a relatively new technique known as Conditional moment closures (Klimenko, 1990; Bilger, 1993; Bilger, 1999; Klimenko and Bilger, 1999). This is based on the experimental observation that the local temperature and composition in a non-premixed flame depend on the local mixture fraction and reaction progress variable. More recently (Bilger, 1999), CMC was used to predict pollutant species during non-premixed turbulent combustion. The method is apparently well suited to problems of pollutant prediction with complex chemical mechanisms. More extensive review of CMC methods has recently been compiled by Klimenko and Bilger (1999).

4.3 Conservation equations, numerical codes and submodels

In general NOx prediction models consider fluid flow and combustion processes, heat transfer dominated by radiation, thermal and predominantly, fuel NOx. The basic combustion model solves a set of nine conservation equations in a grid cell and iterates sequentially through all the cells until convergence is achieved over the whole furnace volume. Briefly, the quantities solved are pressure (mass continuity), velocity in three directions, enthalpy, mixture fraction, mixture fraction variance and two turbulence parameters.

Overall all combustion model codes must describe the release rates and yields of volatiles (produced from coal during combustion), recirculation zones near the burners, flows through the furnace and the rates of consumption and heat release from the coal particles. The mathematical descriptions of these processes are known as submodels. The most popular approaches for each submodel are the turbulent flow characteristics, the chemical mechanisms and the heat transfer equations. In existing coal combustion CFD models, the process is described by three kinetic rates: coal devolatilisation, volatile combustion and char combustion.

The governing mathematical equations of CFD will be briefly explained in this section. Further details, though, may be obtained from Pourkashianan and others (1998) and Eaton and others (1999).

4.3.1 Governing equations for turbulent flows

Fluid flows are characterised by Reynolds number \( R_E \). The size of \( R_E \) determines whether a flow is laminar (small \( R_E \)) or turbulent (large \( R_E \)).

The value of \( R_E \) is mathematically determined as follows:

\[
R_E = \frac{\rho V L}{\mu}
\]  

where:

\( \rho \) : fluid density  
\( \mu \) : fluid viscosity  
\( V \): velocity (as above)  
\( L \): length scales.

During coal combustion, large \( R_E \) are of interest, since this represents a state of turbulence. In turbulent combustion, the flows are very complex due to the vast ranges of time and length scales. Hence the flow equations need to be averaged. However, since the Navier-Stokes equation is non-linear, averaging does not lead to a closed set of equations for the average values of the variables. Hence, a turbulence model is introduced. The most popular one used is the \( k-\varepsilon \) type as previously discussed in Section 4.2. In this model a Bossinesq approximation (equation 19) is used for a non-linear Reynolds Stress to determine the turbulence viscosity \( \mu_T \):

\[
\mu_T = C_\mu \rho k^2/\varepsilon
\]  

where:

\( C_\mu \) is a constant  
\( k \) is the turbulent kinetic energy  
\( \varepsilon \) is the dissipation energy.

Expressions similar to the Navier-Stokes equations are used
to solve $k$ and $\epsilon$. However, the equation for solving $\epsilon$ is often considered to be not well justified (Pourkashanian and others, 1998).

### 4.3.2 Multiphase flow models for reacting flows

In the case of pulverised coal combustion, solid particles interact with a turbulent gas flow, which comprises the reacting oxidiser, that is air, and other reacting and non-reacting species, and the gaseous and solid reaction products. Thus a combustion model must be able to account for each of these phases. Certain methods such as the Eulerian and Lagrangian methods have been used to model multiphase flows. These methods have also been used to determine particle trajectories.

**Eulerian method**

In the calculation of particle trajectories, some authors have opted for an Eulerian calculation (Schnell and others, 1993; Fueyo and others, 1995; Fiveland and Wessel, 1991), whereas others opted for a Lagrangian method. If an Eulerian calculation is chosen for coal combustion modelling, then it is assumed that the coal particles and carrier gas are intermingling but immiscible with one another and that they have equal mean velocities. However, NOx predicted values are slightly higher than the actual ones, when this method is used. More recently, the Eulerian method has been used for the gas phase only, whilst Lagrangian is used to model particle trajectories only (Han and others, 1999; Liang and others, 1999; Visona and Stanmore, 1998a; Fiveland and Jesse, 1994; Boyd and Kent, 1986). In this case, combustion is considered a two-phase system.

In the **Eulerian** approach, the governing transport equations for the gas phase are of the following form (Boyd and Kent, 1986):

\[
\nabla (\rho u \phi) - \Gamma \nabla \phi = S_b
\]

(20)

where:
- $\phi$ is typically the Favre averaged dependent variable of immediate interest (the NO concentration for instance)
- $\rho$ is the fluid mass density
- $u$ is the velocity vector
- $\Gamma$ is the exchange (or diffusion) coefficient in the transport law
- $S_b$ is the mean source term for $\phi$ per unit volume

**Lagrangian method**

The **Lagrangian** equations are used to describe the motion and heating of each individual particle, as it goes through the combustion chamber. The following assumptions are usually made:

- the particles are assumed to be non-deformable and spherical; and
- the particle density is much higher than that of the fluid.

In this approach a number of equations are solved for variables such as, the particle mass-conservation equation, the equation of motion of the particle and the conservation of the particle energy, to characterise the change in particle properties along a particle trajectory as it moves through the gas. The conservation equations have been summarised by Liang and others (1999) and Eaton and others (1999).

### 4.3.3 Radiative energy transport

Radiation is the dominant energy transport mechanism to surrounding surfaces during combustion processes, especially when entrained particles are also present as in the case of pulverised coal combustion. However characterising radiative energy transport is a complex problem during the modelling of coal combustion. In a typical coal-fired utility, radiation includes contributions from both particulates (coal/char, ash and soot) and gases (mainly CO$_2$ and H$_2$O). The accuracy of the overall radiation calculation depends on how accurate the determination of the radiative properties of these species is (Eaton and others, 1999).

The governing equation for radiative heat transfer for a steady-state system is shown below (Eaton and others, 1999; Mengüc and Webb, 1993):

\[
\frac{dI(s, \omega)}{ds} = -(\kappa + \sigma) I(s, \omega) + \kappa I_b + \frac{\sigma}{4\pi} \int_{4\pi} I(s, \omega) \phi d\omega
\]

(21)

where:
- $I(s, \omega)$ are unit vectors
- $\kappa$: local absorption coefficient
- $\sigma$: scattering coefficient
- $\phi$: phase function to characterise the nature of the scattering media

### 4.3.4 Chemical modelling – particle reactions submodels

The chemical pathways leading to the formation of NOx are highly complicated, with the formation of different nitrogenous species among others (Chapter 2). The following section will discuss the effect of including the various species participating in the formation and destruction of NOx.

**Inclusion of CO in NOx modelling**

CO not only affects the temperature shifts, but also the reactions which remove NO. High CO concentrations also cause higher gas temperatures in the furnace, which in turn leads to higher NOx formation. However it is important to include CO formation in NOx models, since neglecting CO effects could induce an over-prediction of NOx especially in LNB configurations (Fiveland and Wessel, 1991). In previous models, no attempts had been made to model CO. However, Fiveland and Weasel (1991) suggested that the inclusion of CO was important particularly in the fuel-rich regions where the CO concentration may be as high as 10$^5$ ppm. They found that neglecting CO caused large errors in the prediction of gas temperature and oxygen concentrations. On the other hand, the model proposed by Visona and Stanmore (1998a) suggested otherwise.
Inclusion of nitrogenous species

Despite the fact that the De Soete (1975) mechanism of NO formation has been criticised for being too simplistic (Visona and Stanmore, 1998a), this model appeared to produce good predictions for the combustion of low-rank coals in a DTF (Visona and Stanmore, 1999a). Although NH3 is a known precursor to NOx, its inclusion in the CFD model led to higher NO predictions. In fact, it was suggested that NH3 might not play a significant role in the formation of NOx inside a bench-scale DTF. However, when NH3 was included with a HC reburn mechanism, there was a general improvement in modelling predictions of NO, especially for higher coal ranks. In the case of higher rank coals, the full chemical mechanism for the production and removal of NOx gave the best results, with good agreement in fuel-lean conditions, and reasonable agreement in the fuel-rich conditions. The combustion modelling of lignites at 1750 K (1477°C) gives much better results whereas poor predictions are obtained at a lower temperature (1250 K; 977°C), since the formation of other nitrogenous species, such as N2O probably become significant, but are ignored. However, N2O is generally believed to be more significant in fluidised bed combustors than in pulverised coal combustion.

Inclusion of volatile matter and devolatilisation step

Recently, Jones and others (1999), focused their study on the chemical aspect of CFD modelling, in which three main submodels were taken into account:

- coal devolatilisation;
- volatile combustion;
- char combustion.

According to the investigators, the devolatilisation step influences the overall reaction of the coal inside the combustor. During this investigation, a DTF was used to assess the influence of this parameter in the overall coal combustion model. Strong emphasis was made on NOx formation. Different modelling approaches were used during this work, to assess their impacts on the predicted results. It was suggested that different predictions were obtained using different modelling approaches. It was also shown that devolatilisation rates had a considerable effect on NOx formation, and yet these are not accurately described.

4.3.5 Overall solution approach

To effectively model the combustion process, the heat transfer and multiphase submodels described previously must be coupled together with the basic turbulent and with the particle reacting CFD equations. Typically, the various submodels provide the numerical values for the source terms in the CFD equations.

During the modelling of pulverised coal it is necessary to separate the overall solution procedure into three main parts:

1. turbulent, reactive, gaseous flow field solutions
2. particle field solution and
3. radiative transport solution. These are summarised in the schematic diagram in Figure 8 (Eaton and others, 1999):

The turbulent gas flow field solution comprises the following:
- continuity;
- momentum;
- energy, that is enthalpy;
- turbulence (solved by k-ε, RSM and/or RNG, etc);
- gaseous chemical reactions (solved by PDF, EBU, etc).

The conservation equations for each of these gaseous flow fields can all be written as a partial differential equation for steady-state, as follows: (Eaton and others, 1999; Chui and Hughes, 1996; Kordylewski and others, 1993):

\[
\frac{\partial}{\partial x_j} \left( \rho u_j \frac{\phi}{\phi_{NO}} \right) = \frac{\partial}{\partial x_j} \left( D \frac{\partial \phi}{\partial x} \right) + S_{NO} \tag{22}
\]

Figure 8 Overall numerical solution procedure for a comprehensive combustion model (Eaton and others, 1999)

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where $\phi$ is the Favre-averaged dependent variable (NO concentration in this case). The left hand side represents the convection of NO species ($D_{NO}$) by fluid flow velocity $u_i$. The right hand side of the equation represents diffusion of NO ($D_{NO}$) with effective diffusion coefficient $D_{NO}$ plus the source term $S_{NO}$ (mean source of NO per unit volume). The essence of NO modelling is to determine how the time-mean source term $S_{NO}$ should be represented based on the rates of the thermal, prompt and fuel NO mechanism reactions. The index-$j$ in equation 22 denotes summation over 3 co-ordinate directions. The momentum transport equation for coal particle/gas mixture can be derived from equation 22, by substituting $\phi$ with the velocity components $U_i$. In this case $\rho$ would be the mean mixture density.

Various techniques have been proposed to model this source term for turbulent coal flames by various investigators such as Fiveland and Wessel (1991) Fiveland and Latham (1993) amongst others. However, according to Chui and Hughes (1996) the modelling of the dominant fuel NO in coal flames is based on global reactions by De Soete (1975), on which many other modellers have based their work.

The only exceptions are the studies conducted by Peters and Weber (1991), which used the eddy-dissipation concept devised by Magnussen and others (1976). However, most of these studies do not take prompt NO into account (Kim and Lior, 1998), since it is often considered insignificant, whilst some of them include the Zeldovich reactions for thermal NO. The inclusion of thermal NOx improves overall NOx prediction (Visona and Stanmore, 1997).

The equations are solved as shown in Figure 9 (Eaton and others, 1999). These equations are elliptic and thus non-linear and must be solved in an iterative way.

**Figure 9** General model solution sequence for turbulent flow processes (Eaton and others, 1999)

4.4 Assumptions and limitations of CFD

CFD modelling has a number of limitations and many assumptions have also been made. These have been reviewed in a previous report by Niksa (1996). The structure and combustion of coal is complex, with the release and combustion of the fuel nitrogen being equally complicated. However, despite the complexity of the reactions taking place during coal combustion and the resulting complications entailed in numerical modelling, most modellers claim that it is possible to achieve good NOx predictions, in full-scale furnaces using simple NOx chemistry. A NO model developed by Abbas and others (1993) assumed a uniform distribution of fuel-nitrogen between the volatile matter and residual char. Volatile-N was assumed to react to HCN whilst char-N was converted to NO as the particle burns out. According to a recent review by Visona and Stanmore (1999b), the reasons why coarse numerical grids may produce good NOx predictions remain unclear. Moreover, the detailed NOx predictions of single burners in simple geometries are less conclusive, whilst several discrepancies in the near burner zones still remain an issue in numerical modelling.

In many instances fast chemical reactions are assumed to take place, to alleviate the complications that might be entailed by turbulence (Niksa, 1996; van der Lans and others, 1997). Furthermore, many nitrogenous species are not accounted for – some modellers have chosen the De Soete model for fuel-N, which has been suggested to be too simplistic.

Overall, much development work is still needed in improving chemistry and turbulence models, and parallel computation must become prevalent before such models may be applied on a daily basis to practical combustion systems (Fiveland and Jessee, 1994). A fundamental assumption is made during the study of gaseous turbulent fluid flow: the gas may be viewed as a continuum, that is, the distance between gas molecules and the mean free path of the molecules is very small compared with the physical dimensions of the geometric scale of interest.

According to Visona and Stanmore (1999a), even in essentially laminar systems, current CFD models of coal combustion have many limitations. Any mixing due to natural convection needs to be omitted, whilst the introduction of volatile jetting tends to improve burnout predictions, but exaggerate NO predictions. The gas temperature also tends to be over-predicted. The model does not work at lower temperatures (for example at ~1000°C), possibly because the authors did not account for every single nitrogenous species that could have been produced.

### i) Reaction mechanisms

Assumptions made during the modelling studies by certain modellers are summarised below:

- it has been assumed that the primary reaction involved in the nitrogen conversion was that volatile nitrogen was converted to HCN and NH₃, and that the quaternary nitrogen was converted directly to NH₃, determined from
the fuel volatile content, as claimed by Kambara and others (1993) (Visona and Stanmore, 1995). Further assumptions were made regarding the remaining volatile nitrogen: it was assumed that this was released either as HCN or NH₃ (Aho and others, 1993). Moreover, it was also assumed that NH₃ was released as a function of O/N ratio;

- HCN was produced directly from chars (Fiveland and Wessel, 1991) and volatiles (Visona and Stanmore, 1995);
- it was also assumed that the char nitrogen converted to NO inside the char particle, but the NO formed could undergo reduction during diffusion out of the particle;
- many modellers adopted the basic gaseous phase reactions proposed by De Soete (1975) whereby:
  
  \[ \text{HCN} + \text{O} \rightarrow \text{NO} + \ldots \text{and} \]
  
  \[ \text{HCN} + \text{NO} \rightarrow \text{N}_2 + \ldots \]

These reactions are considerably simplified:

- the HC reburn mechanism used was that proposed by Miller and Bowman (1989) during which:
  
  \[ \text{HC} + \text{NO} \rightarrow \text{HCN} + \text{O} \text{ and} \]
  
  \[ \text{CH}_3 + \text{NO} \rightarrow \text{HCN} + \text{H}_2\text{O}; \]
- furthermore, the HCN could be converted to NH via the reaction as follows:
  
  \[ \text{HCN} + \text{O} \rightarrow \text{NH} + \text{CO}; \]
- finally, ammonia can react with oxygen to produce NO:
  
  \[ \text{NH} + \text{O} \rightarrow \text{NO} + \text{H}. \]

Overall, one of the major limitations of NOx modelling is that the pathway of NO formation and the reaction mechanisms involved in the evolution of char nitrogen are still not well understood. The use of the De Soete Fuel NOx model has, however, been widespread. Moreover, according to Visona and Stanmore (1996), modellers have often neglected the formation of prompt NOx, since this is only produced in insignificant quantities.

### ii) Volatile and char nitrogen reactions

According to Niksa (1999), equilibrium combustion products are usually assigned based on the assumption that the volatiles have the same elemental compositions as their parent coals. An accurate description of the reaction of the volatile nitrogen is essential for accurate modelling, but to date there is no universal kinetic relationship which adequately describes the progress of devolatilisation (Visona and Stanmore, 1999b). Moreover, the reaction of char nitrogen is often not well described. This area of uncertainty is not treated by the gas phase, that is by the homogeneous kinetic models, but requires a user input. According to Visona and Stanmore (1999b), the release of nitrogen from the char can be handled in a number of ways, either empirically or by a single particle model. The empirical method relies on measured data for a limited range of chars. On the other hand, the single particle model involves a complex numerical simulation, prior to running the CFD.

### iii) Modelling of turbulence

Another problem that faces modellers is the modelling of turbulence (Niksa, 1996; Fiveland and Jessee 1994). Stochastic PDF methods are promising, for improving the chemistry and turbulence predictions. Various methods have been tested for this, however no simulator has correctly simulated turbulence.

### iv) Reactions in the central recirculation zone

Another major limitation of CFD is its failure to accurately describe the central recirculation zone, where most of the chemical reactions of interest occur.

### v) Gas emitted

Assumptions have also been made regarding the gas emitted during coal combustion: all fuel sources in the gas phase are treated as one gas having the composition of the raw gas (less moisture and ash). For the calculation of the gas-phase enthalpy, the volatiles are assumed to be methane (Visona and Stanmore, 1996; Boyd and Kent, 1986).

### vi) Computational time

Computation of mathematical simulations of full-scale utilities may take several hours or even days (Bundschuh, 1999; Holmes and others, 1997). Bundschuh and others (1999) developed the simulation of the transient reactive flow in a 750 MW tangentially-fired coal-fired utility boiler, using the 3-D CFD combustion code, AIOLOS. The calculations were made using up to 8 processors of a parallel vector computer SX-4/32 of NEC, which enabled such large-scale problems to be solved within reasonable time frames (half a day, which would otherwise take 120 days). Schnell and others (1995) used a DEC 3000/500 AXP workstation with 192 MB of main memory. The CPU time for a converged solution (6000 iterations) totalled approximately 43 hours for the decomposed grid (main domain: 50 x 27 x 84 nodes; sub grids: 50 x 22 x 22 nodes). However, operators would much rather obtain instantaneous results as opposed to waiting for lengthy periods.

### 4.5 Comments

Most modellers have been fairly successful at modelling NOx. However, a number of assumptions have been made in order to improve predictions. Various methodologies have been used to model turbulence, the most popular one being the k-ε model, but to date modellers seem to be of different opinions on which turbulence model to use to produce accurate results. Nonetheless, new models such as the CMC methods have been developed, but these have not been universally used yet.

NOx formation is still not well understood by most – various investigators such as Schnell and Visona have suggested different NOx formation mechanisms but none of these mechanisms are universal. Unless the underlying chemistry of NOx formation is fully understood, no CFD model can be expected to produce accurate predictions.

However, extensive research in this field is still ongoing. Despite all the limitations, CFD is a valuable tool and a cheap method for design and evaluating retrofits, without having to resort to full-scale experiments or capital intensive modifications, but also for obtaining trends in pollutant emissions and assessing the effect of plant modifications or coal quality impacts on pollutant levels.
5 Application of computational fluid dynamics

Despite the various limitations, CFD modelling shows promise in predicting NOx emissions. Model validation is an important step in the development of CFD modelling, to ensure reliability of the model. The recent applications of CFD in assessing coal quality impacts, in the modelling NOX formation and reduction, burner designs and in assessing the effects of furnace configurations will be discussed in this chapter.

5.1 Coal quality impacts

As mentioned earlier in Chapter 3, NOx emissions depend largely on the properties of the coal used, more specifically fuel nitrogen, volatile matter content and the rate of release of nitrogen. Briefly,

- **Fuel NOx** from the oxidation of fuel-N is a large contributor to NOx from boilers fitted with LNB. Higher nitrogen containing coals are expected to produce higher levels of NOx;
- **Volatile matter** (VM) content has a strong influence on NOx formation. High VM coals produce less NOx and vice-versa. Such coals release a higher proportion fuel-N into a reducing atmosphere near the burner. However due to the larger proportion of VM, which could thus provide a reducing environment, the fuel-N would more likely be converted to molecular N2 rather than be oxidised to NOx;
- **Rate of release of volatile nitrogen** from the coal during combustion. Slower release of volatile nitrogen will increase NOx, in an oxidising atmosphere. For bituminous coals, the effect of coal fineness on NOx emissions depends on the volatile matter content. Finer grinds of low volatile coals produce higher NOx emissions than high volatile coals;
- **Char nitrogen** found in the fixed carbon (FC) is typically released away from the immediate flame zone. The NO formed from the char is difficult to reduce using LNB techniques which rely on NOx reduction within the flame zone. A high FC to VM ratio (fuel ratio) \( \approx 2 \) or greater is an indication of a coal that is less amenable to NOx reduction strategies.

In general, NO predictions for low-nitrogen subbituminous coals are better than those obtained from high-nitrogen medium volatile bituminous coals, possibly due to the larger content of char nitrogen in the latter coals. According to Visona and Stanmore (1996), it is still rather difficult to model char nitrogen, which is why NOx emissions with medium volatile bituminous coals are under predicted. Field testing to characterise NOx emissions from coal-fired boilers and identify NOx control options has become an ongoing effort for utilities as they strive to comply with the increasingly severe NOX legislation. NOx emissions and coal quality impacts are both strongly dependent upon the coal combustion process and the site-specific boiler firing practices. The interrelationship between coal quality impacts, NOx emission characteristics and boiler thermal performance over the load range can be complex. This is particularly true with low NOx firing modes involving combustion modifications such as OFA and staged combustion. For these reasons, some utilities have recognised the benefits of integrating coal quality impacts and NOx emissions field test programmes into one large programme conducted with the test coals.

Coal quality impacts are also important parameters in natural gas reburning systems (Hesselmann and others, 1997a). Similar NOx reduction may be achieved for a wide range of coals if the coal nitrogen is evolved before the addition of reburn fuel. However, the ease of nitrogen release is strongly dependent on the coal. Some modellers have used simple 1-D engineering codes to assess coal quality impact. However 3-D CFD codes have proved to be more popular and successful.

5.1.1 Use of 1-D combustion model

A simple 1-D model was developed by van der Lans and others (1998), to assess the impact of coal quality on NOx emissions in a full-scale utility (tangentially-fired, 400 MW) and in a pilot-scale rig (160 kW), using three coals:

- a South African medium volatile bituminous coal;
- a Colombian high volatile bituminous coal; and
- a high volatile bituminous Polish coal.

The volatile contents of these coals were determined using a heated wire mesh reactor (HWM). The 1-D mathematical model described coal combustion, char deactivation and radiation heat transfer in full-scale furnaces. The authors claimed that 1-D modelling was more useful as a tool for engineers in the power industry, than computational fluid mechanical codes. The model used includes a heat balance for calculation of the gas and particle temperatures as a function of furnace height, and with zone-volumes represented by plates. Performance of that model was tested against experimentally measured furnace temperatures as well as carbon in ash concentrations.

The pilot-scale 160 kWth furnace was fired under two different configurations: single stage and two-stage.

NO and O2 concentrations were monitored throughout the experiments. Similar experiments were conducted on the full-scale furnaces. NO concentrations were measured at the boiler outlet prior to the air preheater. The study showed no clear correlations between coal type and carbon in ash content. This was probably due to inherently good coal burnout in the furnaces studies, making differences in burnout between coals smaller. Moreover, the 1-D combustion and radiation heat transfer model for solid fuels was able to predict the temperature profiles in the boilers reasonably well without any fitting parameter. On the other
hand, the model failed to correctly predict the influence of coal quality on the temperature profile. This was partly due to the oversimplification of the mixing pattern and volatile combustion model, and partly to variation in the radiation emission by particles and furnace wall with coal type. NOx predictions were not reported.

5.1.2 Use of 3-D combustion models

The effects of coal quality on NOx emissions from large pulverised coal fired furnaces were also investigated by Hesselmann and others (1997b), using a 680 MW power station in Hong Kong, using a high volatile Indonesian coal and a low volatile South African coal. Tests were performed on this furnace before and after retrofitting with low-NOx axial burners. NOx emissions were similar pre-retrofit with both coals, whilst the Indonesian coal produced significantly less NOx after retrofitting. Moreover, mathematical modelling using CFD was undertaken for both coals. According to the author, NOx emissions were well predicted for these coals, but the level of agreement between the model and the test data became progressively worse for the lower volatile coal. However, only two coals were tested in this study and thus it might be slightly misleading to assume this as being a generality of all low volatile coals. Thus it was concluded that further development of the model was required in order to be able to correctly predict coal quality effects for a range of coals fired in large utility plants.

More recently, the effects of coal quality on NOx emissions and LOI were investigated by O’Connor (1999), using various coals, fired in pilot-scale and full-scale utilities. A model that could calculate the detailed temperature and chemical composition within the furnace, together with the data on the chemical kinetics affecting both NOx production and char burnout, was required. Only four coals were used for this study, so it was not possible to develop or test a correlation based on generic coal properties. The simplest NOx model was to use proximate volatile matter and nitrogen content to model NOx. This approach could be made more accurate if a correlation based on high temperature volatile yield was used instead of the proximate. Furthermore, a more detailed model would need to include char and volatile nitrogen conversion efficiencies. However, a larger number of different coals would be required for testing the model and to improve its accuracy.

5.1.3 Coal quality impact CFD model-FLASHCHAIN™

Niksa (1995) developed a commercial software known as FLASHCHAIN™ to assess the impact of coal quality on NOx emissions during pulverised coal combustion. The input required for the software is:
- coal properties (proximate and ultimate);
- performance of the current coal load, O2, NOx and LOI;
- boiler information, for example, firing type;
- alternative coal properties (to assess the effects of coal change on NOx emissions or if working with a blend).

According to Niksa and Cor (1997), FLASHCHAIN™ does not require an extensive laboratory support to define its input data. A Windows® based software, to assess coal quality impacts on NOx and LOI was developed by EPRI (Niksa and others, 1999a; 1999b). This NOx LOI Predictor, which also incorporates the FLASHCHAIN™ submodel for devolatilisation and fuel-nitrogen release, apparently does not address many design considerations, such as, how adjusting burner settings would affect emissions from the coal.

As seen earlier, many studies have attempted to relate NOx emissions to coal quality using coal properties determined from proximate and ultimate analyses (O’Connor, 1999; van der Lans, 1998). However, although these depict the correct qualitative trends, according to Niksa (1999), they have not able to predict NOx within useful quantitative tolerances, for a number of reasons:
- NOx emissions depend on operating parameters and on fuel properties – these two parameters are difficult to separate;
- the proximate analysis might not be relevant because it does not represent the extent of devolatilisation under the rapid heating conditions in large flames.

Furthermore, the volatile yield and nitrogen released during coal combustion are different to those measured by proximate analysis. This difference may have a substantial impact on NOx formation mechanisms. Although the algorithms of the NOx LOI Predictor are still correlation based, a method more representative of rapid combustion was used to obtain devolatilisation rates. Thus a high heating rate device such as a DTF was used. The FLASHCHAIN™ model was chosen for the development of the NOx LOI predictor because it has proved to be very successful in accurately predicting volatile yield and volatile nitrogen evolution and the retention of nitrogen in the char (Niksa, 1997). It can also resolve the nitrogen partitioning among char-N, tar-N and HCN. The NOx LOI Predictor was able to successfully forecast the changes in emissions when new coals were fired.

FLASHCHAIN™ has also been used to predict coal quality impacts on near burner coal flame phenomena (Niksa and Cor, 1997) as well as predicting the compositions of fuels that actually burn in the pulverised coal flame (Niksa, 1999). The latter includes soot formation via a secondary volatiles pyrolysis (which are in turn produced during primary devolatilisation of the coals). In this case tar (a primary devolatilisation product) is converted to soot, whilst all gaseous hydrocarbons are converted to CH4 and C2H2. Soot may be considered as the slowest burning component in pulverised coal combustion (Niksa, 1998).

5.2 Chemistry modelling

A number of chemical pathways and reaction mechanisms are involved during NOx formation and NOx reduction as seen previously in Chapter 3. The De Soete NOx formation mechanism (De Soete, 1975) has been used by a number of modellers as a basis for all systems, despite the fact that it has been accused of being too simplistic (Visona and Stanmore, 1999b) and should be used with caution (Pedersen
and others, 1998). Visona and others (1995, 1996) developed the nitrogen chemistry model, during which more emphasis was made on the precursors of NOx from the volatiles and on different models for the conversion of char nitrogen to NO. Details of the kinetics of the gas-phase (homogeneous) reactions involving NO, HCN and NH₃ were later reported (Visona and Stanmore, 1999a).

Recently, Pedersen and others (1998) presented a chemical engineering model for NOx formation. According to the authors, some assumptions were made, which were not experimentally confirmed. For instance, the type of char-N species released was not resolved. However, HCN formation was measured during char combustion, confirming the results of De Soete (1990). Nelson (1996) suggested that char-N was probably released as HNCO, NCO or CN. Although the formation of HNCO during devolatilisation has been measured, that of CH and NCO radicals is less obvious (Nelson, 1996).

Similarly, a number of modellers have proposed various models for NOx destruction/reduction by reburn. Alzueta and others (1998) developed a reburn model, using C₁ (CH₄ for instance) and C₂ (for example C₂H₅) hydrocarbon as reburn fuels. Modelling predictions and pilot-scale experiments were in agreement with each other. The model was also used to assess the potential of the reburn process at low temperatures (1300 K) and to provide guidelines for process optimisation. Results showed that the low temperature gas reburn process has a significant potential for NO reduction. Low temperature reburning has also been studied by Bilbao and others (1997). Most CFD work is geared to the modelling of NOx reduction as will be discussed in the following sections.

5.2.1 Reburn modelling

Earlier work undertaken by Miller and Bowman (1989) also attempted to use CFD codes to model NOx reduction by reburning using a mathematical expression for the formation and reduction of the NO and NH₃ which was then integrated in a CFD code. To account for the effects of CO, the authors used an empirical effective temperature $T_{eff}$ rather than the predicted temperature in the rate expressions as follows:

$$ T_{eff} = T + S(CO) $$

(23)

where the source term $S(CO) = 17.5 \times \ln([CO]) - 68.0$, and [CO] is the concentration of CO (Miller and Bowman, 1989). These expressions were obtained from curve-fitting to match predictions with the full mechanisms, using CHEMKIN. However, the model proved to be too specific to consider important factors such as the effect of O₂, CO and H₂O concentrations.

The chemical pathway of the reburning mechanism was previously explained in Chapter 2. Under fuel-rich conditions, the conversion of fuel-N to NO has commonly been observed to be incomplete. Several elementary reaction steps have been suggested by a number of investigators according to Chen and others (1996a). These steps include a ‘reburning-NO mechanism’, which can be globally expressed as follows:

$$ NO + C_{i}H_{j} \rightarrow HCN + \ldots $$

(24)

where $C_{i}H_{j}$ is the pool of gaseous hydrocarbon species. Mathematically this equation can be expressed as follows:

$$ \Sigma C_{i}H_{j} + NO \rightarrow HCN + \ldots $$

(25)

Chen and others (1996a) reported global rate expressions for the reaction above, for use in turbulent, diffusion flames, from predicted concentrations of species profiles using the CHEMKIN code.

The integration of the mechanisms of NOx reduction by advanced reburning in CFD codes has been reported by a number of workers. Moreover, from the comparisons with a full mechanism, Zamansky and others (1996) reported that these published full mechanisms still do not quantitatively describe experimental results due to insufficient understanding of reactions of NO and carbon-containing species. However, according to Zamansky the main reactions of reburning are as follows:

$$ NH_{3} + OH, O, H \rightarrow NH_{2} + \ldots $$

(26)

$$ NH_{2} + NO \rightarrow N_{2} + H_{2}O $$

(27)

Visona and Stanmore (1995, 1996) proposed an engineering approximation for the concentrations of the HC free radicals. The radicals were assumed to be either CH or CH₃. The concentration is based on the amount of volatiles released into a computational cell. For instance, if the amount of volatile matter released gives a fuel-rich mixture, then a reburn reaction (CH + NO or CH₃ + NO) is assumed to occur. The concentration of these HC radicals is assumed to be some fraction of the concentration of volatiles in the fuel-rich computational cell which was determined to be 1.0, for simplified NOx chemistry. This value produced the best result for the modelling of premixed coal flames. Fractions of less than 1 did not produce the required reduction in exit NOx concentration in fuel-rich mixtures. During a previous study conducted by Chen and others (1996b), the ratio of the concentrations of HC radicals and inlet HC was approximately 1:25. However, the use of this ratio produced very small reburn effects and did not fit the simplified NOx chemistry proposed by Visona and Stanmore. Moreover, these authors assumed that the NH radicals had the same concentration as NH₃ (Visona and Stanmore, 1999a). Furthermore, thermal NOx was not modelled, because synthetic air, which was a mixture of oxygen and inert gas was used as oxidant for all the experiments reported by the authors.

Recently, an advanced NOx model was used to predict NOx emissions from air-staged and fuel-staged combustion of pulverised coal, during which methane and coal were used as reburn fuel (Förtsch and others, 1998). An Eddy Dissipation Concept was used to model the interaction between chemistry and turbulence. The NOx formation model included different stages of combustion such as primary pyrolysis, secondary
reactions of tar, soot and char burnout. Each of the pyrolysis products contain nitrogen, the distribution of which depends on the functional groups within the coal, the coal properties and pyrolysis conditions. The authors suggested that tar nitrogen was released as HCN during secondary reactions as seen in Figure 1(d) in Chapter 2. In the modelling approach, char and soot are released as highly reactive intermediates. Certain assumptions were made, namely that the rate of volatile nitrogen released was assumed to follow the rate of primary pyrolysis. Moreover it was also assumed that the decay of NH radicals was infinitely fast. The 3-D CFD code included submodels describing the flow field, heat transfer by radiation and the proposed combustion and NOx model. Turbulence was solved by the standard k-ε model. The 3-D CFD model was, however, validated using a bench-scale rig and not at full-scale. Results suggest that experimentally determined measurements of NOx agreed with predicted values. Overall, the predicted and measured NOx concentrations were in agreement from air-staged and fuel-staged combustion of pulverised coal where methane and coal were used as reburn fuel. However, some discrepancies were observed especially near the injection point of burnout air and in the near-burner region. The NO reduction at the near-burner appeared to be over-predicted. Furthermore, an over-prediction of the NO concentration was observed near the injection point of burnout air, whereupon oxidation of the char nitrogen occurred. Under reducing conditions during reburn, the NO released from oxidation of char nitrogen, may be reduced to molecular nitrogen. However, this was not modelled, thus possibly accounting for the difference in predicted and measured NO concentrations.

Han and others (1999) presented a two stage Lagrangian model (TSL) to simulate advanced reburning processes in a practical furnace. This model includes the full chemical kinetic elementary mechanisms and accounts for the effects of turbulence on the reactions. However, this model is quite limited since certain equations are not solved. Thus this model cannot be generally applied to many possible advanced reburning process configurations and conditions.

5.2.2 Coal as a reburn fuel

Østberg and others (1998) also presented a coal reburning process, which is based on a kinetic model for the gas-phase reactions as well as some important heterogeneous reactions. These reactions include the devolatilisation of the coal (thus producing char and soot) and subsequent char and soot oxidation, NO reduction on the char and soot surfaces, and radical recombination on the soot and char surfaces. The model was validated against bench- and pilot-scale data from the literature. Use of natural gas as a reburning fuel has received much attention on full-scale furnaces, whereas little has been reported on coal as a reburning fuel, despite the similar efficiencies in reducing NOx.

This model was developed to analyse and extrapolate bench- and pilot-scale reburning results and to evaluate the suitability of various coals as reburning fuels. The aim was to predict NO reduction with respect to coal types (as reburn fuel) and process conditions. Moreover, this model was used as an optimisation aid. The model involved a detailed description of gas-phase chemistry and simplified devolatilisation, mixing and heterogeneous gas/solid mixing. However, this model was validated by comparison with bench and pilot-scale data only from the literature, not from experiments conducted by the authors.

According to the authors, the model produced good results of reburn, with gas and coal but underestimated the reduction of NO obtained with char and lignite coal as reburn fuels. The results also showed that for the bituminous coals used, soot was important in reducing NO as well as reducing the concentration of free radicals as a result of reactions on the soot surface. However, the weakness of this work lies in the fact that no experimental validation was attempted by the authors, who relied on literature data. It might be desirable to conduct experimental work for validation.

Coal reburning modelling was also recently undertaken by Morgan and others (1998), using a 2.5 MW semi-industrial IFRF single-swirl burner. The reburn coal injector of the furnace had initially been designed using FLUENT. The injector was designed to provide an even distribution and adequate penetration of the reburn fuel, into the primary zone products. The effects of coal-over-coal reburn were investigated at three reburn fuel fractions (10, 20 and 30%), with varying stoichiometry (0.6 to 1.16), using two coals (with different volatile matter content).

Overall it was concluded that coals with high volatile matter content and high char reactivity were more effective as reburning fuels. Similar conclusions were made by Hampartsoumian and others (1995). It was suggested that higher volatile matter content promotes the formation of CH radicals necessary to reduce NOx (Morgan and others, 1998). The investigation stressed the importance of maintaining sufficient hydrocarbon radicals to reduce NO during reburning. However, further research is required to investigate whether the mixing of hydrocarbon radicals and the primary zone NOx would result in lower overall NOx emissions.

A similar study was also undertaken by Yang and others (1998), using a smaller capacity pilot-scale furnace (0.2 MW). A mathematical model was developed to investigate the sensitivity of the reburning process to the devolatilisation behaviour and mixing rates of the reburn coal. The model considers the main NO reduction pathways using a global chemistry approach such as hydrocarbon fragments, volatile fuel-nitrogen species and heterogeneous NO reduction by char particles. The predicted and experimental results showed that increased volatile yields and faster devolatilisation rates lead to improved NO reduction, as observed by various co-workers (Morgan and others, 1998; Williamson and others, 1998).

The modelling of coal over coal reburn was investigated by Hesselsmann (1997), Hesselsmann and others (1997b) and Hesselsmann and Chakraborty (1998) using a 160 kWth pilot-scale combustion plant (NRTF), using Polish and Illawarra coals. The investigations comprised studies on the
effects of stoichiometry and residence time to provide basic process design information, fineness, reburn coal fraction and the quality of the reburn fuel (use of a variety of coals compared to natural gas). The optimum reburn stoichiometry was established at 0.9. It was found that very long residence times did not make much difference to the overall reburn efficiency since gas phase reduction reactions normally occur on relatively short time scales. Coal fineness did not have significant impact on NOx. The quality of the reburn coals did not have much impact on the overall NOx emissions and thus it was concluded that the quality of the primary coal was more important than that of the reburn. More importantly it was seen that the overall efficiency of NOx reductions of natural gas reburn was similar to that of coal reburn.

The use of coal-over-coal reburn was then extended to a 630 MWe opposed wall fired plant (Hesselmann, 1997), as well as a 600 MWe plant and a 320 MWe power station (Hesselmann and Chakraborty, 1998). The furnace was modelled using FLUENT code, to determine the optimum arrangement of reburn injectors and OFA ports. It was concluded during the course of this study that process information obtained during pilot-scale testing was successfully applied to the utility plant. The experimental data obtained were used to optimise the performance of the reburn installation in the full-scale plant and hence a standard coal-over-coal reburning design was produced based on the modern 630 MWe furnace. It was also found that the reburn process was more efficient than furnace air-staging normally used in LNB. This was due to the combustion of the primary coal in a relatively oxygen rich atmosphere, which in turn is more beneficial in that less aggressive conditions prevail in the furnace causing less wall corrosion. Overall the use of CFD was, according to Hesselmann (1997) and Hesselmann and Chakraborty (1998) successful in optimising the full-scale utility, using process information from pilot-scale data.

5.2.3 Reduced reaction scheme for NOx formation during reburn

Pedersen and others (1998) developed a reduced HCN/NH3/NO model, applicable for modelling pulsed combustion. The authors deemed it necessary to have an adequate description of the CO/H2 chemistry to be able to model HCN oxidation and hence NO formation. For this purpose, two reduced CO/H2 models were developed, one including eight active species and the other with six active species (a three-step model). These gave good predictions of CO formation. The HCN oxidation model developed included HCN, NO, NH3 and N2, as active species. According to the authors, the reduced model showed very good agreement with the detailed chemical kinetic model used for pulsed coal. However, comparison of HCN oxidation models from the literature and the one presented by Pedersen, showed that the prediction of HCN and NO formation were different from each other. Most of the models presented in the literature included the same number of active species. The main difference to the one presented by Pedersen was the much shorter computational time to calculate the reaction rates. Recent work carried out by Xu and others (1998), involved the computational modelling of NOx reduction by advanced reburning (hydrocarbon followed by ammonia), using the CHEMKIN combustion code. These authors postulated a seven-step and 11 species reduced mechanism for the prediction of NO concentrations for advanced reburning, during which NH3 was injected. These main seven reactions used in the mechanism are as follows:

1. \( \text{H}_2 + \text{O}_2 \rightarrow 2\text{OH} \)
2. \( \text{O}_2 + 2\text{CO} \rightarrow 2\text{CO}_2 \)
3. \( \text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \)
4. \( \text{O}_2 + \text{N}_2 \rightarrow 2\text{NO} \)
5. \( \text{H}_2 + \text{O}_2 + \text{CO}_2 + \text{NO} \rightarrow 2\text{OH} + \text{CO} + \text{NO}_2 \)
6. \( \text{H}_2 + \text{O}_2 + \text{CO}_2 + 2\text{N}_2 \rightarrow 2\text{OH} + \text{CO} + 2\text{N}_2\text{O} \)
7. \( \text{OH} + 2\text{CO} + 3\text{NO} + \text{NH}_3 \rightarrow 2\text{H}_2 + \text{O}_2 + 2\text{CO}_2 + 2\text{N}_2 \)

According to the authors, the predictions of the above seven-step reduced mechanism were in good agreement with those of the full mechanism over a wide range of parameters applicable to coal, gas and oil combustion. The major equilibrium species required for the combustion code are \( \text{H}_2\text{O}, \text{CO}_2, \text{N}_2, \text{O}_2 \) and CO. The other six remaining species which are NO, NH3, H2, NO2, N2O and OH, are non-steady species. NO and NH3 are very dilute species. However, during the determination of the concentrations of certain species, it was shown that the partial equilibrium or steady-state assumptions made were not adequate (Xu and others, 1998). Furthermore, the partial equilibrium assumptions made for O2 and CO at low concentrations could induce errors in the final calculation. Nevertheless, it is possible to calculate the concentrations of these species using a species-continuity equation, but this would take a considerable amount of computational time.

More recently, Xu and others (1999b), developed a simpler reduced mechanism to reduce the otherwise long computational time involved in the seven-step mechanism. A simpler four-step, eight species (\( \text{CO}_2, \text{H}_2\text{O}, \text{N}_2, \text{O}_2, \text{NO}, \text{NH}_3, \text{CO} \) and OH) mechanism was developed. This method proved to be in reasonable agreement with the skeletal mechanism. The authors also reported that the model was in agreement with three independent sets of experimental data, which showed the influence of CO concentration, O2 concentration and the ratio NH3/NO. This revised four-step mechanism was integrated in a CFD code known as PCGC-3, which also contained the thermal NOx (Boardman and Smoot, 1993; Smoot and others, 1993), fuel NOx (Smoot and others, 1993) and finally, reburning NOx submodels (Chen and others, 1996a). The equilibrium values for three species, namely, \( \text{CO}_2, \text{H}_2\text{O} \) and \( \text{N}_2 \) were used. Species conservation equations for \( \text{OH}, \text{CO} \) and \( \text{O}_2 \) were solved, and combined with species continuity equations for NO and NH3. This advanced reburning submodel was activated immediately upon the injection of NH3. The model calculations for turbulent coal combustion cases show that the advanced reburning submodel integrated with the PCGC-3 code gave realistic predictions. The predicted impacts of temperature, CO, O2 and NH3/NO ratio on advanced reburning were apparently consistent with observations based on laminar flame mechanism studies, earlier undertaken by Xu and others (1998).
5.3 Burner and furnace designs

To meet the increasingly stringent legislation, plant operators are having to purchase new equipment to reduce NOx emissions. All these techniques require large capital investments and so operators are faced with the dilemma of analysing the most effective solutions for their unique situations. As a result most operators have opted for conducting numerical simulation analyses such as numerical combustion and numerical flow distribution studies by CFD.

According to King and others (1996) numerical simulation of boiler systems has advanced to the point where the best 3-D CFD models can provide considerable information and can be used to carry out design studies for the optimisation or improvement of combustion efficiency, emissions, corrosion and erosion damage, heat transfer, slagging, fouling and flow distribution. Furthermore, CFD modelling is extremely cost effective, both when applied to upgrading existing hardware and when used to provide independent and objective assessment of new equipment installation. The comparison between experimental and computational techniques for the design of LNB was undertaken by Ahmed and others (1994), using FLUENT. The study proved useful in prompting greater understanding of the complex mechanisms, hence leading to improved burner designs. More recently, Moyeda and others (1999) assessed a LNB design and operation for a coal fired utility, using FLUENT code. According to the modellers, FLUENT offers an extensive set of physical and chemical reaction models for the simulation of pulverised coal 3-D flows. Moreover, FLUENT provides maximum flexibility to efficiently tackle complex 3-D geometries, due to its unstructured meshing capabilities. The design of the LNB provided effective air-staging into the flame during the combustion process. This staging allowed for coal devolatilisation and subsequent release of fuel-bound nitrogen to occur under fuel-rich conditions, hence resulting in low NOx emissions. Moreover, the burner design provided good control over flame shape and length during initial optimisation, but also did not cause any flame impingement on the wall. NOx emissions from the LNB were <0.45 lb/million Btu (269 ppm).

5.3.1 Application of CFD for optimisation

Numerical modelling has successfully been used to design a LNB for utility burners, as well as assess the effects of modifications of the combustion process and pollutant formation (Del Taglia and Gass, 1999; Epple and others, 1995). The model used by Epple and others (1995) was developed by Fiveland and Latham (1993). This model was first used to design the LNB for a pilot-scale furnace. Successful results proved that the novel design could also be used on a full-scale utility.

Del Taglia and Gass undertook the optimisation of a 450 kW combustion chamber, using CFD simulations. Apart from the pollutant models, the model included combustion models (which is a modified Eddy Dissipation Model) and thermal radiation and temperature dependent heat capacities, which would help improve accuracy. Based on the experimental and numerical results for that chamber, four modified geometries were proposed, and analysed by numerical experiments. However, results showed that an improvement in one parameter lead to the degeneration of another. For instance, a variation in residence time that could lead to NOx reduction, could cause an adverse effect on CO emissions. However, two design modifications were made which lead to an improvement in NOx emissions by:

- introducing a heat exchanger in the combustion chamber at a suitable distance from the burner; and
- collecting flue gas exiting the chamber bottom using a plane bottom. Normally a round bottom (shown in Figure 10) near the outlet of the combustion chamber is adopted in order to collect gases and to prevent flow instabilities in the outlet region. In the simulations, the round bottom was replaced by a plane bottom which is more economical to construct.

However, it remains to be seen whether these modifications would be effective for a full-scale utility.

Multiburner systems

Epple and others (1995) used CFD codes to simulate pulverised coal combustion in two full-scale plants: 490 MW and 150 MW. The comparison between measured and predicted data indicated reasonable results for unstaged and air-staged modes. The aim of the project was burnout improvement in a coal-fired furnace with six swirl burners. The burnout air nozzle was optimised to enhance the degree of burnout. The predicted NOx emissions were in agreement with measurements.

Moreover, a new strategy for modelling multiburner furnaces was investigated by the authors. The near-burner zones were modelled using finer grids, whilst the rest of the furnace was modelled using coarser grids. This method allowed local grid refinements close to the burners enhancing the accuracy of the important burner details. This operation proved cheaper than if the furnace were to be uniformly decomposed into a single grid. This method could also be extended to more complex burner arrangements, such as tangentially-fired combustion systems. Furthermore, the simulation process
CFD models were also used to explore the influence of burner spacing on NOx emissions (Azvedo and others, 1999). Modelling results showed that reducing the burner pitch below two burner diameters led to a sharp increase in NOx with four burners in the test rig used.

**Improved fuel-air mixing**

According to Pitsko (1997), three of the coal fired plants operated by Southern Company’s Georgia Power Co. subsidiary began optimisation programmes to improve plant efficiency following the installation of LNB. Plant operators believed that improved air mixing to the pulveriser mills would enhance performance. Thus engineers at the Southern Company Services Inc (SCS) started investigating the use of thermal mixers and flow straighteners to improve mill flow characteristics. Computer simulations and CFD were extensively used to accelerate the development efforts and optimise the mixer design, so as to prevent the risk of fire (caused by localised ‘hot spots’) during the drying of the coal. The aim of the optimisation of mixing was thus to reduce thermal gradients and hence the formation of localised ‘hot spots’ in the air supplied to the pulverisation mills and improve the operating efficiency of the plant. Live tests would have been far too time consuming, costly and involved shutting down of the plant. Thus CFD was used to simulate different mixing arrangements of the mill.

The analysis of the CFD results led to the conception of a new mixer design to improve mixing. This new design consisted of rectangular strips across the face of the cold and hot air ducts, thus dividing the airflow into slices. Increasing the surface area between the cold and hot air minimised turbulence and hence improved air mixing. CFD simulations showed that increasing the number of slices produced improved thermal mixing. To optimise the design of the new mill, additional CFD simulations were conducted with different parameters, such as turning vanes, and cold/hot air volume ratios in the mixer. The mill inlet ducts were consequently modified according to the design. Plant test results showed improved flow profile as well as a temperature stratification.

Weber and others (1998), undertook studies on the mixing of reburn fuel (which could reduce NOx emissions by up to 80%) with primary combustion-zone products. Natural gas was used as the reburn fuel. The mixing was controlled by reburn jet parameters, such as jet size (or diameter), momentum, injection location, number of jets and nozzle design. The aim of that study was to assess the ability of CFD for predicting the properties of these jets as well as to develop a methodology for scaling the results obtained for isothermal flows into combustion flows in full size boilers and municipal incinerators. CFD codes seemed to be the perfect tool for optimising the mixing. Simple fluid-flow simulations could be carried out, leading to proper selection of the nozzle geometry and injection momentum of the jets. For this study, the commercially available CFD code, FLUENT was used, whilst the experimental data were obtained from an IFRF furnace (wall-fired, 660 MW, 48 main burners in 4 rows) for studying flows in boilers and municipal incinerators. This boiler operated at 10% excess air.

The jet velocities and penetration were measured and compared with their corresponding simulated values. The velocities were measured at various traverse positions of the model burner namely at 270 mm depth, 180 mm depth, and 90 mm depth. This is shown in Figure 11. The results showed that the velocity profiles predicted were very similar for all traverses. On the other hand, the penetration depth differed by 5-12% from the experimentally observed trajectories. The authors presented a set of correlations for estimating the jet penetration depth under isothermal and combustion conditions. The measured and predicted values of penetration were in good agreement with one another in that case. However, it is important to note that each type of boiler has its own characteristic flow pattern resulting from a specific geometry, burner type and burner configuration, and also from burner load. Hence, when correlations are applied careful attention must be paid to the boiler flow pattern, which determines optimum positioning of the reburn-gas injectors.

**5.4 Validation of CFD modelling**

The evaluation of the quality of the predictions obtained from combustion models requires a level of accuracy from experimental measurements. However, the question to be asked is whether to use laboratory or full-scale experimental measurements for reliable model validation. Schnell and others (1995) suggested that 3-D modelling often lacks
detailed and symmetric evaluation due to the shortage of experimental data in large-scale boiler geometries.

Experimental research work requiring an in-depth understanding of pulverised coal combustion demands a test rig that is able to reproduce full-scale results. For this purpose, Schnell and others (1993) developed a 500 kW semi-industrial scale furnace, which apparently reproduced the combustion conditions in industrial furnaces. NOx measurements on the 500 kW furnace and predictions agreed with one another, but although this furnace reproduced full-scale conditions, no comparison was made between full-scale measurements and predictions. Moreover, only one type of coal, a German hard coal, was used for this investigation.

Gibb and others (1995) claimed that the combustion test furnace (CTF) was designed to provide a realistic simulation of combustion in real plants and should thus produce similar NO emissions. Reasonable agreement was apparently obtained between the CTF and full-scale utility under unstaged conditions. More recently, Gillespie and Hough (1999) used pilot-scale combustion results to complement CFD work in order to understand the performance of lower volatile Vietnamese anthracites in comparison with Chinese coal, with both approaches producing comparable results.

Schnell and others (1995) applied a general 3-D combustion code for turbulent reacting flows to simulate a semi-industrial (350 kW) pulverised coal combustion facility. After validation of the model using the semi-industrial furnace, the codes were applied to several full-scale furnaces with wall fired systems using swirl burners and tangentially-fired units for the combustion of bituminous and brown coal. These furnaces were equipped with LNB and multiple air-staging facilities. Promising results were obtained, although it was generally accepted that the model had some limitations and restrictions in the near burner and near-wall regions. Nevertheless, the model was able to replicate some experimental trends, although it was considered at the time that development work was far from complete.

On the other hand, O’Connor (1999) suggested that test rig data were more suitable than full-scale data for model validation, since results obtained from test rigs tend to be more accurate, due to the much smaller coal samples used. Similarly, Förtsch and others (1997) conducted experimental and numerical assessments of NOx reduction of various fired systems using swirl burners and tangentially-fired units for the combustion of bituminous and brown coal. These furnaces were equipped with LNB and multiple air-staging facilities. Promising results were obtained, although it was generally accepted that the model had some limitations and restrictions in the near burner and near-wall regions. Nevertheless, the model was able to replicate some experimental trends, although it was considered at the time that development work was far from complete.

Overall, it appears that many investigators are still of different opinions when it comes to using full-scale, pilot-scale or laboratory-scale experiments for model validation. Moreover, the creation of ideal sets of validation data for a wide variety of cases has not yet been fully realised (Eaton and others, 1999). Obtaining accurate data for model validation poses a number of difficulties and challenges, one of them being the harsh conditions of the combustion environment.

5.4.1 Laboratory-scale experimental data

The successful predictions of NOx concentrations requires the correct representation of fluid flow, heat transfer and NOx chemistry. In the absence of turbulence and a swirling burner geometry, the fluid dynamics inside a bench-scale, laminar DTF are comparatively simple. They can thus provide a test of the chemistry producing NOx without the flow modelling complications which otherwise arise in NOx predictions in industrial flames. The use of the DTF has thus proved to be popular amongst a number of modellers such as Visona and Stanmore (1999a), Conn and others (1995) amongst others. However, one complication arises in the modelling of DTF due to the release and concentration of coal particles along its vertical centerline. Brewster and others (1995) showed that comparison of experimental data from a DTF and a two-dimensional axisymmetric model were as follows:

- for a fully laminar flow within the furnace, the predicted NO concentration tended to be lower than measured (70 ppm vs 170 ppm); whereas
- a laminar turbulence model overestimated NO concentration (270 ppm versus 170 ppm).

Although the furnace is designed for laminar flow, the study concluded that in terms of NOx formation the influence of turbulence needed to be considered in the model.

Other laboratory-scale furnaces included the 0.2–0.4 MW Controlled Profile Reactor (CPR) which was used by Tree and others (1998) to obtain data for model validation. Measurements obtained include, particle velocity, radiation, gas temperature, concentration measurements of gas species (including NOx, HCN and NH3 amongst others), wall temperature, etc. Gas temperature was measured using a novel instrumentation technique, Coherent Anti-Stokes
Raman Spectroscopy (CARS). According to Tree and others (1998), the measurements have led to an improved understanding of the combustion process as well as an understanding of the strengths and weaknesses of combustion models.

5.4.2 Comparison of full-scale, pilot-scale and laboratory-scale data

O’Connor (1999) presented NOx models for various coals and furnaces, ranging from bench-scale to coal-fired utilities (160 kWh to 500 MWe). One of the objectives of that study was to demonstrate the ability of mathematical modelling using laboratory-scale coal characterisation data to predict NOx in full size wall fired utility boilers equipped with LNB, and other more advanced NOx reduction techniques.

During this study, laboratory coal characterisation procedures (using a DTF and HTWM test rig) were coupled with combustion experiments over a range of scale to generate data for model validation. Models would then be able to accurately predict the NOx levels produced as well as the carbon burnout in a utility boiler. However accurate predictions require full-scale plant (40 MW single burner and 500 MW full-scale plant) trials to establish a baseline with a known coal. These tests were carried out to produce a set of comprehensive data to compare with mathematical modelling and characterisation data. Combustion studies at various scales were essential. All tests were performed using a LNB. Coal quality effects were also studied using a 160 kW pilot-scale plant. The objective of these tests was to generate data on the sensitivity of each coal’s NOx formation behaviour to combustion parameters, giving a set of data of gas flows, temperatures and compositions for model validation.

The results of that study concluded that:

- in contrast to large-scale plants, test rig data proved more suitable than full-scale power plant data for model validation and to assess coal quality impacts, since rig measurements tend to be more accurate than those made on full-size plants. In general, test rigs are able to pick up any slight differences between coals, due to the small amounts of coals used during the experiments. On the other hand, much larger quantities of coal are fired in a full-scale plant thus making comparisons between coals much more difficult;
- it was suggested that in order to confidently and accurately predict NOx emission from a coal, it would be necessary to use either a rig test, or possibly, a model of a rig test;
- there were significant coal quality effects on NOx at rig-scale which were successfully modelled. On the other hand, coal quality effects were less conspicuous on full-scale plants, due to added effects such as tramp air, non-uniform air or fuel split between burners. These cannot be measured accurately on full-scale plants, hence making them more difficult to model accurately.

5.4.3 Applications of CFD for the simulation of full-scale burners

CFD models have proved to be successful for predicting NOx emissions in full-scale utility boilers (Fan and others, 1998, 1999a; Liang and others, 1999; Visona and Stanmore, 1999a; O’Connor, 1999, Coimbra, 1994; Eppe and others, 1995). However, inclusion of certain parameters such as tramp air is deemed necessary to improve NOx prediction. Moreover, the accuracy of modelling predictions of utility boilers is limited by uncertainties in the plant conditions that are difficult and expensive to measure (Eaton and others, 1999). For instance, it is nearly impossible to measure some important plant boundary conditions, such as the location and quantity of tramp air. These uncertainties have, however, been accounted for by their impact on measured NOx levels and unburnt losses. NOx predictions using CFD for a full-scale plant were generally accurate to about 10% and within the range of experimental error, in most cases, according to O’Connor (1999).

Fiveland and Weasel (1991) successfully modelled the formation of NO in a 1.76 MW test furnace. This consisted of four conventional swirl burners and two pairs of LNB cells. Equations for mass, momentum, energy and turbulence were solved using a Favre averaged form of the 3-D flow equations. The standard k-ε equation was used to model turbulence. Particle flow was modelled using an Eulerian approach. Chemical reactions were assumed to be very fast. The combustion rate was controlled by turbulent mixing using the EBU concept. Radiation was also modelled and a De Soete mechanism for HCN and NO formation was adopted. Thermal NOx was considered whilst prompt NOx was ignored. CO was also modelled as the authors proposed that the incorporation of CO in a NOx model was important, due to its importance in correctly modelling the oxygen concentrations and gas temperatures. The model further assumed that all the fuel nitrogen, including char nitrogen, was released via HCN. Using a very simple chemistry Fiveland and Weasel achieved remarkably good NO predictions in the LNB and the standard burner configuration. This work was extended to a 605 MW opposed fired boiler.

Coimbra and others (1994) simulated the formation of NO in a 300 MW front wall fired boiler. The model solved the full set of transport equations (mass, momentum, energy and k-ε), but unlike the model proposed by Fiveland and Wessel (1991), the particle trajectories were modelled using
Lagrangian particle dynamics. Eddy dissipation model was used to solve for volatiles, O₂ and CO₂. Fuel NOx was also modelled using the De Soete model (1975), whilst thermal NOx, prompt NOx and char/NO reduction were ignored. It was assumed that both char and volatile fuel nitrogen were released as HCN, and that the nitrogen was equi-partitioned between the volatiles and char. The results suggested a good agreement between measured and predicted NOx. Again this work apparently showed that it was possible to produce good predictions of NOx using very simple NOx chemistry. Similar results have also been obtained by Visona and Stanmore (1996) who used NOx chemistry that included hydrocarbon reburn and NH₃ to model a 275 MW front wall furnace (40.3 m high x 12.9 m wide x 9.2 m deep). More recently Visona and Stanmore (1998b) presented results of a predictor that combines fuel nitrogen conversion and furnace flow models. In order to test the performance of the NOx predictor, seven Australian coals were used. The units modelled ranged from 120 to 660 MW, with various firing configurations that is, front and opposed wall and tangential firing systems, using a variety of bituminous coals. Detailed evaluation was also made using axisymmetric test results obtained from the IFRF. This showed that good predictions were produced for simple boiler configurations but performance was variable in more complex boiler environments. This led to the conclusion that CFD models cannot be considered as reliable. According to Visona and Stanmore (1999b), the gasification mechanism of char nitrogen represents the highest area of uncertainty in CFD simulation. The aim of this work was to evaluate the current generation NOx model developed by Visona and Stanmore (1998a) as a generalised predictor over a range of boilers. A model developed by Boyd and Kent (1986), which consists of more efficient algorithms was used. This model is apparently faster than other multipurpose codes (such as FLUENT). 100,000 to 250,000 grid cells were used. The model developed by Visona and Stanmore consists of NO, NH₃ and HCN as well as seven other reactions (see Chapter 2). Seven different boilers were modelled, and the results showed that the model was sensitive to coal properties and firing configurations. For instance, the predictions of a 24 burner wall fired boiler were in good agreement with measured values. This was not the case with a BOOS boiler.

**Effects of swirling in the near burner zone**

One of the most important parameters to influence NO formation is the aerodynamics in the near burner zone. This suggests that reasonable NO modelling results can be obtained by modelling a single burner, as long as the boundary conditions can be estimated to produce the correct flame shape and temperature. According to Visona and Stanmore (1996), reasonable NO predictions may be obtained from the modelling of a single standard swirl burner (since most NO is produced at the near-burner field), provided that the appropriate boundary conditions may be estimated to produce the correct flame shape and temperature.

Recently, Visona and Stanmore (1999b) presented results of the simulation of the near-burner behaviour of full-scale burners on a 350 MW opposed-wall fired furnace, using De Soete NOx kinetics together with hydrocarbon reburn and NH₃ chemistry. Three burner designs were considered in this work: a conventional duel-register circular burner, the same burner without the spreader, and a LNB. According to the authors, the simulated NO profiles consisted of finer features than the actual measurements as shown in Figure 12. Moreover, accurate predictions were obtained. Modelling was most accurate with the inclusion of the reburn chemistry mechanism. The simulation of full-scale burners has been complicated by the presence of swirl burners, as finer grid meshes are required to obtain a reasonable result in the near burner zone. This is why more modelling work has been carried out on simple burner geometries such as tangentially-fired furnaces as opposed to more complicated ones.

Mathematical simulations of a swirling pulverised coal flame of 2 MWth input were performed by Breussin and others (1996) and compared with in flame measurements. The flame was a low NOx type characterised by a fuel jet penetrating through the swirl induced reverse flow zone (IRZ). The computations were undertaken using Renormalisation Group Theory-k-ε, (RNG-k-ε) and Reynolds Stress (Transport)

![Figure 12](Visona and Stanmore, 1998b)
Model (RSM) of turbulence in order to examine their potential for predicting the near burner zone flow field of Type-1 flames. The following were concluded from this investigation:

- the flow pattern was better predicted using the RSM. The k-ε and RNG-k-ε failed to predict the jet penetration;
- the flame length and volume, the near burner zone temperatures and oxygen concentrations were directly affected by jet penetration. The RSM predictions were in good agreement with the experimental measurements, whilst on the other hand the other two models predicted too short and too intensive flames;
- the physical size of the fuel-rich region and subsequent NOx predictions appeared to be strongly dependent on the calculated jet penetration. The failures in predicting properties of the fuel-rich zone while using either the k-ε or the RNG-k-ε model, resulted in excessive NO flue concentrations.

Effects of OFA

Three situations have been studied by Visona and Stanmore (1996) as follows:

- standard burner configuration without OFA;
- standard burner configuration with OFA;
- long flame.

Figure 13 shows the velocity patterns of the different cases. In the case of 13(a), that is without OFA, there is a considerable external recirculation zone (ERZ) above the burners. When OFA is introduced, as in 13(b), the amount of air to the burners is reduced, thus reducing the strength of the ERZ. OFA penetrates about 60% of the width of the furnace, and hence forces the main flow of the burners towards the rear wall. As a result of the jet effect of the OFA, an additional ERZ is induced above the jets. Hence the lower axial momentum in case 13(b) gives longer residence time for the particles in the main burner belt.

Figure 14 shows the particle trajectories in the furnace (Visona and Stanmore, 1996). In cases 14(a) and 14(b), the smaller particle size fractions tend to burn close to the firing wall. However, this is not the case with the long flame 14(c). The 20 µm particles penetrate over half the width. In cases 14(a) and (b), oxygen is consumed very rapidly near the burner exit as suggested by the contour data. With the longer...
flame on the other hand, there is less rapid mixing of the pulverised coal particles and the air, leading to higher oxygen concentrations in the middle of the furnace. In this case, oxygen values are as high as 13%, whilst the oxygen levels in the swirl-burner cases (that is with or without OFA) are not more than 6%. The findings of this investigation suggest that modelling was able to predict the correct NOx trends. In the case without OFA, the measured NO value at 7% O2 was \( \approx 1052 \) ppm, whilst the predicted value was 1000 ppm. The predicted value of NO in the long-flame case was \( \approx 626 \) ppm, whilst the measured value was \( \approx 635 \) ppm. With OFA, a NO reduction of 15% was obtained, whilst the predicted value was \( \approx 5\%\). According to the authors, NO predictions were better with subbituminous coals than with medium volatile coals. Thus NO modelling prediction techniques are very selective, implying that a model which works for one coal type might not work for another. Moreover, when the medium volatile coal was fired using a more advanced NOx reduction technique such as BOOS and the use of a long flame, NO predictions were considerably improved.

Application of CFD modelling to a tangentially-fired unit

Tangentially- and wall-fired units fitted with LNBs normally give roughly similar NOx emission levels. NOx reduction is achieved by the same basic principle of air staging in both cases, so the techniques applying to wall-fired will be applicable to a tangentially-fired furnace. As mentioned in earlier reports and in Chapter 2, tangentially-fired units rely on a fireball in the centre of the furnace to maintain flame stability, whereas wall-fired units rely on flame attachment devices. Thus the interaction between coal properties and burner aerodynamics will be different and hence would need to be treated separately. Coal particles behave differently in each of these units. Modelling of tangentially-fired units using CFD is relatively easier since the flame stability does not depend on external flame attachment devices as in the wall-fired units (Visona and Stanmore, 1999b). Hence a coarser mesh may be used for a similar size boiler. Overall, the detailed aerodynamics of wall fired units are different to tangentially-fired units and thus different tuning of test rigs and geometrically different mathematical models would be required.

Recently, a ‘no-cost strategy’ was developed for a tangentially-fired, 680 MWe South African coal-fired boiler using a 400,000 cell grid (du Plooy and others, 1999). Emissions data were collected for various loads, mill
combination and different levels of OFA for model validation. The study concluded that measured and predicted NOx values compared reasonably well with one another. The model can confidently be used to predict the effects of load, mill combination and stoichiometric conditions, according to du Plooy and others (1999). On the other hand, the model failed to predict char burnout. In general, the AIOLOS code proved to be reliable in predicting NOx for tangentially-fired plants with or without air staging. From this study, it was concluded that pseudo OFA (that is, without any plant modification) would be an effective option for NOx reduction in that particular South African plant, but according to the authors, pseudo OFA could lead to fireside corrosion and other problems.

Fan and others (1999b) developed a simplified post-processor NOx chemistry model in conjunction with a gas-particle fluid flow model as opposed to using a complex NOx chemical model, which could consist of a large number of reactions. This was then used to model NOx emissions from a tangentially-fired 600 MW coal-fired plant. The authors claimed good agreement between predicted and measured NOx.

### 5.4.4 Scaling properties

Peters and Weber (1994) developed a NOx post-processor for pulverised coal combustion, which was then validated with industrial-scale experiments. These results were then to be used to develop full-scale industrial burners. The difference of this model is that the modellers used an eddy-break up approach, as opposed to a k-ε. Moreover they did not use the De Soete chemical reaction mechanisms, which have been used by other modellers. A project known as SCALING 400 was then developed. However, this was relevant for gas combustion rather than pulverised coal combustion, but the theory should be the same for pulverised coal combustion.

Weber and Breussin (1998) investigated the scaling properties of swirling pulverised coal flames from a 176 kW to a 50 MW thermal input plant. The objective of their work was to provide guidelines for scaling of swirl-stabilised burners fired with pulverised coal, emphasising NOx emissions. The 50 MW furnace represented a full industrial-scale burner, whilst the 176 kW furnace represented a laboratory-scale burner. For the purpose of this study, two scaling methodologies were used namely, a constant velocity or constant residence time principles; at lower thermal inputs of the order of 2–3 MW, the NOx emissions decrease with thermal input. According to the authors, in order to obtain identical NOx emissions in a prototype experiment, carried out at a thermal input less than 1 MW, the constant residence time scaling would be recommended, and the pulverised fuel would have to be milled finer;

- both scaling methodologies were successful for low NOx penetration flames, over a range of thermal inputs. In that case, the key to NOx scaling was the localisation of the devolatilisation zone inside the reverse flow region.

According to the authors, these conclusions are valid for internally air staged burners where NOx reduction is achieved by interactions between the swirl-induced recirculation zone and the coal particles. In the prototype experiments certain parameters need to be kept constant. These are the burner confinement (defined as the ratio of furnace diameter to burner diameter) and the total heat extraction (ratio of heat extracted to thermal input). Small deviations from these would not affect the similarities between the NOx emissions of a full-scale and prototype furnace. However, larger deviations would cause discrepancies in the results.

Payne and Moyeda (1994) undertook scaling up and modelling of gas reburning, using a scale up methodology which involves the use of computational and physical models. A combination of physical and flow modelling was used, involving the construction of a $l_{10}$ to $l_{15}$ scale physical flow model of the full-scale boiler. The potential impacts of the reburn system on the boiler performance were then evaluated. This was done using furnace heat transfer models, which are used to predict boiler heat absorption and gas temperatures. The final step in the design process aimed at estimating the efficiency of NOx reduction by the reburn process. This was done in two ways:
- by using small-scale data – this would represent a theoretical reduction;
- by using a computational model of the reburn process previously developed by Wu and others (1992).

For the most part of this work, modelling predictions agreed with full-scale NOx measurements.

Gillespie and Hough (1999) undertook CFD modelling to validate design developments which included the assessment of alternative burner designs and the scale-up procedure to enable confident designs of 600 MWe furnaces.

### 5.5 Effects of using different CFD codes on NOx prediction

Eaton and others (1999) compared the predictive capabilities of the commercially available CFD codes, PCGC-3 and FLUENT. There are two major differences between FLUENT and PCGC-3. PCGC-3 is limited to rectangular mesh elements with a staggered-grid solution approach, whereas FLUENT uses a body-fitted coordinate mesh structure. The FLUENT mesh cells may be fitted to coincide with a curvilinear surface, whilst PCGC-3 mesh requires the use of
a stair-step approximation to fit the same surface. The other difference between FLUENT and PCGC-3 is that they both ‘use’ different methods to model radiation. During this study, only thermal NO production was considered. Figure 15 shows the difference between measured thermal NO and predicted thermal NO by FLUENT (Eaton and others, 1999). The predicted and measured profiles are not in agreement; measured NO values were around 40 ppm, whilst calculated values were about 16–18 ppm in the CPR. The difference is possibly due to the under prediction of the gas temperature near the burner, and since thermal NO is temperature dependent, it is not unexpected that the thermal NO is under predicted. However, no temperature measurements were made by the investigators to support this theory. It was also suggested that the higher NO measurement was probably due to the formation of prompt NO. Thus to improve the prediction of NO, a devolatilisation submodel was added to the existing one. This was designated as the FLUENT-CPD code. The PCGC-3 code also includes a two-step devolatilisation model. The three codes (PCGC-3, FLUENT and FLUENT-CPD) were compared and are shown in Figure 16 (for fuel-NO). Measured peak fuel NO was about 600 ppm near the centre line of the furnace, whilst the computed maximum was about 400 ppm in the same region. All three codes gave different results; however, the authors claimed that PCGC-3 was the best (axial distance 0.30 m).

Full-scale furnaces have additional complexities. The results are shown in Figure 17. Similar to the CPR, the FLUENT-CPD and PCGC-3 codes show completely different predictions, but the PCGC-3 code predicted NO to within about 60–80 ppm of the observed value of 500 ppm. On the other hand, NO values were very low with FLUENT-CPD. According to the investigators FLUENT and FLUENT-CPD...
data were similar and thus the FLUENT data were not shown. With more detailed measurements, it might be possible to identify the causes of differences between the predictions and measured data, and then improve calculations by both codes. A similar study was conducted by O'Connor (1999). O'Connor (1999) showed in his work that there were a few discrepancies between the various codes that were used. For example, for the NRTF rig, CFX and FLUENT codes had been used, and both predicted different flame shapes as well as different NOx performance, depending on coal kinetic parameters.

5.6 Commercial CFD codes

A number of software houses have developed commercial CFD codes. These are listed on the CFD Resources Online web on: www.cfd-online.com and on www.icemcfd.com. The list below consists of some of the major CFD developers in coal combustion. Further details on these codes may also be obtained from the worldwide web.

CFX – 3-D multipurpose CFD code developed by CFDS Inc. of AEA Technology, UK. This company is now a multinational with offices worldwide.

CINAR – developed by Prof F Lockwood and his research group of Imperial College is also focused on coal combustion. It has been used both in the UK and in Europe and is marketed by CINAR Ltd.

FLUENT – considered as being the leading CFD code and the company Fluent Inc is based in the US. The code incorporates a thermal NOx routine which gives good predictions for gas flames. It also incorporates a fuel NOx model for solid fuels, but according to Visona and Stanmore (1999a,b), this has not been successful.

PHOENICS – developed by Prof Spalding and is one of the first commercial CFD codes. The original PHOENICS appeared in 1981.

FLASHCHAIN™ – developed by NEA (Niksa)- predicts weight loss, the yields and weight percentages of nitrogen and oxygen in char, tar yields, yields of CO₂, H₂O, CO, HCN and non condensible HC gases.

Star-CD – developed by Computational Dynamics Ltd. Recently, National Power have evaluated the code.

NOx LOI Predictor – developed by EPRI. The software has recently been updated (Niksa and others, 1999a,b).

AIOLOS – developed by the IVD, University of Stuttgart, Germany – a 3-D coal combustion code for quasi-stationary turbulent reacting flows, based on a conservative finite-volume procedure.

FW-FIRES (Fossil fuel, Water-walled furnace integrated reaction and emission simulation) – developed by the Advanced Combustion Energy Research centre – a 3-D code which simulated furnace combustion, heat transfer and pollutant formation based on fundamental principles of mass, momentum and energy conservation.

PCGC-3 – Pulverised Coal Gasification and Combustion, 3 dimensional. This code is developed by ACERC of Brigham Young university. It incorporates submodels for all physical processes that are necessary for characterising a turbulent reactive gas flow with entrained particles.

5.7 Comments

CFD has been widely used in boiler designs, retrofits and optimisation. CFD modelling is far more cost effective than furnace testing for evaluating the effect of coal quality and furnace designs on NOx emissions. Most modellers have used 3-D models, but 1-D modelling has also been applied. The use of 1-D modelling is limited to simple cases. It is only valid for one dimensional cases or where reaction is taking place in one direction only. It cannot be applied to industrial combustors for good simulation. 3-D modelling is more accurate since three co-ordinates (x, y and z) are taken into account.

Model validation using experimental data is very important in order to produce reliable models. However, some modellers have resorted to bench-scale rigs for model validation whereas others have resorted to full-scale plants. Although it has been claimed that some bench-scale rigs such as the DTF are able to replicate full-scale furnaces, it would be advisable to use full-scale data for model validation, since the behaviour of coal at bench-scale and at full-scale is different.
CFD modelling has become a quick and cost effective method for predicting NOx emissions as well as assessing coal quality effects and plant design changes on NOx emissions without having recourse to more expensive plant trials. However, further work needs to be done to improve predictions as well as to obtain results in relatively shorter periods of time.

The following summarises the conclusions made on various aspects of CFD modelling.

**Simulation time and computational limitations**
Combustion models have combined features to account for the main physico-chemical interactions that occur during gaseous and in dilute-dispersed solid particle and droplet fossil fuel combustion processes such as in pulverised coal combustion. However, these submodels incorporated in combustion modelling do not have the level of complexity, accuracy and sophistication that stand alone submodels of the same phenomena have. Moreover, combustion models should be able to combine submodel sophistication with computational ability, that is, the combustion model should be made of submodels that can simulate the phenomena of interest in a reasonable amount of time. This may be achieved by simulating turbulence, coupled with finite-rate chemistry and complex reaction schemes. However, this is not possible at the present time due to hardware limitations. Thus most research in combustion modelling is geared towards the improvement of computational efficiency, as well as improving hardware and software and simulation techniques.

**Model validation**
Validation of the CFD models is an important aspect in evaluating how well the model predictions match the observations, both qualitatively and quantitatively. Many modellers have used full-scale or laboratory-scale furnaces to validate their models and most of them appear to have different views of whether full-scale data or laboratory-scale data are best. Some modellers are of the view that laboratory-scale furnaces are not only cheaper to use but are also easier to control, and thus ensure better accuracy throughout an experiment. However, the question one may ask is to what extent are such furnaces representative of full-scale utilities.

Due to the large number of variables and parameters in combustion models, it is difficult to identify the reasons for the lack of agreement between predicted and modelled values, when this happens. It has generally been agreed that CFD has many limitations as follows:

**CFD codes**
Different CFD codes seem to produce different predictions of the same furnace under the same combustion conditions. Certain codes seem to work better than others under different conditions.

**Turbulence**
Turbulence still remains a problem for modellers. Modellers in general would quite obviously claim that their particular model ‘works’, but to date a universal model, which would correctly predict, regardless of furnace configuration or coal type needs to be seen. According to Eaton and others (1999) the most popular k-ε method is inadequate particularly for strongly swirling flows.

**NOx formation and reduction**
Unlike SOx, NOx formation relies on a number of parameters, such as furnace configuration, coal type and volatile matter. A number of modellers still rely on the De Soete NOx (1975) formation reaction mechanism. This reaction route has been deemed too simplistic and thus erroneous. NOx formation is not as simple and straightforward as this reaction route suggests. As long as the formation of NOx is not well understood, it will be difficult to predict accurately its formation during pulverised coal combustion. The most suitable NOx model is probably one that considers all the main possible intermediates, such as nitrogenous species as well as tar and soot. The model proposed by Förtsch and others (1998) appears to be the most realistic. The Visona and Stanmore NOx model (1998a,b) is also quite elaborate but does not include the individual tar formation, but considers the formation of volatile matter (which would probably include tars). This might produce slight differences in the final CFD models. These new models still overlook many other reactions, such as the reduction of NO by soot or char nitrogen chemistry to give accurate fuel-N to NO conversion estimates. The char nitrogen chemistry can be solved by a combination of experimental testing to identify the conversion processes, and modelling to describe these processes. It might be possible in the future to reduce the complex interactions in the system to only one variable, for instance an effectiveness factor.

**Assumptions and limitations**
Operators are more interested in using simple and user-friendly as well as cost effective predictive models. The complication arises when modellers produce such simple models. In such cases, a number of assumptions would have been made, which could then jeopardise the reliability and accuracy of the prediction tool.

Despite the various limitations, the accuracy of CFD models continue to improve.

Overall, the following conclusions may be made:
- it is still too early and dangerous to rely solely on CFD. CFD needs to be used as complementary to physical experiments;
- CFD modelling is being used to design boilers and to make modifications to existing designs thus reducing the requirements for experiments and equipment manufacture and hence overall costs;
- CFD codes are being used by engineers and plant
operators to gain an insight into complex phenomena of a reacting flow and to perform more analysis on more design alternatives. CFD is providing increasing understanding of the effects of certain physical parameters on NOx emissions for instance.

**Future of CFD modelling**

CFD modelling as a whole is an invaluable predictive tool. But a universal code has yet to be developed which could work for different furnaces and different coals, without having to make too many drastic assumptions. To date, modellers have made a number of assumptions which may prejudice predicted values. One model could work for one furnace, but not necessarily for another.
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