Effects of Small-Scale Turbulence on NOx Formation in Premixed Flame Fronts

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Abstract
A flamelet-based approach that accounts for turbulence-chemistry interaction has been formulated to simulate NOx formation in turbulent lean premixed combustion. In the simulations, the species NO is transported and solved with the chemical source term being modelled through its formation in flame fronts and its formation rate in post-flame regions. The flame-front NO and post-flame NO formation rate are obtained from 1-D freely propagating premixed flames with detailed chemical kinetics. For turbulent premixed flames located in the thin-reaction-zones regime, small-scale eddies could penetrate into the preheat zone of the flame and enhance the mixing process. In this study, their effects on the flame-front NO are investigated through the incorporation of turbulence induced diffusion in the preheat zone of the 1-D premixed flames. One-dimensional methane/air premixed flames are simulated with the 53-species GRI-Mech 3.0 mechanism at both atmospheric and engine conditions with different turbulence intensities. It is found that the NO generated in flame fronts decreases with increased intensity of small-scale turbulence and the effect is more profound at high pressures. At high pressures, the turbulence induced diffusion in the preheat zone can reduce the flame-front NO by more than 40%.

1. Introduction
Oxides of nitrogen (NOx) emissions from combustion process are harmful to the environment. It will cause the ozone depletion, and is the main contributor to the acid rain and photochemical smog [1]. Recently, more stringent emission regulations are pushing toward the development of more fuel efficient and low emission gas turbine systems. Turbulent lean premixed combustion now plays a predominant role in reducing NOx due to the low flame temperatures. Extensive experimental studies have been performed to investigate the effects of mixture inlet temperature, equivalence ratio, pressure, as well as swirling on NOx formation in premixed systems operating at both atmospheric and engine conditions [2-10]. At the meantime, simulations have also been used to explore the underlying physicochemical processes for emission formation in turbulent premixed combustion [11-15].

Detailed chemical kinetics is a key component needed for accurate emission prediction. One approach to incorporate chemical kinetics in simulations is to transport and solve all the chemical species in a mechanism and perform chemical calculations on-the-fly. This approach includes linear eddy models [16, 17] and composition transported probability density function methods [18, 19]. Despite chemistry acceleration tools like storage/retrieval (e.g. [20]), mechanism reduction [21] and dimension reduction [22], etc., the computational cost of this approach remains high. In contrast, the flamelet approach [11, 12, 23, 24] assumes that the compositions occurring in turbulent flames are similar to those of a laminar flame and reside in a low-dimensional manifold. Thus a laminar flame generated manifold can be employed to describe turbulent flames. This flame generated manifold can be parameterized by very few variables, e.g. the mixture fraction and/or the progress variable, which are transported and solved in simulations. With the flamelet approach the reduction in simulation time is significant, not only because of the reduced number of transport equations, but also because the computationally expensive chemistry calculations can be performed a-priori.

The flamelet approach can successfully describe the flame structure for a relatively weak turbulent premixed flame, in which the smallest turbulence eddies are larger than the flame thickness, and turbulence wrinkles

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and convolutes the premixed flame interface, increasing its area but not altering its internal structure. The flamelet concept, however, does not apply to flames in the broken-reaction-zones regime, in which eddies can penetrate into the thin reaction zone and the flame stretch by turbulence changes the chemical reaction rate and often leads to flame quenching [25]. Sophisticated models such as LEM and PDF are needed to resolve the intense turbulence-chemistry interaction. For turbulent premixed flames between these two extremes, large eddies will convolute and stretch the premixed flame interface while eddies smaller than the flame thickness can penetrate into the flame zone and thicken the flame preheat zone, but are still too large to influence the thin reaction zone. In this thin-reaction-zones regime in which most gas turbine combustors operate, there still exists a flame front that separates the unburnt and burnt mixtures. The flamelet approximation can still be employed, but have to be revised to take into accounts of the flame thickening effects on the flame speed, structure and pollutant formations. For example, Kim and Menon [13] developed a turbulent flame speed model for this regime that explicitly accounts for flame broadening effect. However the effect of the small-scale turbulence on NOx formation in premixed flame fronts is still not clear.

In the present effort, a flamelet-based approach for NOx prediction has been formulated for turbulent premixed flames in the thin-reaction-zones regime. In the simulations, species NO is transported and solved and its chemical source term is obtained from 1-D freely propagating premixed flames with detailed chemical kinetics. NO formation in 1-D premixed flames is characterized by its formation in flame fronts and formation rates in post-flame region. The effects of the small-scale-turbulence/chemistry interaction on flame structure and NO formation are accounted for through the incorporation of turbulence induced diffusion in the preheat zone of the 1-D premixed flames. As an outline of the paper, in Section 2, the NOx formation in unstretched laminar premixed flames is studied and then the flamelet-based approach for NOx prediction in turbulent flames is formulated. Effects of small-scale turbulence on NO formation in premixed flame fronts are studied in Section 3. Discussions and conclusions are presented in Section 4.

2. NOx formation in freely propagating premixed flames

One-dimensional methane/air adiabatic laminar premixed flames are simulated with GRI-Mech 3.0 [26] at both atmospheric and engine conditions. The values of the three controlling parameters, equivalence ratio, \( \phi \), pressure, \( p \), and temperature of the unburnt mixture, \( T_{in} \), are listed in Table 1. The base case is \( p = 15 \text{ atm}, \phi = 0.6 \), and \( T_{in} = 700 \text{ K} \). The NOx formation in these freely propagating flames is firstly characterized and then the flamelet-based approach for NOx modeling is formulated.

<table>
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<th>( p ) (atm)</th>
<th>1</th>
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<th>30</th>
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<td>( \phi )</td>
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<td>0.6</td>
<td>0.7</td>
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<td>( T_{in} ) (K)</td>
<td>600</td>
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2.1 Flame-front NO and post-flame NO formation rate

Figure 1 shows the profiles of temperature, NO mass fraction, and NO formation rate from a 1-D premixed methane/air flame. It is noticed that in the 1-D adiabatic flame, the NO profile has two distinct behaviors: a rapid increase in the flame front region and a linear growth in the post-flame region where temperature almost reaches the adiabatic flame temperature and NO formation rate is a constant. Consequently, if a location in the linear growth region is defined as the boundary between the two regions, the NO profile in the post-flame region can be quantified by [11]

\[
Y_{NO} = Y_{NO}^{ff} + \omega_{NO}^{pf} t^*,
\]

(1)

where \( Y_{NO}^{ff} \) is the flame-front NO (i.e., species NO mass fraction at the boundary location), and \( \omega_{NO}^{pf} \) is the constant post-flame NO formation rate, and \( t^* \) is the residence time (with \( t^* = 0 \text{ ms} \) being at the boundary location). In this study, the boundary is taken to be the location where 99% carbon in the mixture has been
converted into carbon dioxide. As shown in Fig. 1, the boundary point is within the linear growth region and meanwhile is close to the rapid growth region.

Figure 1. Temperature, NO mass fraction, and NO formation rate against time in the 1-D laminar methane-air flame with \( p = 15 \text{ atm}, \phi = 0.6, \) and \( T_{in} = 700K \). The vertical line (with \( t^* = 0 \)) is the starting point of the post-flame region.

Figure 2 illustrates the contribution of NO formations from the prompt and thermal mechanisms. The prompt NO is obtained by performing a separate calculation with the following three reactions being removed from the GRI-Mech 3.0 mechanism

\[
\begin{align*}
N_2 + O & \rightarrow NO + N \quad \text{R1} \\
O_2 + N & \rightarrow NO + O \quad \text{R2} \\
N + OH & \rightarrow NO + H \quad \text{R3}
\end{align*}
\]

These three reactions are responsible for producing thermal NO. The thermal NO is obtained by subtracting the prompt NO from the overall NO formation. As shown, prompt NO increases rapidly in the flame front region and then remains almost flat in the post-flame region. NO formed in the flame front has contributions from both prompt and thermal mechanisms, whereas the NO formed in the post-flame region is primarily due to the thermal mechanism.

Figure 2. The NO formations from prompt and thermal mechanisms in the 1-D laminar methane-air flame. The vertical line (with \( t^* = 0 \)) is the starting point of the post-flame region.

In 1-D laminar premixed flames, \( Y_{NO}^{ff} \) and \( a_{NO}^{ff} \) depend on \( \phi, p, \) and \( T_{in} \). As shown in Fig. 3a) and 3b), both \( Y_{NO}^{ff} \) and \( a_{NO}^{ff} \) increase with an increased \( \phi \) or \( T_{in} \). An increased value of \( \phi \) or \( T_{in} \) results in a higher flame temperature and that increases the thermal NO both in the flame front region and post-flame region. An increased value of \( \phi \) also increases the concentrations of intermediate species such as CH and CH\(_2\) and consequently also increases the prompt NO in the flame front region. The effects of pressure are more interesting. As shown in Fig. 3c), an increased pressure will result in an increase in \( a_{NO}^{ff} \), whereas a decrease in \( Y_{NO}^{ff} \). This is due to the fact that a higher pressure leads to a higher flame temperature and consequently a
higher $\omega_{NO}^{pf}$. However as shown in Fig. 4, a higher pressure reduces the residence time in the flame front region and therefore $\gamma_{NO}^{ff}$ decreases.

Figure 3. Effects of a) equivalence ratio, b) temperature of the unburnt mixture, and c) pressure on flame-front NO, $\gamma_{NO}^{ff}$, and post-flame NO formation rate, $\omega_{NO}^{pf}$, in 1-D premixed methane-air flames.

Figure 4. Temperature profiles at different pressures in 1-D premixed methane-air flame. The point $t^* = 0$ is the start of the post-flame region.

To predict NOx formation in turbulent premixed flames, the flame-front NO, $\gamma_{NO}^{ff}$, and post-flame NO formation rate, $\omega_{NO}^{pf}$ are pre-computed from the 1-D laminar premixed flames as functions of equivalence ratio, temperature of unburnt mixture and pressure. In the simulations of turbulent flames, the mean concentration of species NO is transported and solved at the turbulence model level according to

$$\hat{\rho} \frac{\partial \gamma_{NO}^{ff}}{\partial t} + \hat{\rho} \mathbf{V} \cdot \nabla \gamma_{NO}^{ff} = \nabla \cdot \left( \hat{\rho} D_{eff} \nabla \gamma_{NO}^{ff} \right) + \hat{\rho} \hat{\omega}_{NO}^{ff},$$

(2)

where $\hat{\rho}$ is the mixture density, $\mathbf{V}$ is the resolved mean velocity, $\hat{\omega}_{NO}$ is the chemical source term, and $D_{eff}$ is the effective diffusivity that consists of the molecular and turbulent contributions. The chemical source term $\hat{\rho} \hat{\omega}_{NO}^{ff}$ is modeled as

$$\hat{\rho} \hat{\omega}_{NO}^{ff} = -\rho \frac{\partial \gamma_{fuel}^{ff}}{\partial t} \gamma_{NO}^{ff} + \hat{\rho} \hat{\omega}_{NO}^{pf},$$

(3)

where $\gamma_{fuel}^{ff}$ is the mass fraction of fuel in the unburnt mixture and $\hat{\omega}_{fuel}$ is the local consumption rate of fuel. The first RHS term in Eq. 2 represents the NO formation in flame fronts. The second RHS term represents the post-flame NO formation and is only active in the post-flame region. The (instantaneous) flame front in a simulation is constructed using the same criteria as in the 1-D laminar premixed flames. That is, the boundary between flame front and post-flame regions is the surface where a specified percentage of carbon in the local mixture has been converted into carbon dioxide. To use Eq. 2 for NO prediction, combustion models such as LEM, PDF are needed to primarily predict the global heat release and the flame characteristics. For example,
Eggenspieler and Menon [12] employed a thin flame propagation model in conjunction with LES to track the flame front in a full-scale DOE-HAT combustor.

3. Effects of small-scale turbulence on NOx formation in premixed flame fronts

The flame front in a premixed flame generally consists of two zones, referred to as preheat zone and thin reaction zone. For turbulent premixed flames in thin-reaction-zones regime, large eddies convolutes and stretches the flame front while eddies smaller than the flame thickness can penetrate into and thicken the flame preheat zone, but are still too large to influence the thin reaction zone. In this regime, in addition to equivalence ratio, temperature of unburnt mixture and pressure, turbulence can also affect the NO formation in flame fronts. Therefore the flamelet approach for NOx prediction has to be revised to account for the flame thickening effects. Specifically, the dependence of the flame-front NO, $Y_{NO}^{ff}$, on small-scale turbulence has to be quantified.

3.1 Incorporation of turbulence induced diffusion in 1-D unstretched premixed flames

In the preheat zone, reaction is not important and diffusion and convection balance each other, whereas in the thin reaction zone, the dominant balance is between diffusion and reaction. In this study, the boundary between these two zones is taken to be the location where the heat release rate reaches half of its maximum in the flame. The effects of small-scale turbulence on NOx formation in flame fronts are investigated through incorporating the turbulence induced diffusion into the preheat zone.

![Figure 5. Profiles of temperature, normalized heat release rate $q^*$ (with $0 \leq q^* \leq 1$), and function $\delta(x)$ (with $0 \leq \delta \leq 1$) in 1-D premixed methane-air flame with $p = 15 \text{atm}$, $\phi = 0.6$, and $T_{in} = 700K$.](image)

Specifically, turbulence induced diffusivities are added to the species and energy equations of the 1-D flames as follows:

Species: \[
\dot{m} \frac{dy_k}{dx} + \frac{d}{dx} (\rho V_k Y_k) - \dot{\omega}_k W_k = 0,
\] (4)

Energy: \[
\dot{m} \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left( \rho \lambda_{eff} \frac{dT}{dx} \right) + \frac{1}{c_p} \sum_{k=1}^{K} \rho Y_k V_k c_{pk} \frac{dT}{dx} + \frac{1}{c_p} \sum_{k=1}^{K} \dot{\omega}_k h_k W_k = 0,
\] (5)

where \(\dot{m}\) is mass flow rate per unit area, \(c_p\) is mass-averaged heat capacity, \(\rho\) is density, \(\lambda_{eff}\) is the effective thermal conductivity consisting of both the molecular and turbulent contribution, and \(K\) is the number of species in the mechanism. For the \(k\)-th species, \(Y_k\) is its mass fraction, \(V_k\) is its diffusion velocity, \(c_{pk}\) is its heat capacity, \(\dot{\omega}_k\) is its reaction rate, \(h_k\) is its enthalpy, and \(W_k\) is its molecular weight. The diffusion velocity \(V_k\) in the energy and species equations is given by:

\[V_k = \vartheta_k + V_c,
\] (6)

where \(\vartheta_k\) is the ordinary diffusion velocity and \(V_c\) is the correction velocity for all the species to satisfy \(\sum_{k=1}^{K} Y_k V_k = 0\). Turbulent diffusivity \(D_{turb}\) is added when computing \(\vartheta_k\) as
\[ \theta_k = -(D_{km} + \delta D_{turb}) \left( \frac{1}{X_k} \frac{dx}{dx} \right) \]

where \( D_{km} \) is binary mass diffusivity and \( \delta(x) \) is specified as

\[ \delta(x) = \frac{\text{atan}(T^* - T(x))}{\pi} + 1/2, \]

with \( T^* \) being the temperature on the boundary between preheat and reaction zones. As shown in Fig. 5, the function is chosen so that it is one in the preheat zone and zero in the thin reaction zone and post-flame zone. This implies that the turbulence induced mixing dominantly affects the preheat zone. The effective thermal conductivity \( \lambda_{\text{eff}} \) is given by

\[ \lambda_{\text{eff}} = \lambda + \delta \lambda_{\text{turb}}, \]

where \( \lambda \) is the laminar conductivity and \( \lambda_{\text{turb}} \) is turbulent conductivity computed as

\[ \lambda_{\text{turb}} = \rho c_p D_{\text{turb}}. \]

### 3.2 Effects of small-scale turbulence on species profiles and NOx formation in flame fronts

The effect of turbulent diffusivity on flame structure is illustrated in Fig. 6, which compares the temperature and radical profiles from the cases with and without turbulent diffusivity. The value of the turbulent diffusivity, \( 4 \text{ cm}^2/\text{s} \), is about ten times of the laminar diffusivity of major species at 2000K. As shown in Fig. 6a), the added turbulent diffusion significantly broadens the temperature distribution in the preheat zone. The distributions of radicals such as CH and O are also thickened, but not as greatly as temperature distribution since radicals are confined near the thin reaction zone. Notice that turbulent diffusion can also affect the peak radical concentrations. However, with turbulent diffusion, laminar flame speed increases since it is proportional to the square root of the effective diffusivity. The reaction time for the unburnt mixture in the flame front is actually reduced as shown in Fig. 6b). When plotted against time, the radical profiles are narrower than those without turbulent diffusion.

![Figure 6](image-url)

**Figure 6.** Temperature and mass fractions of species CH and O against (a) distance and (b) time in 1-D methane-air flames with and without turbulence induced diffusion. The location \( t^* = 0 \) is the start of the post-flame region.

The effects of turbulent diffusivity on NO formation are demonstrated in Fig. 7, which compares the NO profiles from the cases with and without turbulent diffusivities. In both cases, the NO mass fraction increases greatly in the flame front, and then increases linearly in the post-flame zone. The turbulence induced diffusion increases the peak NO formation rate in the flame front due to the modification of flame structure (see Fig. 6) At the meantime, however, it reduces the residence time of mixtures in the flame front. Overall the small-scale-turbulence induced diffusion in the preheat zone reduces NO formation in the flame front. Since the temperature profile in the post-flame region is unchanged, the NO formation rates with and without turbulent diffusivity in this region are the same as indicated by the slopes of the NO curves.
Figure 7. NO mass fraction and its formation rate as a function of time in 1-D premixed methane-air flame. The location $t^* = 0$ is the start of the post-flame region.

The effects of small-scale turbulence on flame-front NO are studied over a range of equivalence ratios, temperatures of the unburnt mixtures, and pressures. As shown in Fig. 8, for all the cases considered, turbulence induced diffusion reduces the flame-front NO. For the three different equivalence ratios considered, $Y_{NO}^{ff}$ can be reduced by up to 42%. Similarly, for the three temperatures of unburnt mixture considered, it can be reduced by more than 40%. The effects of small-scale turbulence at different pressures are more interesting. As shown, turbulence induced diffusion almost has no impact on flame-front NO at atmospheric pressure. However, its effect becomes profound at high pressures. At $p=30$ atm, it can reduce flame-front NO by up to 48%. That is because the flame thickness at atmospheric pressure is larger than those at high pressures. The flame thickening at atmospheric pressure does not significantly modify the flame structure and consequently does not affect flame-front NO.

Figure 8 The flame-front NO, $Y_{NO}^{ff}$, as a function of turbulent diffusivity at $^a$ different equivalence ratios, $^b$ different temperatures of the unburnt mixture, $^c$ and different pressures.

4. Discussions and conclusions

A flamelet-based approach that accounts for turbulence-chemistry interaction has been formulated for NOx prediction in turbulent lean premixed flames. In the approach, species NO is transported and solved at turbulence model level, and its chemical source term is modeled through NO formed in flame fronts and its formation rate in post-flame regions. The flame-front NO and post-flame NO formation rate are obtained from 1-D upstretched laminar premixed flames with detailed chemical kinetics. For turbulent premixed flames located in the thin-reaction-zones regime, the effects of small-scale turbulence on NOx formation in flame fronts have been quantified through the incorporation of turbulence induced diffusion in the preheat zone of the 1-D premixed flames. One-dimensional methane/air premixed flames have been simulated with the GRI-Mech 3.0 mechanism at both atmospheric and engine conditions with different turbulence intensities. It is shown that the NOx generated at flame fronts decreases with increasing intensity of small-scale turbulence.
and the effect is more profound at high pressures. Small-scale turbulence induced diffusion can reduce the flame-front NO by over 40% at high pressures. The small-scale turbulence induced diffusion in the preheat zone reduces the flame-front NO through modifying the flame structure and more importantly through reducing the residence time of mixtures in the flame front.

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References