Characteristics and NO\textsubscript{x} formation mechanism of thermodiffusively unstable premixed hydrogen flames

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In this study, the formation of NO\textsubscript{x} pollutants in thermodiffusively unstable premixed hydrogen flames is investigated. At first, the overall NO\textsubscript{x} formation characteristics are analyzed, and the effects of the computational setup (2D vs. 3D) on the NO\textsubscript{x} formation are quantified. Then, reaction path analyses are conducted to identify the relevant reaction pathways that make important contributions to the formation of NO\textsubscript{x} pollutants. Finally, the performance of the flamelet model in predicting the NO\textsubscript{x} species is evaluated through an a-priori analysis. The results show that the computational setup has significant effects on NO\textsubscript{x} formation, e.g., the peak value difference of NO mass fraction is around 50%. For the condition studied, the NNH and N\textsubscript{2}O pathways are dominant for the NO formation. The flamelet model gives accurate predictions of NO\textsubscript{x} species in the positively curved region, while discrepancies exist in the negatively curved region.

1. Introduction

Hydrogen is drawing rapidly growing attention around the world. The advantage of the deployment of hydrogen is that its thermochemical conversion does not lead to emissions of the greenhouse gas CO\textsubscript{2}. However, nitrogen oxides (NO\textsubscript{x}) can be formed during the combustion of hydrogen in air. For non-premixed or fuel-rich premixed combustion, the formation of NO\textsubscript{x} by the thermal pathway is found to be the primary reaction pathway due to the high temperatures (Correa 1993). In fuel-lean premixed hydrogen flames, NO\textsubscript{x} emissions can be reduced due to the overall lower flame temperatures.

For fuel-lean hydrogen combustion, the thermodiffusive instability, which is associated with the disparity between the heat flux leaving the reaction zone and the mass flux of the fuel entering the reaction zone, is significant due to the lower effective Lewis number of the unburned mixture (Law & Sung 2000; Matalon 2007). The intrinsic instability in premixed hydrogen flames leads to cellular structures, which directly influence local heat release, local fuel air ratio and, hence, the distributions of temperature in the burned gas region. The NO\textsubscript{x} formation reactions take place within the flame, and their significance depends on the local temperatures. NO\textsubscript{x} pollutants are expected to be enhanced in super-adiabatic regions and suppressed in extinguished pockets, which leads to a complicated global NO\textsubscript{x} formation mechanism. However, the underlying physics governing the interactions between the thermodiffusive instability and NO\textsubscript{x} formation are still unclear.

For thermodiffusively unstable premixed hydrogen flame, various direct numerical simulations (DNSs) have been conducted; see, for example, Matalon (2007), Day et al. (2011b), Berger et al. (2019, 2022), and Wen et al. (2022a,b). However, most of these

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Figure 1. Numerical setups of the planar thermodiffusively unstable premixed hydrogen flames in the (a) 2D and (b) 3D computational domains. The isosurface of $T_{iso} = 1000$ K colored by the local value of $Y_{NO}$ is shown in (b) for illustration of the perturbed initialization fields, with $H_2$ mass fraction being superimposed as the background color.

studies adopted 2D configurations to approximate the combustion behavior, or NO$_x$ formation was not considered. As the effects of strain rate and curvature are significantly different in three dimensions, it is desirable to investigate the NO$_x$ formation mechanism of thermodiffusively unstable premixed hydrogen flames in a 3D computational domain. For this, the 3D simulation domain of Berger et al. (2022) is significantly enlarged to capture the full range of possible flame corrugations.

Modeling a thermodiffusively unstable premixed hydrogen flame is challenging due to the wide ranges of scales, strain rate and curvature (Wen et al. 2022a,b). Modeling NO$_x$ formation is even more difficult due to the existence of different reaction pathways, i.e., thermal-NO, NNH and N$_2$O pathways (Glarborg et al. 2018). The interactions between the flame-intrinsic instabilities and the various NO$_x$ formation pathways challenge combustion models. The performance of the flamelet model (Peters 1984) in predicting NO$_x$ formation in a thermodiffusively unstable premixed hydrogen flame was rarely evaluated in previous studies.

The motivation of the present work is to investigate the NO$_x$ formation in the thermodiffusively unstable premixed hydrogen flame through DNS for both 2D and 3D computational domains to understand the effect of dimensionality. Based on the DNS data sets, the characteristics of NO$_x$ formation in the thermodiffusively unstable premixed hydrogen flame are first investigated, and the effects of the computational setup on the NO$_x$ formation are quantified. Then, reaction path analyses are conducted to identify the key contributors to the formation of NO$_x$ pollutants. Finally, the performance of the flamelet model in predicting NO$_x$ pollutants is evaluated.

2. Computational setup

In this work, thermodiffusively unstable premixed hydrogen flames stabilized in 2D and 3D computational domains are simulated with DNS. The computational setups are shown in Figure 1. For the 2D computational domain, it is a square field with a length ($L_x = L_y$) of 100 thermal flame thicknesses of the corresponding 1D unstretched premixed flamelet. This domain size is validated to be sufficiently large to not affect the flame dynamics (Berger et al. 2019). The unburned mixture of hydrogen-air with an equivalence ratio $\phi_0$
of 0.4, a temperature $T_0$ of 298 K and a pressure $p_0$ of 1 atm flows into the domain at $y = 0$ with a velocity $u_0$ of 0.63 m/s. For the corresponding 1D freely propagating premixed flame, the laminar flame speed $u_L$ is calculated to be 0.21 m/s, the flame thickness $l_F$ is 0.62 mm and the adiabatic flame temperature $T_{ad}$ is 1421 K using the FlameMaster package (Pitsch 1998). The inlet fluid velocity is around 2.9 times the laminar flame speed, so that the flame remains within the domain for a sufficient long time interval. In addition, with the selected inlet velocity, the flame front stays away from the inlet boundary to avoid the inlet influence on the flame dynamics. The computational domain is initialized with the 1D freely propagating premixed flame along the $y$-direction. As in Berger et al. (2019), the flame front is perturbed with a weak harmonic function described by $F(y) = A_0 \sin(2\pi y/\lambda)$. The parameter $A_0$ is the amplitude of the perturbation, and $\lambda$ is the wavelength of the perturbation. To trigger the flame instabilities, the initial thermochemical quantities are obtained by mapping the 1D flame solutions along the $y$-direction of the computational domain, and the parameters of $A_0$ and $\lambda$ are set to be the same as those in Berger et al. (2019), i.e., $A_0 = 7 \cdot 10^{-4}$ m and $\lambda = 7 \cdot 10^{-3}$ m. A periodic boundary condition is applied in the $x$-direction, while a constant inlet boundary condition is set at $y = 0$ and an outlet boundary condition is specified at $y = L_y$.

For the 3D computational domain, it is a cuboid field with a length of 100 $l_F \times 150 l_F \times 100 l_F$ in the $x$-, $y$- and $z$-directions, respectively, as shown in Figure 1(b). The unburned mixture flows into the computational domain from the $x$-$z$ plane at $y = 0$, and the burned products flow out of the domain through the $x$-$z$ plane at $y = 150 l_F$. Different from the 2D case, the inlet velocity is set to be 1.044 m/s, which is around 5 times the laminar flame speed. This inlet velocity is higher than that in 2D, since the flame speed in the 3D domain is larger than that in 2D. As in 2D, the initial thermochemical quantities are obtained by mapping the 1D flame solutions along the $y$-direction according to $F(y) = A_0 \sin(2\pi y/\lambda) \cdot \sin(2\pi z/\lambda)$, where the parameters of $A_0$ and $\lambda$ are set to be the same as those in the 2D case. A periodic boundary condition is set in the $x$- and $z$-directions, a constant inlet boundary condition is set at $y = 0$ of the $x$-$z$ plane and the $x$-$z$ plane at $y = 150 l_F$ is suppressed with an outlet boundary condition.

For both computational setups, the mesh resolution is set to be sufficiently fine so that there are at least 10 grid points to resolve the corresponding flame thickness. For the 2D case, $1024 \times 1024$ grid points are uniformly set in the $x$- and $y$-directions, respectively, as in Berger et al. (2019). For the 3D case, $1024 \times 1536 \times 1024$ grid points are uniformly set in the $x$-, $y$- and $z$-directions, respectively, resulting in about 1.6 billion grid points. The chemical reaction mechanism developed by Glarborg et al. (2018) is adopted, which contains 21 species and 109 elementary reactions. Considering the detailed chemistry, the 3D simulation results in nearly 34 billion degrees of freedom. The simulation ran on 36864 cores and consumed 40 million CPU hours to achieve converged results.

3. Modeling method

3.1. Governing equations and numerical scheme

The governing equations for the momentum, species mass fractions and temperature in the low Mach limit (Tomboulides et al. 1997) are solved. The mass diffusivity of each species is calculated using the thermal conductivity, density, specific heat capacity of the gas mixture and the Lewis numbers for each species. The constant non-unity Lewis numbers are calculated from the burned gas region of the corresponding 1D unstretched
premixed flamelet. The molecular diffusion due to the Soret effect is considered using the reduced thermal diffusion model proposed by Schlup & Blanquart (2018).

The DNS is performed with the CIAO code (Desjardins et al. 2008) using a time- and space-staggered finite-difference reactive Navier-Stokes solver on Cartesian grids. The momentum equations are discretized with a fourth-order-accurate central difference scheme, while a fifth-order, weighted essentially non-oscillatory scheme (Jiang & Shu 1996) is adopted to discretize the species and temperature governing equations. For the time integration, a second-order-accurate Crank-Nicolson scheme (Crank & Nicolson 1947) is utilized. The Poisson equation is solved with the algebraic multigrid (AMG) solver hypre Boomer AMG (Falgout & Yang 2002). The symmetric operator splitting method proposed by Strang (1968) is utilized to efficiently advance the stiff advection-diffusion-reaction equations for species and temperature. A time-implicit backward difference method is employed to integrate the chemical source terms, as implemented in the stiff ODE solver CVODE as part of the SUNDIALS suite (Hindmarsh et al. 2005).

3.2. Reaction path analysis

Reaction pathway analyses are conducted to quantify the importance of different NO$_x$ formation pathways in the thermodiffusively unstable premixed hydrogen flame. In the reaction path analysis, the flux is calculated based on the molecular element conservation (Androulakis et al. 2004). For instance, the flux of element N between species A and species C in reaction $j$ of $A + B \leftrightarrow C + D$, $\mathcal{J}_{AjC}$, is calculated according to

$$\mathcal{J}_{AjC} = \frac{n_{N,A} \cdot n_{N,C}}{\delta_{N}} M_N \cdot \dot{\omega}_j,$$

where $n_{N,A}$ and $n_{N,C}$ are the number of atom N in species A and species C, respectively. The parameter $\delta_{N}$ is the sum of the number of atom N on either side of the reaction $j$, $M_N$ the molecular weight of the element N and $\dot{\omega}_j$ the net reaction rate of reaction $j$. Considering all reactions that convert species A to species C, the net reaction flux of element N between the two species can be calculated as

$$\mathcal{J}_{AC} = \sum_{j=1}^{N_r} \mathcal{J}_{AjC},$$

where $N_r$ is the number of reactions in the chemical reaction mechanism. To investigate the relative importance of the flux between species A and species C with respect to the other fluxes, the flux ratio $\xi_{AC}$ is introduced, which is calculated by normalizing the individual flux to the magnitude of the sum of the flux between N$_2$ and the other species,

$$\xi_{AC} = \frac{\mathcal{J}_{AC}}{\sum_{k=1}^{N_r} \mathcal{J}_{N_2,k}} \times 100\%,$$

where $\mathcal{J}_{N_2,k}$ is the flux between N$_2$ and species $k$.

3.3. A-priori analysis of flamelet model

In this work, the performance of the flamelet model in predicting the NO$_x$ species in the thermodiffusively unstable premixed hydrogen flame is evaluated through an a-priori analysis. The flamelet table is generated by solving 1D freely propagating premixed flames at an unburned gas temperature of 298 K and a pressure of 1 atm for various equivalence ratios ranging from 0.32 to 2. The chemical reaction mechanism and the
transport model used in the flamelet table generation are the same as those in the DNS. The thermochemical quantities \( \Psi \) in the resulting flamelet table are tabulated as a function of the Bilger mixture fraction \( Z_{\text{Bilger}} \) (Bilger et al. 1990) and normalized progress variable \( PV \), i.e., \( \Psi = \mathcal{F}(Z_{\text{Bilger}}, PV) \). The variables \( Z_{\text{Bilger}} \) and \( PV \) are defined as

\[
Z_{\text{Bilger}} = \frac{(Z_H - Z_{H,2})/2M_H - (Z_O - Z_{O,2})/M_O}{(Z_{H,1} - Z_{H,2})/2M_H - (Z_{O,1} - Z_{O,2})/M_O}, \quad PV = \frac{Y_{PV} - Y_{PV,u}}{Y_{PV,b} - Y_{PV,u}},
\]

where \( Z_H \) and \( Z_O \) are the local mixture fraction of elements H and O, respectively. The subscripts 1 and 2 indicate pure fuel and pure air, respectively. In this work, \( Y_{PV} \) is defined as \( Y_{PV} = Y_{H_2} - Y_{H_2} - Y_{O_2} \) following previous works (Wen et al. 2022a, b). The parameters \( Y_{PV,u} \) and \( Y_{PV,b} \) in Eq. (3.4) are the corresponding values on the unburned and burned sides, respectively.

In the \textit{a-priori} analysis, \( Z_{\text{Bilger}} \) and \( PV \) are calculated from the DNS. The thermochemical quantities are extracted from the flamelet lookup table (FLT) according to

\[
\Psi^{\text{FLT}} = \mathcal{F}(Z_{\text{DNS}}^{\text{Bilger}}, PV_{\text{DNS}}),
\]

The performance of the flamelet model is evaluated by comparing the tabulated values \( \Psi^{\text{FLT}} \) against the corresponding reference results \( \Psi^{\text{REF}} \) from the DNS.

4. Results and discussions

4.1. \( NO_x \) formation characteristics

The instantaneous distributions of the NO mass fraction \( Y_{NO} \) in the 2D and 3D cases are shown in Figure 2. In the 3D domain, the isosurface of \( T_{iso} = 1000 \) K colored by the local value of \( Y_{NO} \) is shown for illustration of the cellular flame structure, with the \( H_2 \) mass fraction \( Y_{H_2} \) being superimposed as the background color. It can be observed that for both 2D and 3D computational domains, the peak value of \( Y_{NO} \) locates at the region with positive curvature \( \kappa_c \). As in previous works (Berger et al. 2019; Wen et al. 2022a), the curvature \( \kappa_c \) of the flame front is defined as \( \kappa_c = -\nabla \cdot \vec{n} = -\nabla \cdot (\nabla PV/|\nabla PV|) \). In addition, the overall cellular flame structure is significantly different in different computational domains. In the 2D computational domain, a finger-like large

\[ \begin{align*}
Y_{NO} & = 10^{-7} \times 10^2 \times 10^5
\end{align*} \]

\[ \begin{align*}
0 & \quad 0.05 \quad 1
\end{align*} \]

\[ \begin{align*}
0 & \quad 0.15 \quad 1
\end{align*} \]
Figure 3. Comparing the conditioned NO and NO\textsubscript{2} mass fractions in the progress variable space obtained from 1D, 2D and 3D computational domains for the same operating conditions.

scale flame front can be observed, while in the 3D domain, many differently sized square patches make up the flame front.

To quantitatively investigate the effects of the 2D and 3D domains on the NO\textsubscript{x} formation, Figure 3 compares the conditioned NO and NO\textsubscript{2} mass fractions in the normalized \textit{PV} space obtained from the 1D, 2D and 3D computational domains for the same operating conditions. The symbol \langle \cdot \rangle denotes the spatially conditioned values. It can be observed that the peak value of \langle Y_{\text{NO}} \rangle in the 3D domain is much higher than that obtained from the 1D and 2D domains. This is considered to be associated with the fact that the 3D flame front corrugations feature higher curvature values, which promotes the accumulation of H\textsubscript{2} due to differential diffusion. For the distribution of \langle Y_{\text{NO}_{2}} \rangle in Figure 3(b), a significantly larger value can be observed in the 2D domain, in the range of \textit{PV} = 0.4 \sim 0.8. The reason for this will be investigated in detail in the next step. Overall, the results show that 3D effects can significantly alter flame propagation and NO\textsubscript{x} formation.

4.2. Reaction path analysis

To quantify the relevant reaction pathways that make important contributions to the NO formation, a reaction path analysis was conducted. Figure 4(a) shows the reaction path diagram for the 2D DNS case, which is obtained by integrating over the whole computational domain. The percentages superimposed in the pathway are calculated according to Eq. (3.3). For comparison, the reaction path diagram for the 1D freely propagating premixed flame calculated at the same conditions as in the DNS is shown in Figure 4(b). Only the pathways with percentages larger than 0.1\% are shown. The dashed lines in Figure 4(b) indicate the thermal-NO relevant pathways, which are shown even if they are below the 0.1\% threshold. The red line indicates the thermal-NO pathway N + NO \leftrightarrow N\textsubscript{2} + O, the blue line corresponds to the NNH pathway NNH \leftrightarrow N\textsubscript{2} + H and the violet line is the N\textsubscript{2}O pathway N\textsubscript{2}O + M \leftrightarrow N\textsubscript{2} + O + M. For the operating conditions studied, the NNH and N\textsubscript{2}O reaction pathways are much more important than the thermal-NO pathway. The thermal-NO reaction pathway only contributes 0.32\% to the N\textsubscript{2} consumption, which is an expected result due to the overall low temperatures (T\textsubscript{max} \approx 1600 K). In addition, the fluxes flowing into NNH (48.9\%) are close to those away from NNH (34.8\%+6.88\%+6.21\% = 47.89\%), which indicates that the NNH species is in quasi-steady state. For the NO fluxes, the only important pathway for consumption of NO is to form HONO. The corresponding reaction path diagram for the 1D flamelet, shown in Figure 4(b), indicates that the N\textsubscript{2} \rightarrow NNH pathway becomes less important for the consumption of N\textsubscript{2} compared to the thermodiffusively unstable premixed flame studied. The increased importance of the NNH pathway in the thermodiffusively unstable
premixed flame is considered to be due to the accumulation of the H radical at positively curved regions, which promotes the NNH formation through N$_2$ + H → NNH. Day et al. (2011a) reported that the N$_2$ → NNH flux becomes more important as the equivalence ratio of the unburned mixture increases. Thus, the existence of intrinsic instability has locally similar effects to increasing the fuel mixture equivalence ratio. Compared to the 2D DNS, the thermal-NO reaction pathway becomes negligible (0.03%) in the 1D flamelet, which indicates that the thermodiffusive instability promotes the thermal-NO pathway. Such effects are expected to be amplified in fuel-richer or preheated conditions.

Note that the above reaction path analysis and the a-priori analysis (see the next section) are currently only based on the 2D data set, while the corresponding analyses for the 3D data set are still ongoing.

4.3. Flamelet modeling of NO$_x$ formation

The performance of the flamelet model in predicting NO$_x$ formation in thermodiffusively unstable premixed hydrogen flames is evaluated through an a-priori analysis. The results shown in Figure 2 confirm that the NO$_x$ formation is affected by the flame front corrugations and, hence, curvature. To investigate the effects of curvature on the performance of the flamelet model, two representative flame segments are extracted from the negatively and positively curved regions, given as FNeg and FPos in Figure 2(a).

In Figure 5, the tabulated NO and NO$_2$ mass fractions and their source terms, referred to as FLT, are compared to the corresponding reference DNS results, referred to as REF. The left column shows the comparison for FNeg representing the negatively curved flame segments, while the right column shows the comparison for FPos representing the positively curved ones. The NO$_x$ species in the positively curved flame segment (FPos) can be accurately predicted by the flamelet model, while discrepancies exist for the
negatively curved flame segment (FNeg). The budget analysis of the generalized premixed flamelet equations (Wen et al. 2022a) shows that the tangential diffusion, which is not considered in the 1D flamelet table, is significant only in the negatively curved flame segments, while it is negligible in the positively curved region. This could be one of the reasons for the inaccurate prediction of the NO species in FNeg. For both FNeg and FPos, the reaction source terms cannot be accurately predicted, as shown in Figures 5(c, d). The reason why the prediction accuracy of the NO and N2O mass fractions is higher than the corresponding source terms could be associated with the fact that the reaction source terms are more sensitive to the local curvature, which is, however, not considered in the flamelet table. From the profiles of NO and NO2 source terms, it can be observed that the production of NO2 is significant only in the 0.1 < PV < 0.4 region, while the production of NO mainly takes place in the region with PV > 0.6.

To investigate the reactions in the small progress variable region, a conditioned reaction path analysis is conducted for FPos and the results are shown in Figure 6(a). The flux magnitude of the NO → NO2 pathway is dominant and is at least one order of magnitude larger than the others. Note that the significant flux ratio is due to the normalization. This indicates that in the small progress variable region, the main reaction is to convert NO to NO2. Figure 6(b) shows the comparison of $\Omega_{NO+NO2} = (\dot{\omega}_{NO}/M_{NO} + \dot{\omega}_{NO2}/M_{NO2})$ between the flamelet predictions and the reference results for the FPos flame segment.

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**Figure 5.** Profiles of (a, b) NOx species mass fractions and (c, d) NOx reaction source terms, comparing the reference simulation (referred to as REF) and the a-priori flamelet predictions (referred to as FLT). The left column shows FNeg, while the right column shows FPos.

**Figure 6.** (a) Reaction path diagram of nitrogen atom conditioned in the 0.1 < PV < 0.4 region, as normalized in Figure 4. (b) Profiles of the sum of NO and NO2 source terms divided by their respective molecular weights, comparing the reference simulation (referred to as REF) and the a-priori flamelet predictions (referred to as FLT) for the FPos flame segment.
The value of $\dot{\Omega}_{NO+NO_2}$ is close to zero in the $0.1 < PV < 0.4$ range, which is predicted. This indicates that NO$_x$ formation is in a quasi-steady state close to the unburned side. The NO$_x$ species is mainly produced in the range of $PV > 0.6$, which is, however, underpredicted by the flamelet model.

5. Conclusions

NO$_x$ formation in thermodiffusively unstable premixed hydrogen flames is investigated through DNS. To quantify the effects of the computational setup on NO$_x$ formation, both 2D and 3D configurations are considered. The results show that for both 2D and 3D configurations, the peak NO mass fraction occurs at the positively curved regions. In the 3D domain, various sizes of square patches can be observed that do not exist in the 2D domain. The peak value of NO mass fraction in the 3D domain is larger than that in the 1D and 2D domains, while locally high values of NO$_2$ mass fraction can be observed in the 2D domain. The reaction path analysis shows that the NNH and N$_2$O pathways are dominant, while the thermal-NO pathway is negligible for the fuel-lean premixed flame studied. The NNH species is in quasi-steady state in the thermodiffusively unstable premixed flame. Compared to the 1D flamelet, the existence of thermodiffusive instability tends to increase the importance of the $N_2 \rightarrow$ NNH pathway due to differential diffusion of the H radical, which is similar to the effect of an increase of the equivalence ratio. The NO$_x$ species in the positively curved region can be accurately predicted by the flamelet model, while large discrepancies exist in the negatively curved region. For the reaction source terms of the NO$_x$ species, the flamelet model cannot give accurate predictions due to the curvature effects. It is found that the NO in the cooler flame regions is governed by the NO$_2 \leftrightarrow$ NO pathway, and that the flamelet model can accurately predict the relevant pathway in the cooler regions but not in the hot regions.

In future work, the influence of the computational setup on the consumption speed and flame surface area will be quantified, and the analyses conducted in this work will be extended to analyze the 3D DNS data set. Furthermore, the flamelet model will be further extended in order to accurately predict the NO$_x$ reaction source terms in the thermodiffusively unstable premixed hydrogen flame.

Acknowledgments

The authors thank Thierry Poinsot, Andrea Aniello and Davide Laera for fruitful discussions during the CTR Summer Program. Computational resources are provided by the Gauss Centre for Supercomputing e.V. on the GCS Supercomputer SuperMUC-NG at Leibniz Supercomputing Centre.

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