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The effect of hydrogen addition on flammability limit and NO_x emission in ultra-lean counterflow CH_4/air premixed flames

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Abstract

The effect of hydrogen addition to ultra lean counterflow CH_4/air premixed flames on the extinction limits and the characteristics of NO_x emission was investigated by numerical simulation. Detailed chemistry and complex thermal and transport properties were employed. The results show that the addition of hydrogen can significantly enlarge the flammable region and extend the flammability limit to lower equivalence ratios. If the equivalence ratio is kept constant, the addition of hydrogen increases the emission of NO in a flame due to the enhancement in the rate of the NNH or N_2O intermediate NO formation routes. The addition of hydrogen causes a monotonic decrease in the formation of NO_2 and N_2O , except flames near the extinction limits, where the emission of NO_2 and N_2O first increases, and then decreases with the increase in the fraction of hydrogen. Overall, hydrogen enrichment technology allows stable combustion under ultra lean conditions, resulting in significant CO_2 and NO emission reduction. Crown Copyright © 2004 Published by Elsevier Inc. on behalf of The Combustion Institute. All rights reserved.

Keywords: Hydrogen enrichment; NO_x ; Extinction limit; Ultra-lean premixed flame.

1. Introduction

The addition of hydrogen to a hydrocarbon flame is of great interest for combustion scientists and engineers. It can improve the burning stability for ultra-lean combustion and reduce the greenhouse gases and pollutant emission, such as

CO_2 , CO, unburned hydrocarbons, and soot particles. Further, there is interest in ultra-lean combustion as a potential NO_x reduction technology. The development of hydrogen enrichment technology has motivated studies in understanding the effect of hydrogen addition on extinction and NO_x emission characteristics in ultra-lean premixed flames.

The extinction characteristics of stretched methane and hydrogen premixed flames have been extensively studied [1–5]. The influence of hydrogen addition on the response of lean premixed

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CH₄ flames to high strained flows was recently investigated by Jackson et al. [6]. It was demonstrated that the addition of hydrogen to methane extended the stretch extinction limit, and thus could improve the lean premixed flame stability. Another extinction limit at lower stretch rate, known as radiation extinction limit [2–5], was not investigated in [6]. Many researchers have studied NO_x emission in various hydrocarbon and hydrogen flames, such as [7–13]. Rørtveit et al. [14] reported a comparison of low-NO_x burners for combustion of methane and hydrogen mixtures. They indicated that the addition of hydrogen to natural gas or methane resulted in an increase in NO_x for most burners, and a slight decrease in NO_x for one burner. Therefore, further studies are required to understand the detailed effect of hydrogen addition on the extinction limits and NO_x emission.

Theoretically, the addition of hydrogen to a hydrocarbon fuel may reduce the prompt NO due to the decrease in hydrocarbon radicals in a flame, assuming a constant temperature. However, the addition of hydrogen may cause a rise in the flame temperature, which would result in an increase in thermal NO formation. In addition, the NO from NNH mechanism [13] may also increase compared to pure hydrocarbon flames. The combined effects of these factors determine the net influence of hydrogen addition on NO_x emission in lean hydrocarbon premixed flames.

In this paper, the effect of hydrogen addition on the extinction and NO_x emission in ultra lean counterflow CH₄ premixed flames is investigated by numerical simulation. Detailed chemistry, and complex thermal and transport properties were used. The effect of hydrogen addition on the flammable region and flammability limit of ultra lean counterflow methane/air premixed flames is discussed, as well as NO_x emission in hydrogen enriched ultra lean methane premixed flames.

2. Numerical model

The flame configuration studied is an axisymmetric laminar counterflow premixed flame. The simulations assumed the stagnation point flow approximation. The governing equations can be found elsewhere [15]. The potential boundary conditions were used. The calculations were carried out with a code revised from that of Kee et al. [16]. Upwind and center difference schemes were, respectively, used for the convective and diffusion terms in all the governing equations. Adaptive refinement of meshes was done. The arc-length continuation method [17] was employed to obtain the extinction limits. The pressure and the fresh mixture temperature were 1 atm and 300 K, respectively.

A previous investigation [18], using an improved radiation model, in which the radiation

reabsorption was accounted for, showed that the reabsorption has little influence on the extinction limits and temperatures of lean counterflow CH₄/air premixed flames. To simplify the calculation, the optically thin radiation model [3] was used.

The chemical reaction mechanism used is GRI-Mech 3.0 [19]. The thermal and transport properties were obtained by using the database of GRI-Mech 3.0 and the algorithms given in [20,21]. The thermal diffusion velocities of H₂ and H were accounted for, while that of other species was ignored.

It is well known that NO can be formed through the thermal, the N₂O intermediate, and the prompt routes [7–11], based on the initiation reactions by which molecular nitrogen is converted to atomic nitrogen or other intermediate species containing the nitrogen element. Thermal NO formation is comprised of the three reactions: N₂ + O = N + NO; N + O₂ = NO + O; and N + OH = NO + H; of which the first one is the initiation reaction. The N₂O intermediate route is initiated by the reactions: N₂O (+M) = N₂ + O (+M); N₂O + H = N₂ + OH; N₂O + O = N₂ + O₂; and N₂O + OH = N₂ + HO₂; and then the N₂O formed is partially converted to NO. The prompt NO is initiated by the rapid reactions of hydrocarbon radicals with molecular nitrogen [7]. In addition, NO formation can also be initiated by the reactions of molecular nitrogen with other hydrocarbon-free radicals, such as H, OH, and H₂. These reactions include: NH + N = N₂ + H; NH + NO = N₂ + OH; NNH = N₂ + H; NNH + M = N₂ + H + M; NNH + O₂ = HO₂ + N₂; NNH + O = OH + N₂; NNH + H = H₂ + N₂; NNH + OH = H₂O + N₂; and NNH + CH₃ = CH₄ + N₂. Although the last reaction is initiated by CH₄, we also attribute it to this route due to NNH. This route is known as the NNH intermediate route [13]. To identify the relative importance of the four routes in current study, four simulations were carried out for each flame. The first simulation (SIM1) was conducted by the full chemistry (GRI-Mech 3.0), while the second (SIM2) was carried out by removing the initiation reactions of the prompt routes. In the third simulation (SIM3), the initiation reactions of both the prompt and the NNH intermediate routes were removed. All the initiation reactions of the prompt, the N₂O, and the NNH intermediate routes were removed in the fourth simulation (SIM4). Consequently, NO obtained from SIM4 can be attributed to the thermal mechanism. The difference in NO between SIM1 and SIM2 is attributed to the prompt route, and the difference between SIM2 and SIM3 is due to the NNH intermediate route. The NO contributed by the N₂O intermediate route is the difference between SIM3 and SIM4.

3. Results and discussions

Except in the discussion of extinction limits, a stretch rate of 30 1/s was used for all the flames. This choice is arbitrary. The fuel used is a mixture of methane and hydrogen, with α_{H_2} being the volume fraction of hydrogen, i.e., $\alpha_{\text{H}_2} = V_{\text{H}_2} / (V_{\text{H}_2} + V_{\text{CH}_4})$, where V_{H_2} and V_{CH_4} are the volume flow rates of hydrogen and methane, respectively. The variable ϕ is the equivalence ratio. Since the objective of this paper was to study the effect of hydrogen enrichment in ultra lean premixed flames, the equivalence ratio investigated was limited to less than 0.7 and the fraction of hydrogen was up to 0.4 for most cases. However for the sake of comparison, a hydrogen fraction of 1.0 was reached in some cases.

3.1. Effect of hydrogen addition on extinction limits

For a lean CH_4/air or H_2/air mixtures at a given equivalence ratio, there are two extinction limits when the stretch rate varies. One is caused by an ultra high stretch rate due to the shortened residence time, and the other is caused by an ultra low stretch rate because of the radiation heat loss. The former is known as the “stretch extinction limit,” and the latter is known as the “radiation extinction limit.” If all the extinction limits and the corresponding equivalence ratios are plotted in a stretch rate – equivalence ratio plane, a C-shaped curve is formed [3]. The upper branch of the curve is the stretch extinction limit branch, and the lower branch is the radiation extinction limit branch. The region bounded by the two extinction limit branches is the flammable region of counterflow lean premixed flames. At a critical equivalence ratio, the two branches merge at one point. This critical equivalence ratio is the flammability limit of the counterflow lean premixed flame. For equivalence ratios lower than the flammability limit, a steady counterflow premixed flame cannot exist, regardless of the stretch rate.

Since NO_x chemistry usually has negligible effect on flame temperature and structure, the reactions and species related to NO_x formation were removed (except N_2) in the calculations of extinction limits to simplify the calculation.

Figure 1 shows the C-shaped curves of the flames with four different hydrogen fractions being 0.0, 0.1, 0.2, and 0.4, respectively. It should be pointed out that although the reaction schemes used in this paper and in the previous study [3] are different, the same flammability limit (0.42) was obtained for the pure counterflow CH_4/air lean premixed flame. It is observed from Fig. 1 that the addition of hydrogen increases the stretch extinction limit and reduces the radiation extinction limit for a given equivalence ratio lean counterflow CH_4/air premixed flame. The effect of hydrogen addition is enhanced with an increase

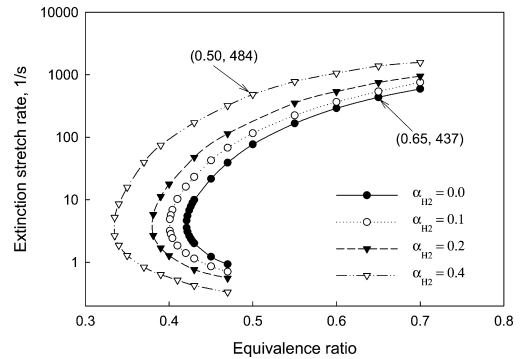


Fig. 1. C-shaped curves of lean counterflow premixed $\text{CH}_4/\text{H}_2/\text{air}$ flames.

in the fraction of hydrogen. When the fraction of hydrogen is increased from 0.0 to 0.4, the flammability limit is extended from 0.42 to 0.335. There are two factors responsible for this phenomenon, the first being that hydrogen has a higher flame speed and a lower flammability limit than CH_4 . Second, the Lewis number of a H_2/air mixture is lower than that of a CH_4/air mixture. The preferential diffusion of H_2 results in higher combustion intensity in a lean $\text{H}_2/\text{CH}_4/\text{air}$ flame than in a lean CH_4/air flame for a given equivalence ratio. As a result, with the addition of hydrogen, the flammable region of the flame is enlarged, and the flammability limit is extended to a lower equivalence ratio. These observations are qualitatively consistent with the results by Jackson et al. [6]. However, the radiation extinction limit was not studied in [6].

Therefore, we can conclude that the addition of hydrogen to a CH_4/air premixed flame can significantly improve the combustion stability. This is a significant advantage of the hydrogen enrichment technology. It allows a combustor to operate under ultra lean conditions, and thus reduce the emission of greenhouse gases, such as CO_2 . For example, the stretch extinction limit of the flame with the equivalence ratio of 0.5 and the hydrogen fraction of 0.4 is even higher than that of the pure CH_4/air premixed flame with the equivalence ratio of 0.65, as shown in Fig. 1.

3.2. NO formation

Figure 2 shows the distributions of NO mole fractions in counterflow premixed flames with equivalence ratios of 0.47 and 0.55, when the fraction of hydrogen varies from 0.0 to 1.0. The value of 0.47 is an equivalence ratio at which the pure CH_4/air flame is close to the stretch extinction limit at the stretch rate of 30 1/s, and the value of 0.55 is a moderate equivalence ratio studied. It is clearly indicated that the addition of hydrogen increases the emission of NO in a counterflow

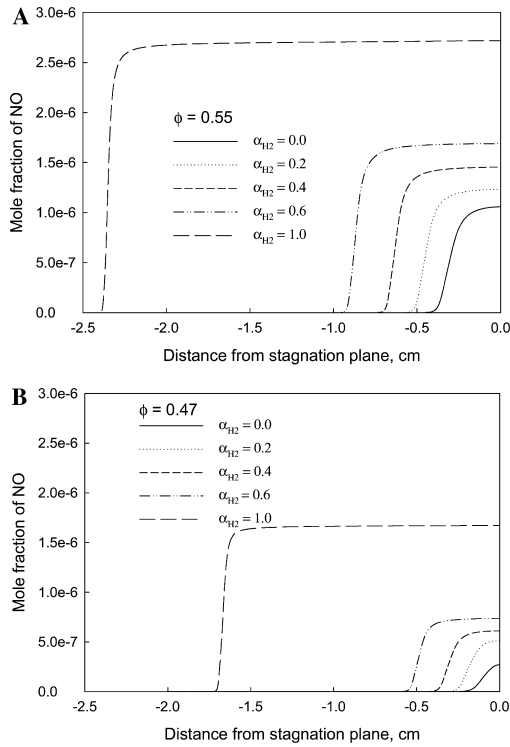


Fig. 2. Mole fractions of NO in flames with equivalence ratios of 0.47 and 0.55.

CH₄/air premixed flame if the equivalence ratio is kept constant. With the increase of the hydrogen fraction, NO concentration rises. The flames of other equivalence ratios have qualitatively similar results.

Figure 3 displays the variations of NO emission indices in the flames of equivalence ratios of 0.47 and 0.55, obtained by the four simulations (SIM1 to SIM4), when the fraction of hydrogen varies from 0 to 1.0. The emission index in this paper is based on the consumption of oxygen, i.e., $EI_{NO} = \frac{\text{mass of NO formed}}{\text{mass of O}_2 \text{ consumed}}$, rather than the conventional definition based on the consumption of fuel. The reason is that hydrogen is not only one of the parent fuels, but also an intermediate species in this study. Although not shown, the variations of the peak NO mole fractions with the increase of the hydrogen fraction have been verified to show a similar trend to the emission index. It is observed that the contributions of the thermal and prompt routes to the total NO emission are very small in these flames. This is because these flames are ultra lean and the temperatures are very low. The two significant routes of NO formation in the pure CH₄/air premixed flames are the N₂O and the NNH intermediate routes. However, with the increase of the

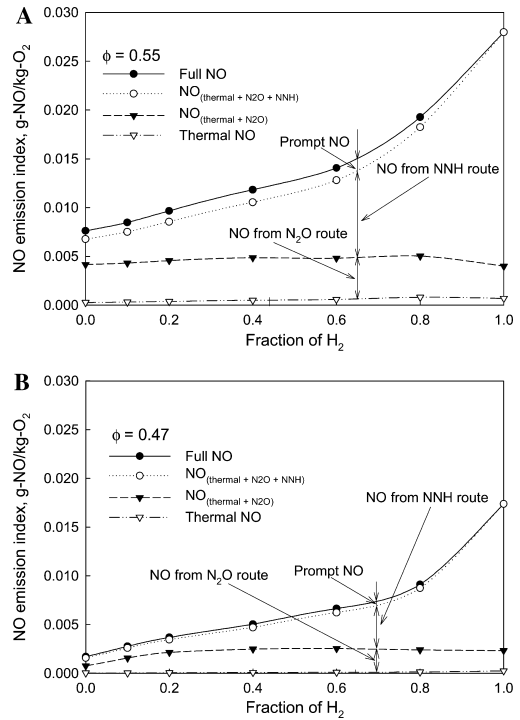


Fig. 3. NO emission indices in flames with equivalence ratios of 0.47 and 0.55.

hydrogen fraction, the contribution of the NNH intermediate route quickly rises, while those of the other three routes exhibit minimal change, except for the flames with the equivalence ratio of 0.47 at lower hydrogen fraction. For the flame with the equivalence ratio of 0.47, when the hydrogen fraction increases from 0.0 to 0.2, the contribution of the N₂O intermediate route rises much faster than the other three routes. When the pure H₂/air premixed flames are reached, the contribution of the prompt route disappears, and the NNH intermediate route dominates the NO formation.

Figure 4 displays the NO emission indices of the flames with the equivalence ratio of 0.7, the highest equivalence ratio considered, when the fraction of hydrogen varies from 0.0 to 0.6. In contrast to the flames with the equivalence ratios of 0.47 and 0.55, the contributions of the thermal and prompt routes in the pure CH₄/air flame are of similar magnitude to the NNH and N₂O intermediate routes. This change is due to the increase in the flame temperatures and methane concentrations. The contribution of the thermal route slowly increases with the rise of the hydrogen fraction. Similar to the flames with the equivalence ratios of 0.47 and 0.55, the contribution of the NNH intermediate route rises faster than the three other routes, when the fraction of hydrogen increases.

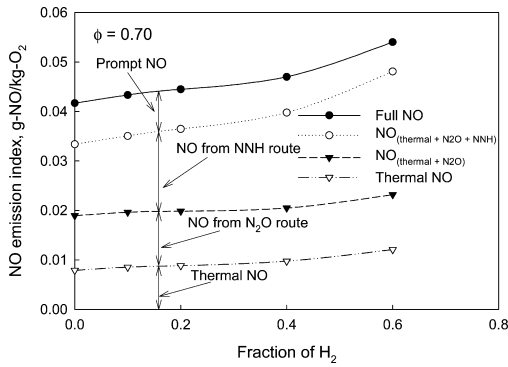


Fig. 4. NO emission indices of the flame with equivalence ratio of 0.70.

From the above results, we can conclude that the rise in NO formation rate with the increase of the hydrogen fraction is mainly caused by the rise of the NNH intermediate route, except for the flames with a very low equivalence ratio and at lower hydrogen fraction where the increase in the N_2O intermediate route is more significant.

A sensitivity analysis indicates that the two most significant initiation reactions of the NNH intermediate route are $NNH = N_2 + H$ and $NNH + M = N_2 + H + M$, and the most important NNH destruction reaction is $NNH + O_2 = HO_2 + N_2$. With the increase of the hydrogen fraction in constant equivalence ratio flames, the concentration of H increases dramatically, and there is a moderate increase in temperature. As an example, this is shown in Fig. 5 for the flames with the equivalence ratio of 0.55. Therefore, the NO formation rate by the NNH intermediate route quickly increases. Later we will show that the N_2O concentration actually decreases with the increase of the hydrogen fraction in the flames with the equivalence ratio of 0.55, which results in a small variation in the NO from the N_2O intermediate route. As a result, when the hydrogen

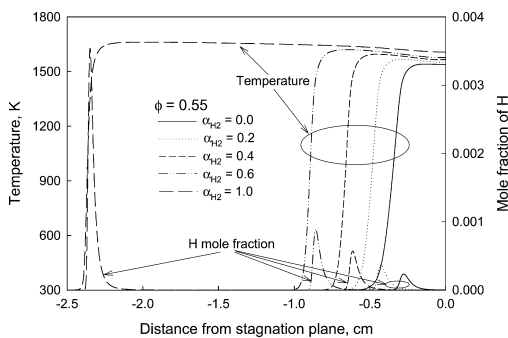


Fig. 5. Temperatures and mole fractions of H in flames with equivalence ratio of 0.55.

fraction is increased, the increase of total NO emission in the flame with the equivalence ratio of 0.55 is mainly due to the NNH intermediate route. The flames with higher equivalence ratios in this study are qualitatively similar to the flame with the equivalence ratio of 0.55.

When the equivalence ratio is 0.47, the pure CH_4 /air flame at the stretch rate of 30 1/s is near the stretch extinction limit. The flame temperature dramatically decreases, and the concentration of oxygen increases, compared to the flames with higher equivalence ratios. The formed NNH is quickly converted back to molecular nitrogen by the reaction $NNH + O_2 = HO_2 + N_2$. Consequently, when the fraction of hydrogen increases from 0 to about 0.2, the contribution of the NNH intermediate route varies little. On the other hand, the N_2O intermediate route dominates the NO formation in these flames. With the increase of the hydrogen fraction from 0 to about 0.2, the increase in the N_2O formation rate is greater than that of its destruction rate, as discussed later. Therefore, the contribution of the N_2O intermediate route quickly increases, which leads to an increase in the total NO emission. With further increases in the fraction of hydrogen, both the temperature and the concentration of H rise to relatively higher levels. The rate of the NNH formation reaction exceeds that of its destruction reaction, and the situation for N_2O formation and destruction reverses. Consequently, the NNH intermediate route dominates the NO formation and causes the rise of NO formation rate as the fraction of hydrogen is further increased, similar to the flames with an equivalence ratio of 0.55.

The above results and discussions indicate that the addition of hydrogen to an ultra lean counterflow CH_4 /air premixed flame causes the NO formation to increase, because the contribution from the NNH or N_2O intermediate route increases. However, this conclusion does not mean that the hydrogen enrichment technology has a disadvantage in terms of NO emission. As indicated before, since the addition of hydrogen can extend the flammability limit to a lower equivalence ratio and enlarge the flammable region, the hydrogen enrichment technology allows a combustor to operate at lower equivalence ratio. Figure 6 shows the NO emission indices for flames with the equivalence ratio varying from 0.47 to 0.70 and the hydrogen fractions of 0.0, 0.1, 0.2, and 0.4. It is seen that the decrease in the equivalence ratio can significantly reduce the emission of NO. If the operating equivalence ratio of a combustor is decreased from 0.65 to 0.5 by 40% hydrogen enrichment (the example illustrated in Fig. 1), the NO emission index is reduced from 0.025 to 0.007 gNO/kgO₂. From this example, hydrogen enrichment has significantly reduced the emission of NO. Similar benefits can be

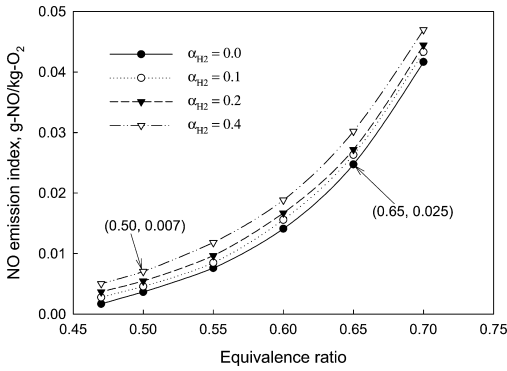


Fig. 6. NO emission index variation with equivalence ratio.

demonstrated for other equivalence ratios and degrees of hydrogen enrichment.

3.3. NO₂ formation

Figure 7 displays the distributions of NO₂ mole fractions in the flames with the equivalence ratios of 0.47 and 0.55, when the fraction of hydrogen is increased from 0.0 to 1.0. Different phenomena are observed for the flames with these

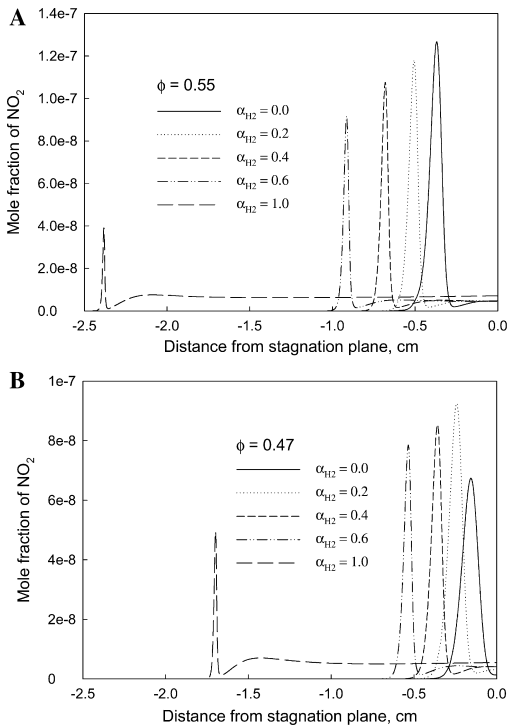


Fig. 7. Mole fractions of NO₂ in flames with equivalence ratios of 0.47 and 0.55.

two equivalence ratios. When the equivalence ratio is 0.55, the peak concentration of NO₂ monotonically decreases with the increase in the fraction of hydrogen. However, for flames with an equivalence ratio of 0.47, the peak NO₂ concentration first increases when the fraction of hydrogen is raised from 0.0 to 0.2, and then decreases with further increase in the fraction of hydrogen.

The main NO₂ formation and destruction reactions are HO₂ + NO = NO₂ + OH and NO₂ + H = NO + OH, respectively. The activation energy of the former one is negative, and the latter one is positive. When the equivalence ratio equals 0.55, both the flame temperature and the concentration of NO increase (Figs. 2A and 5) with the increase in the fraction of hydrogen. As a result of a negative activation energy, the rate of the NO₂ formation reaction HO₂ + NO = NO₂ + OH changes very slowly, in spite of the increase in the concentration of NO. On the other hand, the increase in both the concentration of H and the temperature causes the rate of the NO₂ destruction reaction to increase quickly. The combined variations in the rates of the formation and destruction reactions lead to a monotonous decrease in NO₂ concentration with the increase in the fraction of hydrogen.

For the flames with the equivalence ratio of 0.47, the flame is near the extinction limit, and the temperature is very low. When the hydrogen fraction is increased from 0.0 to 0.2, the increase in the concentration of H, and the temperature is minimal, limiting the NO₂ destruction reaction. However, the concentration of NO rises relatively quickly due to the N₂O intermediate route, as shown in Figs. 2B and 5. Therefore, the NO₂ concentration first increases. With the further increase in the fraction of hydrogen, the situation similar to the flames with the equivalence ratio of 0.55 occurs due to the increased flame temperature and concentration of H.

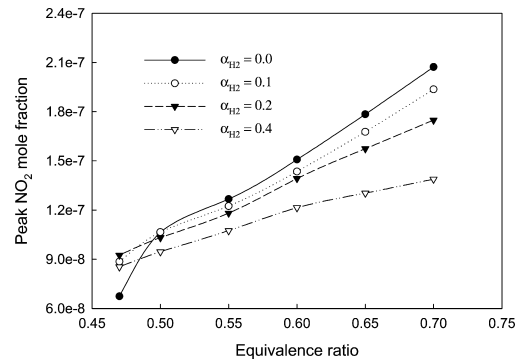


Fig. 8. Peak NO₂ mole fraction variation with equivalence ratio from 0.47 to 0.7 and hydrogen fractions of 0.0, 0.1, 0.2, and 0.4.

Figure 8 illustrates the peak NO₂ mole fractions in flames with the equivalence ratios from 0.47 to 0.7 and the hydrogen fractions of 0.0, 0.1, 0.2, and 0.4. It is found that for the flames with an equivalence ratio greater than 0.5, the NO₂ concentration monotonically decreases with the increase in the fraction of hydrogen. The flames with an equivalence ratio less than or equal to 0.5 have phenomenon similar to flames of the equivalence ratio of 0.47, but their transition hydrogen fraction values are different.

3.4. N₂O formation

The distributions of N₂O mole fractions in the flames with the equivalence ratios of 0.47 and 0.55 are shown in Fig. 9. The concentration of N₂O monotonically decreases with the increase of the hydrogen fraction, if the equivalence ratio is kept at 0.55. Similar to the phenomenon for NO₂, when the equivalence ratio is reduced to 0.47, the concentration of N₂O first rises with the increase of the hydrogen fraction from 0.0 to 0.4. With the further increase of the hydrogen fraction, the N₂O concentration decreases. This is because of the combined effects of flame temperature and concentrations of H and O.

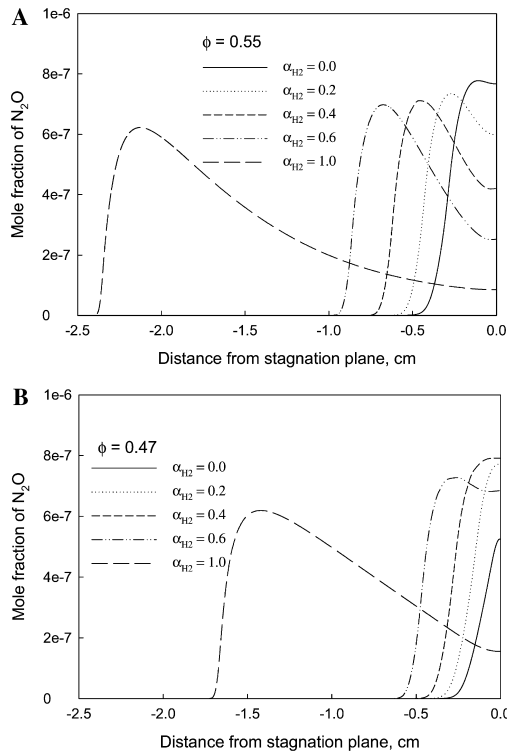


Fig. 9. Mole fractions of N₂O in flames with equivalence ratios of 0.47 and 0.55.

The most important formation and destruction reactions of N₂O are N₂O (+M) = N₂ + O (+M) and N₂O + H = N₂ + OH, respectively. When the equivalence ratio equals 0.55, the increase in the fraction of hydrogen causes the concentration of H to rise quickly, as in Fig. 5, which results in the rate of the N₂O destruction reaction to increase more rapidly than the rate of the formation reaction. Therefore, the concentration of N₂O monotonically decreases with the increase of the hydrogen fraction.

At the equivalence ratio of 0.47, the flame temperature is lower, and the concentrations of nitrogen and oxygen are relatively higher. When the fraction of hydrogen is raised from 0.0 to 0.4, the increase in the rate of the formation reaction is greater than that of the destruction reaction, due primarily to the rise in flame temperature but the minimal increase in H concentration. With further increase in the fraction of hydrogen, the higher concentration of H causes an increase in the destruction reaction rate to exceed that of the formation reaction. Therefore, the concentration of N₂O first increases, and then decreases with the rise in the fraction of hydrogen, when the equivalence ratio is 0.47.

Figure 10 shows the peak N₂O mole fractions for the flames with equivalence ratios from 0.47 to 0.7 and hydrogen fractions from 0.0 to 0.4. As for NO₂, when the equivalence ratio is greater than 0.5, the concentration of N₂O monotonically decreases with the increase in the fraction of hydrogen. If the equivalence ratio is less than or equal to 0.5, the concentration of N₂O first increases, and then decreases, when the fraction of hydrogen is increased.

It is also noted that the N₂O concentration actually increases with the reduction of the equivalence ratio for a given hydrogen enrichment fraction, except at a very low equivalence ratio, Fig. 10. This is a moderately undesirable side effect of the ultra lean combustion technology.

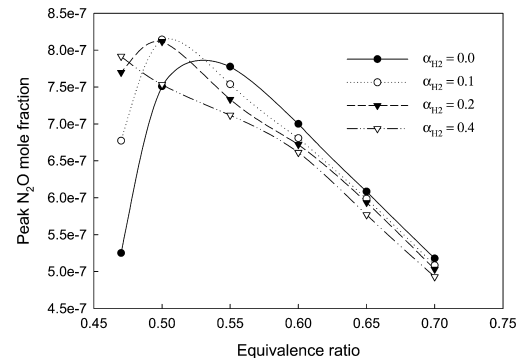


Fig. 10. Peak N₂O mole fractions of the flames with equivalence ratios from 0.47 to 0.7 and hydrogen fractions of 0.0, 0.1, 0.2, and 0.4.

4. Conclusions

The effect of hydrogen addition to ultra lean counterflow CH₄/air premixed flames on the extinction limits and the characteristics of NO_x emission has been investigated by numerical simulation. The results show that the addition of hydrogen can significantly enlarge the flammable region and extend the flammability limit of stretched flame to a lower equivalence ratio. If the equivalence ratio is kept constant, the addition of hydrogen increases the emission of NO in a flame due to the enhancement in the rate of the NNH or N₂O intermediate route. The hydrogen enrichment technology allows combustors to operate under ultra lean conditions, resulting in significant reductions in CO₂ and NO emissions. When the equivalence ratio is relatively higher, the addition of hydrogen causes a monotonous decrease in the formation of NO₂ and N₂O. However for flames closer to the extinction limits, the emission of NO₂ and N₂O, in general, first increases, and then decreases with the increase in the fraction of hydrogen.

References

- [1] J.S. T'ien, *Combust. Flame* 65 (1986) 31–34.
- [2] K. Maruta, M. Yoshida, Y. Ju, T. Niioka, *Proc. Combust. Inst.* 26 (1996) 1283–1289.
- [3] H. Guo, Y. Ju, K. Maruta, K. Niioka, F. Liu, *Combust. Flame* 109 (1997) 639–646.
- [4] Y. Ju, H. Guo, K. Maruta, F. Liu, *J. Fluid Mech.* 342 (1997) 315–334.
- [5] H. Guo, Y. Ju, T. Niioka, *Combust. Theor. Model.* 4 (2000) 459–475.
- [6] G.J. Jackson, R. Sai, J.M. Plaia, C.M. Boggs, K.T. Kiger, *Combust. Flame* 132 (2003) 503–511.
- [7] J.A. Miller, C.T. Bowman, *Prog. Energy Combust. Sci.* 15 (1989) 287–338.
- [8] Y. Ju, T. Niioka, *Combust. Theor. Model.* 1 (1997) 243–258.
- [9] J. Wang, T. Niioka, *Proc. Combust. Inst.* 29 (2002) 2211–2218.
- [10] A. Atreya, H.K. Kim, T. Shamim, J. Suh, *Proc. Combust. Inst.* 26 (1996) 2181–2189.
- [11] S.V. Naik, N.M. Laurendeau, *Combust. Flame* 129 (2002) 112–119.
- [12] R. Fuse, H. Kobayashi, Y. Ju, K. Maruta, T. Niioka, *Int. J. Therm. Sci.* 41 (2002) 693–698.
- [13] G.J. Rørtveit, J.E. Hustad, S. Li, F.A. Williams, *Combust. Flame* 130 (2002) 48–61.
- [14] G.J. Rørtveit, K. Zepter, Ø. Skreiberg, M. Fossum, J.E. Hustad, *Proc. Combust. Inst.* 29 (2002) 1123–1129.
- [15] V. Giovangigli, M.D. Smooke, *Combust. Sci. Technol.* 53 (1987) 23–49.
- [16] R.J. Kee, J.F. Grcar, M.D. Smooke, J.A. Miller, *A Fortran Program for Modelling Steady Laminar One-dimensional Premixed Flames*, Report No. SAND85-8240, Sandia National Laboratories, 1985.
- [17] V. Giovangigli, M.D. Smooke, *Combust. Sci. Technol.* 53 (1987) 23–49.
- [18] H. Guo, Y. Ju, K. Maruta, T. Niioka, F. Liu, *Combust. Sci. Technol.* 135 (1998) 49–64.
- [19] G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R.K. Hanson, S. Song, W.C. Gardiner Jr., V.V. Lissianski, Z. Qin. Available from: http://www.me.berkeley.edu/gri_mech/.
- [20] R.J. Kee, J. Warnatz, J.A. Miller, *A Fortran Computer Code Package for the Evaluation of Gas-phase Viscosities, Conductivities, and Diffusion Coefficients*, Report No. SAND 83-8209, Sandia National Laboratories, 1983.
- [21] R.J. Kee, J.A. Miller, T.H. Jefferson, *A General-Purpose, Problem-independent, Transportable, Fortran Chemical Kinetics Code Package*, Report No. SAND 80-8003, Sandia National Laboratories, 1980.

Comments

Norbert Peters, RWTH Aachen, Germany. It is not easy to unambiguously determine the different contributions to NO formation because the NO-mechanism contains many side reactions. In your case the formation of NO by the NNH path proceeds through the reaction NNH + O → NO + NH. Since NH may effectively reduce NO, the contribution of the NNH path may be overestimated.

Reply. We determined the different contributions to NO formation using four simulations for each flame by gradually removing the initial reactions, which convert molecular nitrogen to atomic nitrogen or other intermediate species containing nitrogen element, of different routes. Although NH may affect the production of NO, this does not significantly over- or underestimate the contribution of the NNH path. The reason is that

the most important formation reaction of NH is NNH + O → NO + NH, and thus the effect of NH on NO is also caused by NNH. By removing the initial reactions of the NNH path, both the direct (through the reaction NNH + O → NO + NH) and indirect (through NH) effects of NNH on NO were removed. Therefore, the method reasonably estimated the contribution of the NNH path.

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Ajay K. Agrawal, University of Oklahoma, USA. Your analysis seems to assume that different NO_x pathways are decoupled. This may or may not be true. One way to verify would be to perform computations with one reaction mechanism at a time. The total NO_x would match with the value obtained using the complete mechanism if indi-

vidual mechanisms were decoupled. Have you done or would you consider performing such a calculation?

Reply. Thanks for your suggestion and we will perform such a calculation in the future.

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A. Koichi Hayashi, Aoyama Gakuin University, Japan. It is not easy to understand the reduction of NO, NO₂, N₂O, by just turning off some of reaction routes since these reactions are complicated and sensitively coupled with each other. You should find another method for the production or reduction of those species. Qualitatively this method might be all right, but not with such a percentage.

Reply. Yes, the formation reactions of NO_x are complicated. However to identify the contributions of different routes, we should concentrate on how the molecular nitrogen is initially converted to atomic nitrogen and other intermediate species containing element nitrogen. For example, the prompt path is initiated by the rapid reactions of hydrocarbon radicals with molecular nitrogen, and the NNH path is initiated by the reactions of molecular nitrogen with some hydrocarbon-free radicals. By turning off the initial reactions of different routes, the sources of different NO formation routes were removed and the contributions of different paths can be reasonably estimated.

We appreciate your comment and will try if there is a better method in the future.