A Mathematical Modeling and Validation Study of NO$_x$ Emissions in Metal Processing Systems

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The model is based on separate calculations of prompt and thermal NO$_x$ and is accomplished using CFD code for flow, temperature and concentration fields in the combustion system. Thermal NO$_x$ is calculated with the Zeldovich model. The prompt NO$_x$ is considered to be independent of residence time and is computed with detailed kinetic data based GRI-Mech version 2.11 and CHEMKIN code by assuming that every computational cell is a perfectly stirred reactor. Three main parameters are considered to be critical in NO$_x$ production: 1) air equivalence ratio, 2) temperature, and 3) mixture dilution with combustion products. All of these parameters and methane oxidation reaction rates are readily available in every cell of the CFD domain. Once NO$_x$ emission index is computed by GRI-Mech in every cell, NO$_x$ reaction rate is easily evaluated by multiplying it with the methane oxidation reaction rate. The NO$_x$ concentration field is then calculated using known CFD transport parameters. Comparison of model predictions with measurements is made for a wide range of industrial natural gas-fired burners installed in combustion chambers and furnaces. The flame temperatures were in the range of 1 400–2 100 K, velocities were in the range of 10–200 m/s, burner nozzles were in the range of diameters 5–550 mm, and the combustion chamber or furnace internal equivalent size in the range of 0.05–3.5 m. Good agreement has been obtained in most cases.

KEY WORDS: NO$_x$ emissions; mathematical modeling; metal processing; combustion systems.

1. Introduction

All gas fired combustion systems produce nitric oxide. Due to their toxic characteristics and the deleterious impact on the environment, the reduction of nitric oxide has become an important issue in industrial combustion systems.

The full kinetic mechanism of NO$_x$ formation is well developed and includes hundreds of reactions. The mechanism is used to calculate an ideal [perfectly stirred reactor (PSR) and plug flow reactor (PFR)] reactors, one-dimensional laminar flames or for validating different types of reduced NO$_x$ formation mechanisms.\(^1\)-\(^3\)

Numerical simulation of NO$_x$ emission in industrial burners requires rather sophisticated approaches due to the complexity of turbulent flows and stiffness problems caused by the large number of nonlinear chemical reaction equations involved. The simultaneous solution of hundreds of equations describing chemical reactions in many thousands of cells is necessary for real industrial applications; however, this problem (even in post-processing CFD mode) is still not practical with modern day computers and computational algorithms available. There are no coupled solutions of full NO$_x$ mechanism equations in complex geometry, practical turbulent flows. Hence, there is a strong motivation to describe some simplified models and approaches for practical applications.

One of the earliest and most efficient approach is the global Zeldovich model which is widely used for many industrial applications.\(^4\)-\(^6\) The main drawback of this model is well known. The model cannot predict NO$_x$ formation with sufficient accuracy in many practical flow patterns, e.g., for high velocity burners, which are used in rapid heating technology or in direct air heating burners where prompt NO$_x$ may be dominant.

Different types of simplified reduced mechanisms of NO$_x$ formation rates have been developed to predict methane–air combustion.\(^7\)-\(^9\) The separate global modeling of thermal and prompt NO has been used successfully as a post-processing code with CFD package to calculate NO$_x$ emission in laminar multi-flame burners for direct air heating\(^10\) and in small industrial rapid heating furnaces.\(^11\) The shortcomings of these schemes are their restriction to a narrow range of designs and operating conditions of the burners and limited industrial validation. In addition, some of the schemes cannot be implemented in practice by the user due to the absence of some reaction rate constants\(^8,10\) and should be employed with caution. Attempts have been made to create simple burner scaling criteria approximations\(^12,13\) based on numerous experiments for laminar and turbulent jet combustion.\(^12,14-16\) However, the correlations obtained describe experimental data with greater deviation than initial experimental data and are far from being universal.

Different types of simplifications have been suggested to
extend the detailed kinetic mechanisms to more complex cases. One of the approaches has been developed for turbulent, non-premixed flames.\textsuperscript{17} The flame jet region is subdivided into two zones: flame sheet and mixture core with prescribed heat and mass exchange coefficients. The flow through the flame sheet is taken to be one-dimensional, uniform and steady. The simplicity of the flow model allows inclusion of a comprehensive chemical reaction model with a relatively large set of reactions. Good agreement with experiments for turbulent diffusion flames developing in cold environment can be achieved. Two drawbacks of this approach are evident: 1) it is based on fortunate (successful) guess of flame zone subdivisions for well explored cases of free flames; hence, the method cannot be readily extended to more complex flow geometries with confined flames in a high temperature furnace environment, and 2) inconvenience of coupling with a CFD package.

The other approaches link detailed kinetic reaction data derived from one-dimensional premixed flame or PSR/PFR computations into two- or three-dimensional solution field obtained using CFD turbulent modeling with two step global combustion model with CO as an intermediate species.\textsuperscript{18} The NO\textsubscript{x} post-processor is based on the Miller and Bowman\textsuperscript{11} mechanism with Zeldovich NO mechanism deactivated and operates in two steps: 1) the one-dimensional adiabatic flame or chemical reactor model is used as a pre-processor to generate a look-up-tables of oxygen atom concentrations and prompt NO reaction rates vs. CO concentrations for a given excess air ratio, pressure and inlet temperature; 2) calls to the look-up-tables provide the CFD code with local values for the oxygen atom concentrations and the rates of nitrous and prompt NO formation. Zeldovich NO formation is then computed using the CFD generated local temperatures.

The authors reported that their approach is successful for NO prediction if applied to lean flames of gas turbine combustors. The advantages in comparison to the above methods of NO\textsubscript{x} modeling are: 1) based on detail chemistry mechanism, 2) simple non-iterative coupling with CFD, and 3) non-iterative fast procedure of local NO\textsubscript{x} concentrations evaluation. The drawbacks of the method are: 1) prompt NO is calculated in fact for adiabatic flame temperatures that may really occur in lean flames of gas turbine combustors, but, for most industrial heat processing apparatus the combustion products and flame temperatures are far below adiabatic due to intense heat extraction by the load (workpiece) and walls; 2) the oxygen atom concentrations needed for accurate thermal NO\textsubscript{x} calculations are also obtained for adiabatic case and so an additional inaccuracy in thermal NO\textsubscript{x} evaluation is possible; 3) mixture dilution with combustion products is not accounted for in the model of the reactor.

The goal of this study is to describe the development of the method for fast and accurate NO\textsubscript{x} emission calculations which combine detailed chemistry of NO\textsubscript{x} formation of the GRI-Mech version 2.11\textsuperscript{19} data base (solved by CHEMKIN package) and detailed flow calculations based on our own CFD code. The approach may be readily used for many practical industrial situations of natural gas combustion systems for a wide range of design and operating parameters.

\section{Analysis and Model Description}

The model is constructed and the solution procedure is developed in four steps. In the first step the flow, temperature and concentration fields are calculated numerically using a CFD code and a standard set of discretized differential equations\textsuperscript{20} for steady-state flows. The standard low Reynolds number $k$–$\varepsilon$ turbulence model and the one step eddy break-up combustion model\textsuperscript{20,21} were used to define the flow characteristics and natural gas (methane) oxidation rates. In the second step, prompt NO\textsubscript{x} emission rates are calculated in all cells of the computational domain. In the third step thermal NO\textsubscript{x} formation rates are determined in all cells. In the fourth step the concentration of NO\textsubscript{x} is calculated over the entire domain using transport coefficients defined in the first step and sum (prompt plus thermal) NO\textsubscript{x} formation rates.

In contrast to many investigators who have described prompt NO\textsubscript{x} formation rates with one global or several step (reduced) models,\textsuperscript{10,11} we have adopted the full kinetic GRI-Mech 2.11 mechanism\textsuperscript{19} for methane oxidation in the calculations. In this mechanism there are considered 49 species and a total of 279 reactions. The model equations and the reaction constants are available on the web\textsuperscript{19} and there is no need to list all of the reactions in the paper. The time consuming calculations using the full GRI-Mech data base can be dramatically simplified if we suppress the reaction time in the prompt NO calculations.

This possibility is demonstrated in Fig. 1 where NO\textsubscript{x} concentrations calculated with the GRI-Mech for a perfectly stirred reactor for which the thermal NO\textsubscript{x} production reactions were disabled. The air equivalence ratio was assumed equal to unity, and smoke ratio $d$ was set to zero. The results show that NO\textsubscript{x} concentrations are practically independent of the reaction time within the range 0.007–0.12 s. Therefore, if we take 0.015 s for the reaction time for all calculations with GRI-Mech, we are confident to obtain results without introducing significant error. Note that the chosen temperature range in Fig. 1 approximates the temperatures of the flame which occur in most types of industrial natural gas furnaces and are widely used for materials processing particularly for heating of metals.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{Dependence of NO\textsubscript{x} emissions on the reaction time and temperature for perfectly stirred reactor. Thermal mechanism is disabled.}
\end{figure}
Inspection of Fig. 1 allows us to make the following assumption. If EI denotes the emission index (grams of NO\textsubscript{x} produced per kg of methane burnt), and if in any cell of a furnace \(M\) kg of methane was burned under some conditions, inevitably \(EI \times M\) grams of prompt NO\textsubscript{x} is generated almost independent of the residence time.

For further simplification we select three dominant global parameters which primarily affect NO\textsubscript{x} production rate,

\[
EI = f(\alpha, d, T) \quad \ldots \ldots \ldots(1)
\]

where the emission index \(EI\) is a monotonic function of air equivalence ratio \(\alpha\), smoke ratio \(d\) (combustion products to unburnt mixture concentration ratio), and temperature \(T\). These dominant parameters which affect the NO\textsubscript{x} production rate the most are well known from experimental and numerical studies and are widely used in design of burners to reduce NO\textsubscript{x}.

Thus, the \(EI\) defined above was calculated with GRI-Mech for a reaction time of 0.015 s and the results have been evaluated for ranges of parameters of interest. A fragment of this \(EI\)-function calculated is presented in Table 1.

This table forms the type of data base with several thousand \(EI\) values for almost all burners of possible practical interest. Some more detailed results illustrating the dependence of the emission index \(EI\) on the relevant parameter (i.e., the temperature \(T\), the equivalence ratio \(\alpha\), and the smoke ratio \(d\)) are given in Figs. 2 and 3.

Now, the prompt \(EI\) can be determined in all cells of the computational domain using a 3-D interpolation of tabulated values of \(\alpha\), \(d\), and \(T\), and then the prompt NO production rate can be calculated from

\[
\frac{\partial NO}{\partial \tau} = EI \frac{\partial CH_4}{\partial \tau} \quad \text{[g/s]} \quad \ldots \ldots \ldots(2)
\]

provided that methane reaction rates \(\partial CH_4/\partial \tau\) together with values of \(\alpha\), \(d\), and \(T\) are taken from the first step of the calculations.

Thermal NO\textsubscript{x} production is calculated with help of the well known Zeldovich\textsuperscript{4} approximation:

\[
\frac{\partial NO}{\partial \tau} = 5 \times 10^{11} \exp \left[ \frac{-43,370}{T} \right] \times \left[ \frac{O_2 \cdot N_2}{T} \right]^{\frac{3}{3}} \exp \left[ \frac{-21,684}{T} \right] \left[ NO \right]^2 \quad \ldots \ldots \ldots(3)
\]

Here \(O_2\), \(N_2\), and \(NO\) are concentrations of oxygen, nitrous oxide in mol/l, and \(\tau\) is the reaction time in s. For the furnace and burners of interest the second term in curly brackets can be neglected, and the expression\textsuperscript{3} may be written in non-iterative form, which is more convenient for use in numerical calculations,

\[
\frac{\partial NO}{\partial \tau} = 5.63 \times 10^{13} \exp \left[ \frac{-65,054}{T} \right] \left[ O_2 \cdot N_2 \right] \quad \ldots \ldots \ldots(4)
\]

where \(O_2\), \(N_2\), and \(NO\) are concentrations in kg/m\textsuperscript{3} and \(\tau\) is the reaction time in s.

After prompt and thermal reaction rates have been calculated in all domains it is easy to solve one set of equations for NO concentration with a source term,
\[
\frac{\partial NO}{\partial \tau} = \frac{\partial NO}{\partial \tau}_{p} + \frac{\partial NO}{\partial \tau}_{k_0}
\]

defined by Eqs. (2) and (4) with the Neumann boundary conditions at all boundaries. The convective and diffusion coefficients are calculated in the first stage of the analysis.

The reaction time is used implicitly in the first step of the model, while we obtain the methane reaction rate with help of global combustion formula in the CFD part of the calculations. In this step the residence time and magnitude of burnt methane depends on the flow field and the model characteristics (velocities, temperature, turbulence, cell sizes, etc.) The methane reaction rate may be regarded as a critical parameter. If it agrees with the experiments, the prediction of prompt NO in the second stage has a good chance of being successful. Prompt NO production depends linearly on the methane reaction rate, and in this sense the combustion conditions in real furnaces are taken into account in the modeling.

The reaction time in question, which is used in the second step of the model, may be regarded as some type of “time boundary line” which separates the “fast” or the “prompt” NO from the thermal NO. Although this time boundary line appears to depend on many factors, but first of all it depends on the temperature. It has been our experience and of others (numerical calculations for ideal reactors or laminar flames) which show that there are some limits in the reaction time in question that affect very weakly the prompt NO emission index for a wide range of initial conditions of an ideal reactor. Therefore, the reaction time for the PSR reactor may be regarded rather as a universal fit parameter, which may be set constant for all cells, and we have found its value to be in the range of 0.01–0.015. This value yields good results for the NO emission index for a wide range of industrial heating furnace and burner conditions, and this is our justification for using the value of the reaction time established empirically.

3. Results and Discussion

Four industrial burner and furnace designs were selected for the present model validation study. They include the following:
1. Direct flame impingement (DFI) multiflame high velocity rapid heating technology,
2. High velocity tunnel burners with almost complete combustion at their outlets which are traditionally used for rapid heating applications,
3. Most widely used conventional “tube in tube” type of natural gas-fired burner without swirl and with both cold and hot combustion air,
4. Powerful (12 MWt) low NO\textsubscript{e} emission combustor with swirling flow of the John Zink Company.

For all cases the two-dimensional Cartesian, axisymmetric grid was used with 2 000–3 000 cells.

3.1. Direct Flame Impingement Furnace

The most detailed calculations were performed for the first case of an industrial rapid heating furnace equipped with multiflame high velocity premixed burners.\textsuperscript{23} This is referred to as direct flame impingement (DFI) technology. The rapid heating of round metal workpiece (100 mm in diameter) is accomplished in a compact furnace (320 mm in diameter) using numerous high velocity (up to 300 m/s) flame jets of premixed methane/air mixture. The stainless steel nozzles to supply the natural gas/air mixture are introduced inside furnace space through the refractory walls. No tunnels or flame holders are needed.

The furnace consists of 32 parts, 1.4 m in length (44.8 m total length), and has a production capacity of up to 50 t/h and gas consumption in the range of 900–1 600 m\textsuperscript{3}/h. Relatively low flame temperature is insured through the extremely high convective cooling of the combustion products with heating a cold load. The temperature is very uniform in the combustion space and there are no peaks. This is a consequence of intense mixing of the combustion products with numerous high velocity jets (about 50–100 per meter length of the furnace).

The furnace firing rate was 60–100 m\textsuperscript{3}/h of natural gas per square meter of the workpiece surface area. This results in high heat fluxes (∼250–400 kW/m\textsuperscript{2}) at the workpiece surface.

DFI technology combines many methods and means used to reduce NO\textsubscript{e} emissions in industrial combustion equipment by lowering combustion temperature, for example, by combustion staging or cooling, intensification of mixing by increasing the number of nozzles and their velocities (in gas turbine combustors) and flue addition in the flame zone as by intense recirculation or reducing the residence time by decreasing the furnace size. A more detailed description of the furnace can be found elsewhere.\textsuperscript{23} The model equations with a set of boundary conditions, combustion and radiation models used for CFD mathematical simulation are described in detail elsewhere\textsuperscript{24} and need not be repeated here.

The NO\textsubscript{e} measurements were made on an industrial furnace in operation using a hot water cooled stainless steel probe and a gas analyzer. The combustion product temperatures were measured with a suction pyrometer. The suction pyrometer and the NO\textsubscript{e} probe were transversed between two neighbouring flames of the multiflame burner in the direction normal to the refractory wall and to the bar surface, e.g., in the zone of complete combustion where the temperature is perfectly uniform. The data obtained were averaged over time and space for every run. In Fig. 4 the data are illustrated for two runs.

Figure 4 demonstrates good agreement between experimental data and predictions. The NO\textsubscript{e} emissions are very low and are at least five to ten times lower in comparison with conventional type heating furnaces which are typically used to heat steel workpieces before forging. The prompt NO accounts for about 80% of the total emissions. The conventional furnaces have typical dimensions of 1.5–3 m in height, 20–50 m in length and 10–12 m in width and are equipped with tube-in-tube type burners with swirled combustion air. The air outlet nozzles are of considerable sizes (0.1–0.5 m) in diameter. Measurements show that the typical NO\textsubscript{e} emissions in such type of heating furnaces are 100–500 ppm and greater due to long residence time in large furnace space and large temperature overshots (strong nonuniformity) on the flame boundaries.
3.2. High Velocity Tunnel Burner

The second case of model validation is an alternative to the DFI rapid heating process which is known as high velocity tunnel burners. These burners can be made of ceramic or stainless steel. The details of design and reliable measurements are available only for two burners (A and B) in question with combustion air cooled steel tunnels. The sizes of the industrial burners are given in Table 2.

The main fraction of the gas-air mixture is burnt inside a very compact tunnel space at high flame temperatures. As a consequence, this contributes to the high NO\textsubscript{x} emissions at the burner exit. Cooling of the tunnel walls with combustion air increases air temperature up to 573 K for a maximum load and to 773 K for a minimum load. This results in an additional rise of the flame temperatures and NO\textsubscript{x} emissions.

Figures 5(a) and 5(b) show an increase in the gas firing rate leads to a decrease of NO\textsubscript{x} emissions due to a decrease in the combustion air temperature and reduction of the residence time. The calculations show that prompt NO\textsubscript{x} contributes about 50% of the total emissions for low gas flow rates and 95% for maximum flow rates in both burners.

The computational model allows easy evaluation of residence times for different temperature ranges. For the A-type burner the residence time for temperature ranges of 1800–1900 K, 1900–2000 K and 2000–2100 K and small loads are accordingly 0.064 s, 0.092 s and 0.176 s, whereas for the largest load and the same temperature ranges they are 0.036 s, 0.079 s and 0.037 s, respectively. Thus, we see that for highest temperature range (2000–2100 K) the residence time is 5 times smaller, although the gas flow rate increases only 2.2 times (from 1.5 up to 3.35 m\textsuperscript{3}/h). This explains the rapid increase in thermal NO\textsubscript{x} emissions which are very sensitive to temperature increase above 2000 K with a load decrease. The same remarks can be made about the B-type burner.

A comparison of the two rapid heating methods described above (DFI technology and high velocity tunnel burners of types A and B) shows the environmental advantage of using the DFI technology. The technology results in high heat fluxes at the load surface with a minimum NO\textsubscript{x} emissions.

3.3. Tube-in-Tube Type Burner

The third case of the model validation deals with the most frequently used simple "tube in tube" type burner without swirl which produces a long diffusion flame with relatively low NO\textsubscript{x} emissions. The gas and air nozzles are 12.5 mm and 65 mm in diameter, respectively. Accordingly, a burner with a gas volume flow rate of 20.4 m\textsuperscript{3}/h was installed at the one end of combustion chamber which was 600 mm in diameter and 3 m long. The combustion air temperature varied from cold (300 K) to hot (843 K).

Figure 6 shows the temperature and NO\textsubscript{x} distributions along the chamber (burner) axis. The heated air strongly enhanced NO\textsubscript{x} thermal emissions which contribute 83% of the total, whereas cold air combustion accounted for only 50% of thermal NO\textsubscript{x} emissions.

The cold air gives rise to relatively small NO\textsubscript{x} pollution emissions —30 ppm which may be explained by the relatively low flame temperature in the chamber (1700–1800 K). For hot air the flame temperatures in the chamber are 200 K higher (1800–2000 K) and NO\textsubscript{x} emissions are 100
The air annulus was 550/350 mm and air velocities were 28 m/s. The experiments were carried out for a cylindrical combustion chamber with water cooled walls. The chamber had a diameter of 3.4 m and was 6.3 m long. The furnace was fired using a large burner (12 MWt) which was installed in one end of combustion chamber. The burner had swirling air flow and multiple natural gas injection for rapid mixing with air. The air annulus was 550/350 mm and air velocities were 28 m/s. The experiments were carried out under the following conditions: gas flow rate of 0.254 kg/s; air flow rate of 4.3 kg/s; swirl number of 0.58; and especially preheated combustion air.

The model developed allows one to predict with good accuracy (30–50%) NOx emissions for both diffusion and premixed methane flames for a wide range of burner sizes, designs and operating parameters.

Another case study for the model validation was carried out for a cylindrical combustion chamber with water cooled walls. The chamber had a diameter of 3.4 m and was 6.3 m long. The furnace was fired using a large burner (12 MWt) which was installed in one end of combustion chamber. The burner had swirling air flow and multiple natural gas injection for rapid mixing with air. The air annulus was 550/350 mm and air velocities were 28 m/s. The experiments were carried out under the following conditions: gas flow rate of 0.254 kg/s; air flow rate of 4.3 kg/s; swirl number of 0.58; and especially preheated combustion air.
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