A NO\(_x\) PREDICTION SCHEME FOR LEAN-PREMIixed GAS TURBINE COMBUSTION BASED ON DETAILED CHEMICAL KINETICS

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ABSTRACT

The lean-premixed technique has proven very efficient in reducing the emissions of oxides of nitrogen (NO\(_x\)) from gas turbine combustors. The numerical prediction of NO\(_x\)-levels in such combustors with multi-dimensional CFD codes has only met with limited success so far. This is at least to some extent due to the complexity of the NO\(_x\) formation chemistry in lean-premixed combustion, i.e. all three known NO\(_x\) formation routes (Zeldovich, nitrous and prompt) can contribute significantly. Furthermore, NO\(_x\) formation occurs almost exclusively in the flame zone, where radical concentrations significantly above equilibrium values are observed.

A relatively large chemical mechanism is therefore required to predict radical concentrations and NO\(_x\) formation rates under such conditions. These difficulties have prompted the development of a NO\(_x\) post-processing scheme, where rate and concentration information necessary to predict NO\(_x\) formation is taken from one-dimensional combustion models with detailed chemistry and provided – via look-up tables – to the multi-dimensional CFD code.

The look-up tables are prepared beforehand in accordance with the operating conditions and are based on CO concentrations, which are indicative of free radical chemistry. Once the reacting flow field has been computed with the main CFD code, the chemical source terms of the NO transport equation, i.e. local NO formation rates, are determined from the reacting flow field and the tabulated chemical data. Then the main code is turned on again to compute the NO concentration field. This NO\(_x\) sub-model has no adjustable parameters and converges very quickly. Good agreement with experiment has been observed and interesting conclusions concerning superequilibrium O-atom concentrations and fluctuations of temperature could be drawn.

NOMENCLATURE

\[ A \] \hspace{1cm} Arrhenius pre-exponential factor
\[ E_A \] \hspace{1cm} Activation energy
\[ Re \] \hspace{1cm} Turbulent Reynolds number
\[ Da, Ka \] \hspace{1cm} Damköhler, Karlovitz number
\[ CO, O_2, NO, \ldots \] \hspace{1cm} Chemical Species
\[ S_L, \delta_L \] \hspace{1cm} Laminar flame speed and thickness
\[ T \] \hspace{1cm} Temperature
\[ \dot{V} \] \hspace{1cm} Volumetric flow rate
\[ Y \] \hspace{1cm} Species mass fraction
\[ a, b, n \] \hspace{1cm} Species, temperature exponents
\[ k \] \hspace{1cm} Turbulent kinetic energy
\[ k_1, k_2, \ldots \] \hspace{1cm} Reaction rate constants
\[ \ell_T, t_T \] \hspace{1cm} Turbulent macro length and time
\[ p \] \hspace{1cm} Pressure
\[ t_c \] \hspace{1cm} Chemical heat release time
\[ w \] \hspace{1cm} Reaction rate
\[ \lambda \] \hspace{1cm} Excess air ratio
\[ \nu \] \hspace{1cm} Dynamic viscosity
\[ \epsilon \] \hspace{1cm} Turbulent dissipation
\[ \eta \] \hspace{1cm} Unmixedness factor
\[ \tau \] \hspace{1cm} Reactor residence time

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INTRODUCTION

For the combustion of fuels without fuel-bound nitrogen at gas turbine conditions, the lean premixed technique has already proven to be an enormously successful primary measure to significantly reduce emissions of oxides of nitrogen \((NO_x)\) (Sattelmayer et al. 1992). Further reductions in \(NO_x\) from gas turbine combustors should be possible with the lean-premixed technique, and there is great interest in the development of such combustors. A numerical \(NO_x\) prediction scheme adapted to these conditions would obviously be a tool of great practical value for the designer. The concept, development and implementation of such a model is presented here.

EXPERIMENTAL SETUP AND OPERATING CONDITIONS

As a test case for the model of \(NO_x\) formation in lean-premixed combustion, experiments were conducted with an ABB Double Cone Burner with 0.1 m nominal diameter mounted in an atmospheric test rig. A Double Cone Burner comprises two halves of a cone that are shifted with respect to each other in the radial direction such that two inlet slits of constant width are formed. A strong tangential component is imparted to the gas entering the burner through these slits. The degree of swirl is chosen such that near the burner outlet the flow undergoes a vortex breakdown, resulting in a zone of recirculation, which acts as an aerodynamic flame holder. This type of flame stabilization in free space is the characteristic property of the double cone burner. More details have been given by Sattelmayer et al. (1992).

The burner used in the experiments is mounted in a movable tube and fires into a SiC-ceramic combustion chamber of square cross section with 0.14 m side length, which in turn is enclosed by a water-cooled steel liner, see Fig. (1). With an electrical heater, the inlet temperature of the combustible mixture can be increased up to 670 K. Typical operating conditions for the atmospheric test rig are inlet temperature \(T_i \approx 630\, K\), a combustible mixture volume flow \(V = 200\, m^3/s\).

In these experiments, fuel is injected far upstream of the burner in order to achieve perfect premixing of fuel and air. As a drawback, flashback occurs for excess air ratios \(\lambda\) below 1.9 (Lean blow-out occurs at \(\lambda \approx 2.2\)).

Sample gas is taken from the combustor with a movable water-cooled stainless steel probe. The concentrations of \(O_2\), \(CO\), \(CO_2\), and \(NO_x\) are determined with the paramagnetic, the NDIR, and the chemiluminescence principle, respectively. An uncoated Pt – PtRh thermocouple, mounted on an uncooled ceramic suction probe, is used to measure temperature. No corrections for radiation loss are made. In addition to the temperature and species measurements in the reacting flow, LDA measurements of velocity were conducted in a water model of the burner and combustion chamber in order to determine appropriate inlet conditions for the two-dimensional numerical model, and to assess the quality of the turbulent flow modeling; this is discussed in more detail by Polifke et al. (1995).

TURBULENT FLOW AND HEAT RELEASE MODELLING

A commercial CFD code – finite volume based with "standard" SIMPLE(C) pressure correction algorithm (Patankar, 1980) – was used as the basis for the implementation of the turbulent combustion model and the \(NO_x\) post-processor. The geometry of the burner and the combustion chamber were mapped to a 2D cylindrically symmetric cartesian grid with 6000 cells. Although both the burner and the combustion chamber are not exactly cylindrically symmetric, this simplification seems appropriate to keep memory and CPU time demands at an acceptable level.

Flow conditions at the inlet section of the 2D model are not uniform and must be based on experimental measurements or 3D numerical predictions of the flow in the double cone burner's inlet slits. Experiments were conducted in a water model of the burner at the appropriate Reynolds number. Axial, tangential and radial velocity and turbulent intensity along the inlet...
slits and downstream of the burner were measured with standard LDA equipment. Additionally, a 3D, boundary-fitted grid of the double cone burner was generated, which includes also the test rig section upstream of the burner. It has been found that the numerical predictions of the flow through the burner’s inlet slits are rather insensitive to the details of the boundary conditions prescribed at the inlet of the 3D model and are in good agreement with experiment.

Inlet flow conditions for the 2D geometry were then set to reproduce along the burner’s inlet the fluxes of mass, and axial and azimuthal momentum observed in the 3D flows. The boundary values for turbulent kinetic energy $k$ and dissipation $\varepsilon$ were determined similarly from the 3D data by appropriate averages. The inflow distributions resulting from this prescription appear entirely reasonable, and characteristic features of the flow inside the combustor — e.g., the size and location of the recirculation bubble — obtained with these boundary conditions are in good agreement with experiment and 3D computation.

It is well known, see e.g. Sloan et al. (1986), that the standard $k-\varepsilon$ model is not well suited for modeling swirling flows and use of a full differential Reynolds stress model (RSM) is usually recommended for such cases. However, the use of an RSM turbulence model entails significantly longer compute times and often severe convergence difficulties. The swirl number of the Double Cone Burner, defined as the ratio of azimuthal radial length scale is less than unity. Such a level of swirl is essentially reasonable, and characteristic features of the flow through the burner’s inlet slits are set to reproduce along the burner’s inlet the fluxes of mass, and axial and azimuthal momentum fluxed divided by a characteristic radial length scale of this prescription appear entirely reasonable, and characteristic features of the flow inside the combustor — e.g., the size and location of the recirculation bubble — obtained with these boundary conditions are in good agreement with experiment and 3D computation.

As discussed below, $CO$ concentrations are required to predict $NO_x$ formation rates with our model. This requires at least the use of a 2-step global reaction mechanism with $CO$ as an intermediate:

$$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O,$$ \hspace{1cm} (1)

$$CO + \frac{1}{2}O_2 \rightarrow CO_2.$$ \hspace{1cm} (2)

Rate expressions for the forward reactions are of a generalized Arrhenius form, based on reactant concentrations $[R_4]$ and temperature $T$:

$$w_f = AT^n[R_4]^a[R_5]^b \exp \left( -\frac{E_A}{RT} \right),$$ \hspace{1cm} (3)

with pre-exponential factor $A$, temperature and species exponents $n, a, b$ and activation energy $E_A$ based on the work of Westbrook and Dryer (1981). Heeding the warning given by Coffee (1985), negative species concentration exponents have not been used in this study, as they may adversely affect both the convergence behavior as well as the accuracy of a computation. Table 1 lists the reaction rate constants used in this study.

Rate constants for the reverse of reaction 2 have also been provided by Westbrook and Dryer (1981), i.e. $k_r = 5 \times 10^8 \exp(-1.67 \times 10^8/RT)$. However, the value of the activation energy $E_A$ given for the reverse reaction is equal to that of the forward reaction. The ratio of $[CO]$ to $[CO_2]$ at equilibrium resulting from such a prescription will obviously be independent of temperature, which is not plausible. Indeed, at lean conditions totally unrealistic equilibrium levels of $[CO]$ are obtained with the rate constants suggested by Westbrook and Dryer (1981). Therefore, the reverse rate of reaction (2) was determined from the equilibrium condition $k_f/k_r = K_e$ for the rate constants.

Admittedly, the rate constants have been manipulated in a very ad hoc manner to suit our needs. The justification for doing so is firstly that this work deals with the description of the concept and implementation of a $NO_x$ post-processor, and not with the development or detailed testing of a turbulent combustion model. The results obtained with the set of rate constants listed in Table 1 are qualitatively correct, and this shall suffice to test the validity of our $NO_x$ postprocessor concept. Secondly, the reaction progress limitations imposed by chemical kinetics are only one aspect of turbulent combustion. The limitations imposed by turbulent mixing

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$</th>
<th>$n$</th>
<th>$a$</th>
<th>$b$</th>
<th>$E_A$</th>
</tr>
</thead>
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<tr>
<td>(1)</td>
<td>$4.56 \times 10^{11}$</td>
<td>0</td>
<td>0.2</td>
<td>1.3</td>
<td>$2.03 \times 10^8$</td>
</tr>
<tr>
<td>(2)</td>
<td>$3.16 \times 10^{12}$</td>
<td>0.5</td>
<td>1.5</td>
<td>0.25</td>
<td>$1.67 \times 10^8$</td>
</tr>
</tbody>
</table>

Table 1: Reaction rate constants in SI-Units (m/s/K/J/kmol).

1Westbrook and Dryer (1981) do provide a set of rate constants for a 1-step global mechanism that uses only positive exponents ("Set 3" in Table II of their paper). Note that the exponential prefactor $A_3$ of this set differs significantly from the one for "Set 2", i.e. the set with a fuel concentration exponent $a = -0.3$. Unfortunately, for the 2-step mechanism Westbrook and Dryer provide only a set of rate constants with $a = -0.3$. The product of this prefactor with $A_3/A_2$ is used in the set of rate constants for reaction (1) in this study, see Table 1.

2Note that for reasons of numerical convenience and robustness, the $[H_2O]$ dependence of the CO-oxidation given by Westbrook and Dryer (1981) has been lumped into the prefactor for reaction (2) by assuming that $[H_2O] \approx 2[CO]$, which holds as long as $CO_2$ concentrations are small. Note that this procedure does not affect the equilibrium concentrations of $CO$ and $CO_2$ if the reverse rate is computed from $k_f/k_r = K_e$. 


must—depending on the relative magnitudes of relevant chemical and turbulent time scales—also be considered.

Indeed, it is generally recognized that different types or "regimes" of turbulent combustion can be distinguished (Borghi, 1988, see also Libby and Williams, 1994 and references therein). The regimes are usually characterized by three dimensionless numbers: the turbulent Reynolds number \( Re \equiv u' l_T / \nu \), the turbulent Damköhler number \( Da \equiv t_T / \tau_c \) and the Karlovitz number \( Ka \equiv u' \delta_L / l_T S_L \). Here \( l_T \) is the turbulent macro scale, while \( \delta_L \) denotes the Taylor micro scale, \( t_T \sim l_T / u' \) a mixing time typical of the macro scale turbulent eddies. The laminar flame is characterized by its flame speed \( S_L \) and thickness \( \delta_L \); a typical chemical heat release time \( t_c \) may be expressed as \( t_c \sim \delta_L / S_L \). For the double cone burner atmospheric test stand at typical operating conditions, we estimate \( Re \approx 250 \), while the turbulent Damköhler number is of order unity, i.e. turbulent mixing time scales \( t_T \) are of the same order of magnitude as chemical time scales \( t_c \). Estimates for the Karlovitz number yield \( Ka > 2 \), which indicates that thin laminar reaction layers can be quenched by the smallest turbulent eddies. Following Borghi (1988), the turbulent flame front in the Double Cone Burner should be categorized as a (wrinkled) thickened flame. See also Hoffmann et al. (1994) for a more detailed discussion and experimental results concerning the structure of highly turbulent lean-premixed flames.

This suggests that eddy break-up, eddy dissipation and flamelet models (see, e.g., Libby and Williams (1994) and references therein), all of which assume that the Damköhler number is large and the Karlovitz number not much greater than one, are not appropriate for modeling this type of flame. Instead, a turbulent combustion model has been used in this study that incorporates both turbulent mixing and chemical kinetic rate limitations. The overall reaction rate \( R \) is expressed as:

\[
\frac{1}{w} = \frac{\eta}{w_{Mix}} + \frac{1-\eta}{w_{Kin}}.
\]

See Philip et al. (1991) for a similar formulation. Here we introduce an "unmixedness factor" \( \eta \), based on a non-dimensionalized and normalized gradient of temperature:

\[
\eta = \tanh \left( C_\eta |\nabla T| \frac{t_T}{T} \right). \tag{5}
\]

The tanh function has been chosen for mere convenience to normalize the gradient to the interval \([0,1]\); other formulations should be possible. \( C_\eta \) is an adjustable constant of order 10. It has been observed that computed species and temperature distributions are rather insensitive to the exact value of \( C_\eta \) as long as the resulting unmixedness \( \eta \) is near unity in the vicinity of the flame front and small elsewhere.

What is the rationale behind this formulation? In homogeneous regions of the computational domain, where \(|\nabla T|\) is small, \( \eta \approx 0 \), and \( w \approx w_{Kin} \), i.e. chemical kinetics is rate limiting—as it should be, because mixing processes cannot impede the reaction progress if the temperature and species distributions are already uniform. Furthermore, it is often assumed in turbulence models that temporal or statistical fluctuations are small in regions where spatial gradients are small. From this assumption it follows that in regions where temperature gradients are small, the mean values of temperature (and species concentrations) may be used to determine the mean chemical rates. On the same token fluctuations will be large near the flame zone, where hot products are in proximity with the fresh fuel/air mixture. Due to the strong nonlinearity of the exponential term in (3), rates based on mean values will then underpredict the mean reaction progress. Therefore, turbulent mixing is set to be rate-determining in these regions in intermediate regions both turbulent mixing and kinetics can influence the overall rate. Again, see Philip et al. (1991) for a similar approach.

Fig. 2 shows distributions of temperature and stream function from a computation with a total mass flux of \( 0.089 \text{ kg/s} \), mixture inlet temperature \( T_i = 630 \text{ K} \), methane fuel at an air excess ratio \( \lambda \approx 2 \) and zero heat flux boundary conditions. Presented are contour plots of stream function \( \psi \) (top half) and temperature \( T \) (bottom half) in an axial cross section of the burner and combustion chamber. Near the burner exit, the central recirculation bubble (\( \psi = 0 \)) is visible. The two contour lines of temperature at \( T = 700 \text{ K} \) and \( T = 1600 \text{ K} \) show the location of the flame front.

A detailed comparison (see Polifke et al., 1995) of numerical and experimental temperature and \( CO \) distributions reveals that although the overall flow and temperature distributions agree well with burner design expectations and experimental observations, there is significant disagreement in the vicinity of the flame front. In particular, it seems that the turbulent combus-
tion model employed underpredicts the turbulent intensity and flame speed and overpredicts the equilibration or burn-out rate.

In this work, however, we are mainly concerned with the implementation of the NO\textsubscript{2} post-processing model. Considering that overall flow and temperature patterns are qualitatively correct, and that the predicted peak and equilibrium CO levels are of the correct order of magnitude, one may expect that at least the feasibility of our NO\textsubscript{2} prediction concept can be tested on the basis of the employed heat release model.

**NO\textsubscript{2} Chemistry in Lean- Premixed Combustion**

The formation of NO in lean (\(\lambda = 1.5\) to 2.5), premixed combustors fired on methane or natural gas occurs by the nitrous oxide, the Zeldovich and — to a lesser extent — the prompt mechanisms. This is quite different from the situation in diffusion flames, where the Zeldovich and prompt mechanisms are dominant, and most certainly the reason why the application of a NO\textsubscript{2} prediction module (Missaghi et al., 1990, Dupont et al. 1993) suitable for richer conditions and/or diffusion flames to the double cone burner gave totally unacceptable results.

The rate of NO production by the Zeldovich mechanism under such conditions is given with good accuracy by

\[
\frac{d[NO]}{dt} = 2k_1[N_2][O],
\]

where the rate constant \(k_1\) in the above expression is that of the initial Zeldovich reaction:

\[
N_2 + O \rightarrow NO + N. \tag{7}
\]

A value of \(k_1 = 1.8 \times 10^{11} \exp(-38370/T)\) m\(^3\) kmol\(^{-1}\) s\(^{-1}\) has been used, which is arrived at by applying detailed balancing to the reverse rate constant given by Miller and Bowman (1989).

As \(\lambda\) and \(p\) increase and the inlet air temperature decreases, the ratio of NO formed by the nitrous oxide mechanism to that by the Zeldovich mechanism increases. Indeed, under the leanest conditions and at high pressures, the nitrous oxide mechanism is predominant and can account for essentially all of the NO formed (Nicol et al. (1993)). The nitrous oxide is formed by the following reaction:

\[
N_2 + O + M \rightarrow N_2O + M. \tag{8}
\]

For high pressure combustion, the \(N_2O\) is destroyed mainly by the reverse reaction. Destruction of the \(N_2O\) by free radical attack plays a secondary role. This is different from the situation at atmospheric pressure, in which case destruction by H-atom attack (i.e., \(N_2O + H \rightarrow N_2 + OH\)) is important.

Nitric oxide is formed from \(N_2O\) and \(O\) or \(H\):

\[
N_2O + O \rightarrow NO + NO, \tag{9}
\]

\[
N_2O + H \rightarrow NO + NH. \tag{10}
\]

For high pressure, lean premixed combustion, reaction (9) is predominant, whereas for 1 atm combustion, reaction (10) also is important.

Under lean conditions, the \(NH\) formed by the reaction (10) is converted to NO. This occurs mainly through reaction of the \(NH\) to \(N\) and \(HNO\), followed by reaction of these intermediates to NO. If the steady-state assumption is valid for the \(NH\), \(N\), and \(HNO\), the rate of NO production by the nitrous oxide mechanism is:

\[
d[NO]/dt = 2k_2[N_2O][O] + 2k_3[N_2O][H], \tag{11}
\]

where \(k_2\) and \(k_3\) are the rate constants of reactions (9) and (10).

The third mechanism of interest is the so-called prompt or Fenimore mechanism, i.e., fixation of \(N_2\) by hydrocarbon attack leading to NO. This mechanism, based on available rate data, exerts a negligible-to-weak effect in high pressure, lean, premixed combustion. However, for the flame zone of 1 atm, lean, premixed combustors, the mechanism can be significant and should be considered. The initiating reaction is taken to be:

\[
N_2 + CH \rightarrow HCN + N \tag{12}
\]

The HCN forms in the flame zone, followed rapidly by complete conversion to NO under lean conditions. A second effect is the reduction of NO by hydrocarbon attack, leading to additional HCN and other cyano species (e.g., HCNO). These molecules form in the flame zone and then are recombined to NO. With respect to NO production, the net effect of the attack of hydrocarbons on the nitrogen system is the formation of NO in the flame zone at a rate less than two times the rate of reaction (12), because some of the nitrogen is tied up as cyano molecules, followed by a yield of NO as the cyano molecules are converted to NO.

By comparing PSR/PFR models of turbulent combustion of methane for \(\lambda = 2\) (Nicol et al., 1994), it is possible to determine the contributions of the three NO\textsubscript{2} mechanisms for a range of pressure levels. For lean combustion models, the nitrous oxide mechanism is also produced "promptly" in the flame zone.
premixed combustion at 1 atm, it is found that all of the mechanisms contribute in the flame zone (which is represented by the PSR). Due to the influence of the radicals, the nitrogen oxides are formed mainly in the flame zone (and immediate post-flame zone), rather than in the burnout zone. In particular, the maximum rate of NO\textsubscript{2} production occurs throughout the PSR and initial part of the PFR, until a time of about 3\texttau is reached, where \texttau is the PSR residence time. This is a relatively long time period, which arises because of the slow relaxation of the O-atom towards its equilibrium level. Thus, the nitrous oxide mechanism (which is sensitive to O-atom) persists into the PFR, and has a contribution of NO\textsubscript{x} competitive with that of the Zeldovich mechanism until a time of about 15\texttau is reached. Downstream, in the burnout zone, the Zeldovich mechanism is predominant, though by this point the rate of production of the NO\textsubscript{x} is very low compared to that in the flame zone and immediate post-flame zone. Since the CH radical is very short-lived, the prompt NO\textsubscript{2} mechanism only contributes in the flame zone.

For high pressure combustion (e.g., 14.3 atm in Nicol et al., 1994) the NO\textsubscript{x} behavior is markedly different. The nitrous oxide mechanism is the predominant source of the NO\textsubscript{2} — again the NO\textsubscript{2} forms mainly in the flame zone. The prompt NO\textsubscript{2} mechanism contributes weakly, and the Zeldovich mechanism does not become significant (relative to the nitrous oxide mechanism) until well into the burnout zone. Because of the fast relaxation of the O-atom towards equilibrium in high pressure combustion, the period of maximum NO\textsubscript{x} production is very short. This behavior may explain the lack of a positive pressure dependency of the NO\textsubscript{x}, as observed in some experiments (e.g., see Joshi et al., 1994; and Steele et al., 1995). For 1 atm combustion, because of the persistence of the maximum NO\textsubscript{x} production rate, the radical dominated NO\textsubscript{x} formation is spread over a significant range of eddy sizes, up to times of several milliseconds. However, at high pressure the region of super-equilibrium O-atoms can be very small, although the maximum rate of NO\textsubscript{x} production is very high (e.g., about 10-fold higher at 14.3 atm than at 1 atm; Nicol et al., 1994). The result of these competing effects is that the NO\textsubscript{x} emission does not increase with pressure, and in some situations actually falls off moderately with increasing pressure (Joshi et al., 1994; and Steele et al., 1995).

**THE POST-PROCESSOR CONCEPT**

The total amount of nitrogen oxides formed in lean, premixed combustion is typically (much) less than 100 ppmv, so that the influence of NO\textsubscript{x} formation on the heat release process and the concentrations of stable species and the more important radicals may safely be neglected. It is therefore possible to decouple the prediction of nitrogen oxide concentrations from the "main" heat release computation. This approach is only feasible, if the chemical source terms for NO\textsubscript{x} may be derived from the main solution field with sufficient accuracy. If this is the case, the CFD solver can be used in a "post-processing" step to solve the transport equations of the nitrogen oxides and compute their two- or three-dimensional concentration fields, while keeping the values of the "main" variables frozen.

However, the discussion in the previous section has shown that a sizable chemical mechanism is required to compute the contributions of the three NO\textsubscript{x} formation routes to the source term, especially at atmospheric pressures. It is not always possible to reduce the number of reactions to a value that can be comfortably handled by a CFD code not designed for stiff problems. Empirically fitted global reaction mechanisms have therefore been introduced to predict, e.g., the formation of prompt NO\textsubscript{x}, see References (Missaghi et al., 1990, Dupont et al. 1993).

Furthermore, Eqns. (6) - (12) show that NO\textsubscript{x} formation rates depend directly on the concentrations of a number of radicals which are typically not predicted by the turbulent combustion models that are currently in use for practical applications. It is often suggested to approximate radical concentrations by their respective (partial) equilibrium values, see e.g. Warnatz and Maas (1993) and Missaghi et al. (1990). However, the temperature levels achieved in lean-premixed low-NO\textsubscript{x} combustion systems are too low to allow the use of this approximation. For example, Zeldovich NO\textsubscript{x} formation depends linearly on the O-atom concentration, while at $p = 1$ bar the O/H/OH radical pool is in general not in partial equilibrium at temperatures of interest here.

In order to circumvent these difficulties, the post-processor developed in this study extracts radical concentrations from numerically evaluated dependencies, i.e. look-up tables that are based on local CO concentration. Among the variables predicted by the CFD code, CO has been chosen as the basis of the tables as it is most indicative of free radical chemistry and less sensitive to numerical inaccuracies than temperature. The look-up table is generated (before the post-processor's run) by adiabatic one-dimensional laminar flame or reactor modeling with detailed chemistry. Note that the operating conditions (equivalence ratio, inlet temperature, pressure) for the laminar flame or reactor models with detailed chemistry are always set in accordance with the main simulation. We emphasize that it is not
assumed that there is a "universal" correlation between CO and radical concentration and NO$_x$ formation that is valid over a wide range of operating conditions. It has nevertheless been found that the CO-correlations are surprisingly universal inasmuch as they do not depend on the details of the reactor modeling, provided that the combustion process is (nearly) adiabatic and that the CO oxidation process is not quenched (see below and Nicol et al., 1994).

With the O-atom mass fraction $Y_O$ taken from the appropriate look-up table, the prediction of Zeldovich NO$_x$ formation rate from (6) is straightforward. How are the other formation paths treated? In the high pressure case, Fenimore prompt NO$_x$ may safely be neglected (Nicol et al. 1994), and the nitrous oxide route is well described by Eqn. (11) with the H-atom contribution dropped. Providing CO-correlations for $Y_{NO}$ and $Y_O$ from the detailed chemical model allows then a prediction of the NO$_x$ formation rate via the nitrous oxide route. At atmospheric pressure, which is considered in this study, the situation is more complicated: Fenimore NO$_x$ should not be neglected, and the destruction of N$_2$O by hydrogen atom attack is important. It has therefore been decided to provide the formation rate of NO via the nitrous and prompt route directly to the post-processor.

The NO$_x$ post-processor operates then in two steps: 1) The one-dimensional adiabatic laminar flame or chemical reactor model is used as a pre-processor to generate a look-up table of $Y_O$ and $d[Y_{NO}]/dt$ by the nitrous oxide and prompt mechanisms versus $Y_{CO}$ for the given $\lambda$, $p$ and inlet temperature. The chemical mechanism used is that of Miller and Bowman (1989) with Zeldovich NO$_x$ deactivated. 2) Calls to the look-up table provide the CFD code with local values for the O-atom concentration and the rates of NO production by the nitrous oxide and prompt mechanisms. Zeldovich NO formation is then computed according to equation (6), using also the CFD generated local temperature.

Adopting this special treatment for Zeldovich NO, it appears principally feasible to consider the effect of heat losses and/or temperature fluctuations at least on Zeldovich NO$_x$ formation – which shows the strongest temperature dependence of all NO$_x$ formation paths considered due to the high activation energies involved$^4$. Of course, this would require that the [O] = [CO] corrosion.

$^4$The effects of heat losses on nitrous/prompt NO$_x$ are less important because the relevant activation energies are generally lower and because heat losses in the flame zone, where the nitrous and prompt routes dominate, may be expected to be small as radiative heat transfer may be neglected in lean-premixed flames and cooling air (if any) is usually not injected into the flame zone.

KINETIC MODELLING RESULTS

As discussed above, our NO$_x$ post-processor does not perform detailed chemical kinetic calculations, it merely links – via look-up tables – reaction kinetic data derived from 1D premix flame or PSR/PFR computations into the 2D or 3D solution field obtained from the turbulent combustion modeling. Specifically, O-atom concentrations and prompt/nitrous NO$_x$ formation rates for a given value of CO mass fraction and temperature are extracted from the detailed chemical kinetics computations. Throughout this paper, the detailed mechanism used for combustion of CH$_4$ is that of Miller and Bowman (1989), with low pressure corrections as suggested by Baulch et al. (1992).
This is illustrated in Fig. 3, which shows $O$-atom vs. CO mass fraction taken from a 1D premix flame computation at atmospheric pressure with inlet temperature $T_i = 630 K$, air excess ratio $\lambda = 2.1$ and methane fuel. Also plotted are equilibrium $O$-atom mass fractions obtained with the Chemkin equilibrium code (Kee et al. 1985, 1989) and with the partial equilibrium expression \[ [O] = k_p[O_2]^{1/2}, \]
where $k_p = 34.67^{0.5} \exp(-27123/T)$ as suggested by Warnatz and Maas (1993). Please note that traversing the flame front from the unburnt to the burnt side corresponds to traversing the curves in the diagram in the counterclockwise direction. Equilibrium conditions are near the upper left end of the curves. The portion of the curves with $O$-atom mass fractions below $10^{-8}$ — corresponding to the cold part of the preheat zone — have been omitted from the graph.

It is found that in the flame zone, i.e. near the CO peak, O atom mass fractions are up to 2 orders of magnitude above (partial) equilibrium values, i.e. super-equilibrium radical overshoot is enormous at the rather moderate temperatures that are found in this lean premixed flame. Only with CO nearing its equilibrium value are the $O$ atom concentrations reasonably well approximated by the partial equilibrium assumption. Obviously, at the prevailing conditions $NO_x$ models based upon partial equilibrium $O$-atom concentrations would severely underpredict the production of Zeldovich $NO_x$ in the flame front. The $NO_x$ prediction scheme introduced in this study should be significantly more precise than any such model, even if predictions of $CO$ concentrations are with the available combustion model only qualitatively correct.

Production rates of prompt/nitrous $NO_x$ — which are also input to the $NO_x$ post-processor in the form of look-up tables — are plotted vs $CO$ mass fraction in Fig. 4. Please note that all concentrations are on a wet, actual $O_2$ basis, except where noted otherwise. The prompt/nitrous $NO_x$ production rate of the 1D premix flame (filled diamonds) behaves essentially\(^5\) as expected, i.e. there is a strong production rate peak in the flame zone (upper right corner of the diagram), the production diminishes rapidly in the burn-out zone and is negligibly small near equilibrium conditions (left side of the diagram).

The production of Zeldovich $NO_x$ (open diamonds) also peaks in the CO-rich flame zone with a value of about one fifth of the maximum prompt/nitrous $NO_x$ rate. Zeldovich $NO_x$ production diminishes less rapidly in the burn-out zone and — in this particular case — forms near equilibrium at approximately 1 ppm/s, which is more than five times faster than prompt/nitrous production.

Also shown in Fig. 4 are production rates from PSR/PFR reactor models at lean blow out (PSR residence time $\tau \approx 0.2$ ms, which provides correlations over the greatest range of CO-space, and with a larger PSR with $\tau \approx 0.4$ ms. The larger reactor's volume was set in such a way that the Double Cone Burner's lean blow out equivalence ratio $\phi \approx 0.4$ was reproduced by the reactor model. It can be seen that the production rates taken from the two chemical reactor models are quite close to each other and the 1D premix values, except near the CO-peak, where differences up to a factor of two are observed. The $CO$-$O$ correlations produced by PSR/PFR models differ even less from their 1D premix counterparts (not shown). This is a remarkable observation, considering that the PSR/PFR and laminar flame models correspond to turbulent Damkohler numbers equal to zero and infinity, respectively.

This apparent universality has been further examined using several chemical reactor zone arrangements, including cases with multiple PSRs and PFRs, and cases with recycle zones included. These results, which are described by Nicol et al. (1994), show (for given $\lambda$, $p$, and inlet temperature) that the dependence on the $CO$
concentration of the $O$-atom and $N_2O$ concentrations, and the rate of NO production, is essentially independent of the chemical reactor zone arrangement selected. The provisions are that the combustion process be adiabatic (or nearly adiabatic), and that the combustion process not be quenched.

**POSTPROCESSOR RESULTS**

2D contour plots of total NO$_x$ production rate and concentration obtained with the post-processor are shown in Fig. 5. (Operating conditions are air excess ratio $\lambda = 2.1$, inlet temperature $T_i = 630$ K, pressure $p = 1$ bar.) The production rate rises very steeply on the cold side of the flame front, and a finer grid would be required to resolve this region adequately. Peak production rates in the flame are about 1000 ppm/s, in the burn out zone the production rate decreases rapidly to very small values around 20 ppm/s. Fig. 5 confirms our expectations that the formation of oxides of nitrogen is essentially restricted to the flame zone, where significant concentrations of radicals are found in lean premixed combustion. Only near the burner axis, where residence times in the vortex breakdown and its wake are longer than elsewhere, is post-flame NO$_x$ formation noticeable.

A comparison of measured and predicted NO$_x$ concentrations (dry, 15% $O_2$) at the centerline, 400 mm downstream of the burner exit, is presented in Fig. 6. Mixture inlet temperature was 630 K for both experiment and computation with natural gas and methane used as fuels, respectively. Maximum experimental flame temperatures are near 1750 K due to the risk of flash back at richer conditions (see above). The agreement between experiment and post-processor predictions is remarkable, especially if one considers that the post-processor has no adjustable parameters. The disagreement at higher temperatures can be attributed to heat losses, which increase with temperature in the experiment, while they are not considered in the (adiabatic) computations. However, recalling the shortcomings of the heat release and CO modeling discussed in Section 3, and the neglect of turbulent fluctuations in the present implementation of the post-processor, we must concede that the level of agreement shown in Fig. 6 is most likely at least to some extent coincidental. Nevertheless, the post-processor is conceptually sound, and reproduces qualitative aspects of NO$_x$ formation in lean premixed flames correctly. A more reliable turbulent combustion model would certainly increase our confidence in the NO$_x$-model's quantitative predictions.

A few comments concerning the influence of temperature fluctuations on NO$_x$ formation in lean premixed combustion shall conclude this Section. The formation of Zeldovich NO$_x$ is extremely sensitive to temperature, due to the high activation energy of the rate limiting reaction (7). A Zeldovich NO$_x$ formation rate based on mean temperature can therefore be very different from the actual mean formation rate. This is particularly so in diffusion flames, where significant NO$_x$ production occurs only in near stoichiometric regions where high peak temperatures and strong fluctuations are realized. For such flames, the turbulent fluctuations of temperature must be taken into account in a meaningful way. In the context of a NO$_x$ post-processor, this has been attempted – see, e.g. Missaghi et al. (1990) and Dupont et al. (1992) – by introducing a presumed probability distribution function (pdf) for temperature, which is based on the first two moments, i.e. the mean and the variance. If the variance is not provided by the main combustion model, it may be determined approximately from the mean gradient. Species concentrations enter the rate expressions linearly or with small exponents, therefore their mean values may be used un-
under certain circumstances. It is also possible to use a presumed pdf for species, with species and temperature fluctuating independently from each other. This methodology has been applied by Massaghi et al. (1990) and Dupont et al. (1993) to turbulent diffusion and (partially) premixed flames with some success.

The situation is quite different in (perfectly) premixed combustion. Firstly, the nitrous and prompt \( NO_2 \) formation paths are significantly less sensitive to temperature than the Zeldovich path. Secondly, the momentary temperature is always restricted to values below the adiabatic flame temperature; less than 1800 K at conditions of interest. Finally, the highest radical concentrations and the highest \( NO_2 \) formation rates are found at intermediate temperatures (compare Fig. 4). These observations suggest that the error incurred by neglecting temperature fluctuations altogether is insignificant. This supposition is supported by Fig. 7, which shows the computed \( NO_2 \) formation rate and the temperature gradient sampled from about 500 computational cells in the vicinity of the flame front. The temperature gradient \( VT \) has been non-dimensionalized by the turbulent length scale \( l_T \) and the temperature \( T \) and then normalized to the interval \([0,1]\). It is remarkable that the \( NO_2 \) formation predicted by the post-processor is considerable only in regions where gradients of temperature, and thereby also the fluctuations of temperature, are relatively small. This behavior is consistent with our conjecture.

**SUMMARY**

A \( NO_2 \) prediction scheme suitable for lean-premixed combustion of methane or natural gas at atmospheric and gas turbine conditions has been developed. The model is implemented as a post-processor, i.e. the \( NO \) transport equation is solved after the "main" turbulent combustion simulation has been completed. Source terms for \( NO \) are derived from the "main" solution via correlations based on mean CO-concentration and temperature. These correlations are computed with one-dimensional laminar flame or PSR/PFR models with detailed chemistry and provided to the \( NO_2 \) module in the form of a look-up table. The correlations are not universal; for every operating condition (inlet temperature, pressure, air excess, etc.) of interest an appropriate look-up table must be prepared. However, the correlations are remarkably universal inasmuch as unstrained laminar flame or PSR/PFR models, corresponding in some sense to infinite and zero turbulent Damköhler number, produce very similar correlations.

At atmospheric conditions, which this study is restricted to, correlations for nitrous/prompt \( NO_2 \) formation rate and \( O \)-atom mass fraction, necessary to predict Zeldovich \( NO_2 \), are supplied. At high pressures, prompt \( NO_2 \) may be neglected, and a global expression for the nitrous \( NO_2 \) rate may be used, which is based on \( N_2O_3 \) and \( O \). The effect of turbulent fluctuations on \( NO_2 \) formation rates is not considered in the present implementation. It has been argued, however, that these effects are possibly quite small in lean-premixed combustion.

As a test case, combustion in a swirl-stabilized gas turbine burner at atmospheric pressure has been simulated. Dimensional estimates suggest that this burner operates in a regime where both turbulent mixing and kinetic rate limitations must be considered (\( Da \approx 1, Ka > 1 \)). An extended eddy break-up turbulent combustion model has been developed and implemented, which allows one to consider kinetic limitations in a physically reasonable manner. Qualitatively correct distributions of flow, temperature and \( CO \) mass fraction have been obtained.

For the leanest conditions considered, where effects of non-adiabaticity are smallest, the \( NO_2 \) post-processor predicts concentrations of oxides of nitrogen with excellent quantitative agreement with experiment. Also, the production of \( NO_2 \) occurs mainly in the flame zone, which is in agreement with our present understanding.

![Figure 7: Computed \( NO_2 \) production rate and normalized temperature gradient vs. temperature \( T \) from the vicinity of the flame front. The sudden jump in production rate corresponds to the transition from the low-\( T \) to the high-\( T \) branch of Fig. 4 and occurs because the \( CO \)-concentration reached in the CFD model is lower than the maximum \( CO \)-concentration from the detailed model.](http://mechanicaldesign.asmedigitalcollection.asme.org/GT/proceedings-pdf/GT1995/78804/V003T06A019/2406178/v003t06a019-95-gt-108.pdf)
of NOx formation in lean-premixed combustion. The model shall be applied to high pressure test cases in the near future; the possibility of including effects of turbulent fluctuations and imperfect pre-mixing is being studied.

REFERENCES


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