NO\textsubscript{x} PRODUCTION IN VITIATED AND ADIABATIC COMBUSTION SYSTEMS

Y. LEVY\textsuperscript{*} and P. ARFI

Faculty of Aerospace Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

The accuracy of NO\textsubscript{x} predictions in combustion systems is highly dependent on the temperature and concentration fields inside the combustor. Turbulence-chemistry interaction affects local temperature, local extinction, and hence flame stability. Some of the advanced dry low NO\textsubscript{x} combustion systems are based on exhaust gas recirculation or staged combustion. Combustion with air diluted by combustion products is a known NO\textsubscript{x} reduction technique, however, it may significantly deteriorate combustion stability. Therefore modeling effects of air vitiation on flame stability as well as on fuel and nitrogen chemistry are a key point for improving NO\textsubscript{x} predictions. In the present study, a local extinction phenomenon is considered, based on a perfectly stirred reactor model, representative of the reactive fine structure. It is shown that current CFD models based on global chemistry mechanisms are unable to reproduce local extinction phenomena. However, comparisons to experimental data show that combination of a combustion model accounting for local extinction and a NO\textsubscript{x} model allowing for nonequilibrium O concentrations could improve trend predictions. Results show that even though air vitiation by combustion products impairs flame stability, it can be counterbalanced by an increase in the gas mixture inlet temperature. In addition, the combined effect of high inlet air temperature and air vitiation enables reduction of local temperature peaks and thereby allows significant NO\textsubscript{x} reduction. It appears that the NO\textsubscript{x} species formation, even when based on a detailed chemistry of the hydrocarbon chemistry oxidation, is poorly represented by simplified CFD emission models. In addition, it was observed that the classic approach based on the assumption of fast fuel chemistry, combined with the O–O\textsubscript{2} equilibrium assumption in the emission model, may be inaccurate when finite rate kinetic effects become preponderant.

*Address all correspondence to Y. Levy, levy@aerodyne.technion.ac.il

INTRODUCTION

Before global extinction due to low fuel flow rate or combustion pressure conditions is encountered, localized flame extinction due to intense turbulence stretching may be present and is of importance as a precursor to global extinction and blowoff (Han and Mungal, 2000). Local extinction due to turbulence-chemistry interactions is an important aspect in developing combustion systems based on air vitiation. Many studies of the extinction phenomenon in a simple flame configuration have been carried out to improve understanding of the mechanisms involved, even under diluted or hot reactant conditions (Chelliah et al., 1990, ...
1990a, b; Mastorakos, Taylor, and Whitelaw, 1995). It is generally believed, based on planar stagnation plane investigations, that strain rate, and especially turbulence-induced strain of the flame, plays an important role in local extinction.

The prediction of combustion patterns in practical combustion devices requires calculation of complex, turbulent, three-dimensional flow fields as well as finite rate kinetic chemistry. As a result, the chemistry and its interaction with the turbulent fluctuations must be modeled, the problem being to model not only the turbulent flow and the kinetic evolution of the components, but also the time-averaged reaction rate dependence on the instantaneous field, whereas only time-averaged values are computed in CFD codes. The models currently used in CFD for combustion rate in internal flows are not as accurate as desirable, and they do not address several issues, especially those relating to finite rate chemistry. That is why recent work has focused on the development of methods that can treat finite rate kinetics in a realistic, yet tractable way. Inclusion of full chemical schemes is very difficult. Meanwhile, there exist a number of combustion phenomena, such as ignition, extinction, and \( \text{NO}_x \) formation, in which finite rate chemical reactions play an important role. It appears that when considering the turbulence regimes, finite rate chemistry effects are not only important for the predictions of intermediate species as CO and \( \text{H}_2 \) in hydrocarbon flames, they also provide the basis for mechanisms that lead to local quenching and eventually lift-off and blowout of nonpremixed flames. Vitiation, by reducing the chemical timescale, will tend to bring combustors (especially those based on flue gas recirculation) toward local quenching conditions. The local quenching effects that lead to disruption of the flame surface have important consequences on turbulent diffusion flame stability. Local extinction can significantly influence combustion characteristics and represents a key point in combustion modeling of low-emission combustors. It also has special importance for understanding the limits of low-\( \text{NO}_x \) systems. The present article focuses on a description of the combined effects of air vitiation, inlet temperature, and residence time on \( \text{NO}_x \) formation. It also attempts to understand how CFD combustion model assumptions affect \( \text{NO}_x \) prediction models and to evaluate model accuracy regarding \( \text{NO}_x \) emissions under mild combustion (Cavaliere and De Joannon, 2006; De Joannon et al., 2002) or a flameless oxidation combustion regime.

**Local Extinction in Vitiated Combustion Systems**

When considering vitiated combustion systems (flameless oxidation, secondary staged combustion), it is interesting to understand the effect of dilution on the chemical quenching time. Figure 1 illustrates the effect of dilution by carbon di-
oxide (CO₂) on chemical quenching time, computed in an adiabatic perfectly stirred reactor model (PSR). To allow comparisons, the CO₂ value was varied (as a parameter), while the nitrogen concentration was retained at a constant value of 70% and the molar concentrations of oxygen and fuel were jointly varied so that the fuel:air ratio remained constant (at stoichiometric conditions, φ = 1). It is shown by the present computations that the quenching time increases with CO₂ dilution at a constant air ratio. This effect is extremely strong for low inlet temperatures and becomes relatively weak at very high temperature inlets. Typically, for a 300 K methane–air mixture, the quenching time for a mixture with 15% CO₂ is 300 times greater than for a mixture without any CO₂, while if the mixture is initially at 1200 K, the quenching time is only 7.5 times greater. It is also interesting to note that the minimum temperature of combustion achievable for the given mixture (the "flame temperature at extinction"), as shown in Figure 2, is much lowered by increased CO₂ concentration, most probably because of its high heat capacity effect. It is also shown by the present study that the temperature reduction is not dependent on the initial temperature, so that even at high inlet temperatures the lowering effect of the dilution on quenching peak flame temperature is not affected. High temperature of reactants combined with CO₂ dilution lowers the minimum flame temperature attainable in steady combustion processes (through dilution), while maintaining the quenching time at the same order of magnitude (by increased inlet temperature). This could be of importance in ex-
plaining why diffusion flames with high-temperature diluted air are less sensitive to blowout that will allow eventually reduction of the temperature peaks. This also suggests that in order to estimate the critical residence time for extinction, it is absolutely necessary to account not only for inlet reactant equivalence ratio and temperatures, but also for dilution.

According to the study of the different mixtures, water does not significantly increase the residence time at quenching (the quenching time) and has about the same beneficial effect on temperature reductions. Nitrogen, as an inert species, has a weaker influence on the increase of the chemical quenching time and does not affect temperature as carbon dioxide does.

Even if it appears interesting to understand these effects for each gas component, in flue gas recirculation, the recirculated gas, or in staged combustion, the primary products, are not made of a single component. That is why one considers here dilution by more realistic combustion products. In this study the stoichiometric mixture of methane-air was diluted using typical combustion products. The dilution gases consist of 9.5% CO₂, 19% H₂O, and 71.5% N₂ and represent the perfect combustion products of a stoichiometric air-methane mixture. The results of the adiabatic PSR calculations are shown in Figure 3.

On the basis of the calculated extinction behavior obtained with the comprehensive reaction mechanism, it is observed that quenching time increases with dilution. However, one can observe that increasing the inlet temperature for any mixture makes the critical residence time decrease to values close to those of the
conventional mixture inlet conditions (no dilution, 300 K), i.e., an order of magnitude of 100 µs. This clearly shows that combustion with ambient air, diluted by ambient temperature combustion products, will strongly impair the flame stability by shifting the quenching time to large values (above 0.01 s). However, when recirculating hot combustion products (high mixture temperatures, above 1200 K, which is the required temperature observed experimentally for flameless oxidation systems (Wunning and Wunning, 1997)), the typical quenching time becomes nearly insensitive to the recirculation rate. It can be concluded that dilution with hot combustion products allows reduction to the minimum achievable flame temperature without impairing flame stability.

The results of the present study are in agreement with the numerical study of Gran, Melaaen, and Magnusseen (1994) in PSR and the experimental study of Mastorakos et al. (1995) under laminar opposed diffusion flame conditions.

Local Extinction and Global Mechanisms

When modeling turbulent combustion, it is important to account for the effect of enhanced local micromixing on the local combustion process. If this micromixing is too rapid (or the reactions are too slow), the reactive flow may be locally extinguished. Since current combustion models typically use a global reaction model approach, it is of special interest in the present investigation to consider this local extinction phenomenon in PSR and to discuss the suitability of the current models in CFD modeling of low-emission combustors. Combustion of methane in adi-
abatic PSR was simulated using the two-step model of Westbrook and Dryer (1981) and the three-step mechanism of Brink (Brink, 1998; Magel, 1997). Figure 4 shows the obtained flame temperature profiles versus PSR residence time for the mentioned mechanisms. The results obtained in this study using the detailed mechanism are also shown for reference. It is clearly shown that the two-step mechanism (dotted line) overestimates the extent of reaction and that reactions nearly always occur, even at a residence time several orders of magnitude lower than that of local extinction. The reaction is, in fact, almost instantaneous. The three-step mechanism (dashed line) enables partial reproductions of a temperature drop phenomena (drop to 400 K) at about the time of the theoretical critical residence time. However, as seen by analyzing the species concentration profiles, this time cannot be considered as characteristic of extinction. Figure 4 shows the computed variation of the fuel concentration with residence time. The observed profiles confirm the "fast" characteristic of the two-step model. This also reveals that the three-step reaction model leads to nearly instantaneous methane consumption (conversion to CO) and is also a fast hydrocarbon chemistry model. This indicates that the drop of temperature shown by this model in Figure 5 cannot be interpreted as an extinction point since all the methane is still reacting completely, even for extremely short residence times.

In both Figures 4 and 5, calculations were with a global mechanism and with detailed mechanisms: two-step and three-step calculations for a stoichiometric mixture of methane and air initially at ambient temperature (300 K).
It is clear that global mechanisms fail to reproduce correctly the temperature or concentration profiles for residence times lesser or closer to the critical residence time of extinction. This is an important point that highlights the limitation of the CFD combustion model of extinction and therefore of the correct temperature fields under vitiation conditions. The accurate predictions of temperature as well as intermediate species concentrations are, as will be seen in the next section, of prime importance in NO$_x$ modeling.

**NUMERICAL MODELING OF NO$_x$ EMISSIONS**

**NO$_x$ Chemistry**

The chemical reactions of nitrogen compounds occurring in combustion processes have been the subject of intensive study for more than 50 years. At the present time, many of the complex reaction paths for formation and destruction of nitrogen species in combustion have been established, and rate parameters for many of the elementary reactions have been determined (Miller and Bowman, 1989). Of special interest are the mechanisms and rate parameters for thermal-NO and prompt-NO formation for fuel-NO conversion.

**Thermal-NO**

The extended Zeldovich mechanism is generally considered for thermal-NO formation. The four principal reactions that comprise the thermal-NO formation mechanisms are
\[
\begin{align*}
O_2 & \rightleftharpoons -2O \\
N_2 + O & \rightleftharpoons NO + N \\
N + O_2 & \rightleftharpoons NO + O \\
N + OH & \rightleftharpoons NO + H
\end{align*}
\]

Free oxygen from the equilibrium dissociation of an unburned oxygen molecule (reaction (1)) initiates the chain. The breaking of a strong N$_2$ bond is represented by the high activation energy of reaction (2), which makes this forward reaction the rate-limiting step of the thermal mechanism. A nitrogen atom is liberated, and it reacts with oxygen to form NO (reaction (3)). The nitrogen atom may also react with the OH radicals to form NO (reaction (4)). It may be noticed that equilibrium dissociation of nitrogen molecules is not achieved at temperatures encountered in a turbine reactor, and the only source of nitrogen atoms is reaction (2). The quantity of NO formed is an exponential function of temperature and is proportional to the concentration of N$_2$, the square root of O$_2$ concentration, and the residence time at high temperatures. Maximum NO rates can be expected to be found under conditions of high temperature and high O concentrations.

**Prompt-NO**

NO may be found very early in the flame region, a fact that seems to be in contradiction with the idea of the kinetically slow process of postflame NO formation. The largest discrepancies between measured NO formation rates and rates predicted by the thermal NO equation were observed by Fenimore (1971) in premixed combustion of fuel-rich (hydrocarbon–air) mixtures. This apparently instantaneous formation of NO, observed in hydrocarbon flames, is due to two mechanisms. Part is due to the thermal mechanism, enhanced by rapidly formed superequilibrium radical concentrations of O and OH, which accelerate the rates of reactions in the Zeldovich mechanism. The rest is due to a hydrocarbon-nitrogen mechanism, enhanced by the rapid reaction of hydrocarbon radicals formed in the flame zone or in multiple flame zones (e.g., CH, C, C$_2$, etc.) with molecular nitrogen. This reaction led to formation of cyano compounds (CN group containing intermediates like hydrogen cyanide) and N atoms that subsequently react to form NO.

**Fuel-NO**

The fuel-N route is relevant when the fuel contains bounded nitrogen; hence it is not generally important in gas turbine combustion applications since most fuels used contain little or no bound nitrogen.
For atmospheric diffusion flame conditions the thermal, prompt, fuel, and nitrous pathways contribute to NO$_x$ production, and none can be \textit{a priori} omitted. Nevertheless, thermal NO predominates in conventional diffusion flame combustors, especially when considering high-temperature inlet reactants. However, the relative importance of the mechanisms is highly dependent on the flame structure.

\textbf{NO$_x$ Formation in the Perfectly Stirred Reactor Model (PSR)}

The evolution of nitrogen species was studied in the present investigation in an adiabatic PSR using a detailed chemistry description of the methane-air combustion (Gri-2.11 mechanism) (Bowman \textit{et al.}, 2006).

\textbf{Effect of Mixture Equivalence Ratio and Residence Time}

Figure 6 shows the effect of equivalence ratio on total fixed nitrogen (TFN) formation. The TFN represents the sum of all the molar concentrations of the different nitrogen-containing species, except N$_2$. It is observed that the TFN fraction peaks on the lean side slightly before stoichiometry. Even if the temperature is maximum at an equivalence ratio slightly superior to 1, the maximum is certainly shifted to the lean side because of higher availability of oxygen atoms at lean conditions, favoring N$_2$ reaction with free oxygen. In contrast, at rich conditions, there is competition between nitrogen species and fuel species for available O, which limits nitrogen oxidation reactions. The amount of TFN formed decreases

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.png}
\caption{NO$_x$ species formation as function of equivalence ratio for different N chemistry formulations (with detailed chemistry for fuel oxidation). Adiabatic PSR air–methane mixture. $T_{\text{in}} = 300$ K; $\tau = 100$ ms. Solid line, reference mechanism (detailed); dashed line, simplified thermal-NO model 1; dotted line, simplified thermal-NO model 2.}
\end{figure}
quickly on the lean and rich sides mainly because of the strong decrease in temperature, which has a drastic effect on reaction rates.

Varying the residence time in the reactor for a stoichiometric mixture entering the combustor at ambient temperature shows that FN species require relatively large residence times to be formed in large quantities (at least 0.1 s for 40% of the equilibrium value and 1 s for 90% of the equilibrium value). In addition, it is shown that FN species reach equilibrium values slowly after residence times a few orders of magnitude larger than that for hydrocarbon oxidation. This confirms that NO formation and fuel combustion occur in different turbulent/chemistry regimes.

**Effect of Inlet Temperature and Dilution**

The effect of the inlet temperature and dilution on the TFN formation is of special interest for understanding how flameless oxidation allows reduction of NO\textsubscript{x} emissions even at high air-preheat temperatures. The initial temperature of the mixture entering the PSR was varied between 300 K and 1500 K. The residence time was unchanged (100 ms), and the equivalence ratio was fixed at 1. Figure 7 displays the computed dependence of the NO\textsubscript{x} formation with the initial temperature of the mixture. As expected for a nondiluted mixture, the NO\textsubscript{x} emission increases drastically with the inlet temperature.

Of special interest is the effect of dilution by different combustion products on NO\textsubscript{x} formation. The initial mixture \((T_{\text{init}} = 300 \text{ K})\) was diluted here using

![Effect of inlet temperature on TFN formation](image)

**FIGURE 7** Effect of initial mixture temperature on total fixed nitrogen (TFN). Adiabatic PSR methane-air mixture. Residence time \(= 100 \text{ ms}\). Equivalence ratio \(= 1\).
carbon dioxide as the dilution agent. The equivalence ratio was maintained at 1, and the nitrogen percentage was fixed at 70%. The dilution was varied from 0 to 20 vol % of CO₂. Figure 8 displays the dependence of the TFN on dilution. It is observed that the effect of dilution on NO species is extremely strong.

Indeed, the TFN is of the order of 1000 ppm without dilution and drops sharply to 1 ppm at about 15% dilution. The TFN becomes even negligible for larger dilution values. This effect of dilution can be attributed to (1) the thermal effect of dilution (decrease of temperature because of lower values of reactive components (heat available)); (2) the thermal effect of CO₂ (increasing the total heat capacity of the mixture); and (3) the kinetic effect of CO₂ that may favor the recombination reaction of HCN species to N₂. This kinetic effect is highlighted further in the isothermal reactor study. Here, as a further improvement, a sensitivity analysis of the reaction rate could be conducted to improve the understanding of the chemical impact of dilution.

**Isothermal Reactor Study**

To improve the understanding of NO formation, in our investigation, isothermal conditions at two fixed temperatures (1500 K and 2000 K) for a lean mixture (equivalence ratio = 0.7) are also considered. Calculations are based on detailed mechanisms.

The effect of CO₂ dilution at constant temperature is illustrated for an isothermal PSR reactor at 1500 K and 2000 K in Figure 9. Even if the different
mechanisms have relatively large discrepancies between each other, they both show that the amount of NO$_x$ formed is strongly decreasing with an increased CO$_2$ concentration, especially at high temperatures. In both cases the amount of NO formed after 1 ms at 2000 K is divided by 2 if compared to the nondiluted case. Since the PSR is modeled as isothermal, this effect is purely kinetic and cannot be attributed to a thermal dilution effect. This also suggests that a simplified scheme is not able to predict this kinetic effect since CO$_2$ concentration is not taken into account in the reaction rate expression of the NO formation rate.

**Conclusion on NO$_x$ Study in PSR**

It was demonstrated in the present investigation that the oxides of nitrogen emissions are reduced by air vitiation. The most drastic decrease is due to thermal dilution and lower heat release, however, isothermal PSR simulation shows clearly that a kinetic effect contributes to lower NO$_x$ formation, especially the presence of carbon dioxide. Further sensitivity analyses could contribute to determining which reactions are inhibited or enhanced and which dilution agent is responsible for this effect on the nitrogen chemistry.

**CONCLUSION**

The investigation under PSR conditions of the influence of the description of the chemistry on the temperature and species concentration predictions showed that fi-
nite rate kinetic effects are of special importance in predicting more accurately stability limits as well as temperature distribution within the combustion chamber. Current global chemistry combustion models have important shortcomings and cannot be used accurately when dealing with advanced combustion methods, such as flameless oxidation as well as flue gas recirculation or fuel staged combustion. Reduced mechanisms were also tested under PSR conditions, and it was shown that they might be sufficiently accurate in predicting important finite rate kinetic effects, such as local extinction.

The CFD assumptions’ influence on NO\textsubscript{x} emission models was also studied under PSR conditions, and it was shown that current combustion models may not predict accurately NO\textsubscript{x} emissions because of the lack of knowledge of the intermediate species concentration. This also suggests that inclusion of detailed chemistry, or at least reduced chemistry, is strongly needed in CFD modeling. However, application of such chemical schemes into CFD combustion models is not straightforward because of the need to model in turbulent flames the mean reaction rate based on average values of the state variables. In addition, it may lead to large CPU time increases as well as to numerical instabilities, which may be difficult to manage practically.

The influence of combustion air temperature and oxygen content (dilution) was studied, with special emphasis on the effects on the local extinction phenomenon and NO\textsubscript{x} formation. These, when studied in PSR, enabled a better physical insight of flameless oxidation fundamentals. It was demonstrated that an increase in air dilution (decrease in oxygen content) decreases strongly the chemical quenching time, which is a characteristic of flame stability and is defined as the minimum residence time required for chemical reaction to occur. However, an increase in the vitiated air temperature makes the mixture nearly insensible to dilution, especially far from stoichiometry, giving thereby some indication of the flame stabilization mechanism in flameless oxidation. It was also shown that the minimum achievable adiabatic temperature is strongly reduced by air vitiation and increases in inlet temperature, therefore avoiding local peaks of temperature responsible for NO\textsubscript{x} formation. The PSR studied also illustrated that the NO\textsubscript{x} reduction in flameless oxidation is principally a thermal effect, although NO\textsubscript{x} formation is partially chemically inhibited by the presence of large quantities of combustion products in the combustion air.

References


