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Guo, Hongsheng; Neill, W.; Smallwood, Gregory J.

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A NUMERICAL INVESTIGATION OF NO\textsubscript{X} FORMATION IN COUNTERFLOW CH\textsubscript{4}/H\textsubscript{2}/AIR DIFFUSION FLAMES

Hongsheng Guo  
Institute for Chemical Process and Environmental Technology, National Research Council of Canada  
1200 Montreal Road, Ottawa, Ontario, Canada K1A 0R6  
Fax: (613)957-7869, phone: (613)991-0869  
Email: hongsheng.guo@nrc-cnrc.gc.ca

Stuart W. Neill  
Institute for Chemical Process and Environmental Technology, National Research Council of Canada  
1200 Montreal Road, Ottawa, Ontario, Canada K1A 0R6  
Fax: (613)957-7869, phone: (613)990-2408  
Email: stuart.neill@nrc-cnrc.gc.ca

Gregory J. Smallwood  
Institute for Chemical Process and Environmental Technology, National Research Council of Canada  
1200 Montreal Road, Ottawa, Ontario, Canada K1A 0R6  
Fax: (613)957-7869, phone: (613)993-1391  
Email: greg.smallwood@nrc-cnrc.gc.ca

ABSTRACT

A detailed numerical study was carried out for the effect of hydrogen enrichment on flame structure and NO\textsubscript{X} formation in counterflow CH\textsubscript{4}/air diffusion flames. Detailed chemistry and complex thermal and transport properties were employed. The enrichment fraction was changed from 0 (pure CH\textsubscript{4}) to 1.0 (pure H\textsubscript{2}). The result indicates that for flames with low to moderate stretch rates, with the increase of the enrichment fraction from 0 to 0.5–0.6, NO emission index keeps almost constant or only slightly increases. When the enrichment fraction is increased from 0.5–0.6 to about 0.9, NO emission index quickly increases, and finally NO formation decreases again when pure hydrogen flame condition is approached. However, for flames with higher stretch rates, with the increase of hydrogen enrichment fraction from 0 to 1.0, the formation of NO first quickly increases, then slightly decreases and finally increases again. Detailed analysis suggests that the variation of the characteristics in NO formation in stretched CH\textsubscript{4}/air diffusion flames is caused by the change of flame structure and NO formation mechanism, when the enrichment fraction and stretch rate are changed.

Keywords: diffusion flame, NO\textsubscript{X}, fuel enrichment.

INTRODUCTION

Fuel enrichment combustion is a promising concept for substantial reduction in fuel consumption and pollutant emission. Many studies have been conducted for some fundamental concepts of fuel enrichment combustion. For example, it has been shown that fuel enrichment can improve flame stability and thus significantly reduce NO\textsubscript{X} formation by allowing a combustor to operate at leaner condition [1-4] in premixed flames. For diffusion combustion, fuel enrichment can suppress the formation of soot particles [5,6] and shorten ignition delay [7,8].

Relatively, not enough attention has been paid to the effect of fuel enrichment on NO\textsubscript{X} formation in diffusion flames. In general, NO, the dominant component of NO\textsubscript{X}, is mainly formed by the prompt route in a hydrocarbon diffusion flame. When an enrichment component, such as hydrogen or carbon monoxide, is added to a hydrocarbon diffusion flame, it is expected that the formation of NO by the prompt route can be reduced because of the reduction in radical CH. On the other hand, the addition of an enrichment component may modify flame temperature, which in turn may change the formation of NO by the thermal route. Therefore, the net effect of fuel enrichment on NO\textsubscript{X} formation in a hydrocarbon diffusion flame depends on the relative variations of the thermal and prompt routes. Naha and Aggarwal [9] investigated the effect of hydrogen addition on NO\textsubscript{X} formation in stretched nonpremixed methane and n-heptane flames at a fixed stretch rate (100 s\textsuperscript{-1}). They found that the addition of hydrogen has minor effect on NO\textsubscript{X} formation in methane flames and reduces the formation of NO\textsubscript{X} in n-heptane flames.

In real applications, stretch rate significantly changes. The variation in stretch rate modifies the residence time of reactants in the reaction zone of a flame. The effect of fuel enrichment on NO\textsubscript{X} formation for flames at different stretch rates may differ. It is of interest to further investigate the effect of fuel...
enrichment on NO\textsubscript{X} formation in diffusion flames at various stretch rates.

In this paper, a detailed numerical study on the effect of hydrogen addition on NO\textsubscript{X} formation in CH\textsubscript{4}/air diffusion flames with various stretch rates was conducted. Hydrogen was selected because it has been shown to be an effective enrichment component that can suppress soot formation in diffusion flames [5,6] and shorten ignition delay [7,8]. The fraction of hydrogen changed from 0 to 1.0. The investigated stretch rate covers a wide range.

**NUMERICAL MODEL**

The flame configuration studied is an axisymmetric laminar counterflow diffusion flame, with fuel stream issuing from one nozzle and air from another, as shown in Fig. 1. The simulations assumed the stagnation point flow approximation. The governing equations can be found elsewhere [10]. The calculations were carried out with a code revised from that of Kee et al. [11]. 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 to obtain grid independent results. Radiation heat loss was accounted for by an optically thin model [12].

Two different free stream conditions – potential and plug flow – were alternately used in the literature for counterflow flame simulation. Based on the method by which the jets were produced, one of them may be closer to the experimental measurements than the other. However, both conditions produce similar qualitative results. As a pure numerical study, the potential boundary conditions were used in this paper.

The chemical reaction mechanism used is GRI-Mech 3.0 [13], which is an optimized mechanism for methane combustion. It has been validated over a wide range of flame conditions. The thermal and transport properties were obtained by using the database of GRI-Mech 3.0 and the algorithms given in [14, 15]. The pressure and the fresh mixture temperature were, respectively, 1 atm and 298 K.

**RESULTS AND DISCUSSION**

In all the studied flames, fuel stream consists of methane and hydrogen. The fraction of hydrogen is defined as $\alpha_{H_2} = \frac{V_{H_2}}{(V_{H_2} + V_{CH_4})}$, with $V_{H_2}$ and $V_{CH_4}$ being, respectively, the volume flow rates of hydrogen and methane. The quantity $a$ in all the figures represents stretch rate. Although we are interested in fuel enrichment combustion, which only requires a small amount of hydrogen addition, the studied fraction of hydrogen covers a range from 0.0 to 1.0 at several typical stretch rates for completeness.

Figures 2 and 3 display the distributions of flame temperature and NO mole fraction in flames with stretch rates of 10 s\textsuperscript{-1}, 100 s\textsuperscript{-1} and 300 s\textsuperscript{-1} and containing 0, 50, 60, 98 and 100% hydrogen. Fuel stream comes from the right side, and air from the left side. The three stretch rates were selected because they represent three typical values, a lower, a moderate and a higher one. The higher one (300 s\textsuperscript{-1}) is close to the stretch extinction limit for CH\textsubscript{4}/air diffusion flame at atmosphere pressure and room temperature condition. From Figs. 2 and 3, we first observe that with increasing the fraction of hydrogen addition, the primary reaction zone moves further away from stagnation plane to the air (left) side. This is because hydrogen combustion needs less oxygen than methane. Secondly, the increase in the fraction of hydrogen causes monotonic increase in flame temperature and thickness. It is caused by the higher adiabatic temperature and diffusion coefficient of hydrogen.
However, the variation of peak NO mole fraction shows some complex phenomena.

![Graph of NO mole fraction distribution]

More detailed information can be found from Fig. 4, where the variation of NO emission index ($\text{NO}_{\text{EI}}$), a more reasonable quantity describing the characteristics of NO formation, is shown. Since the fuel stream is a mixture of methane and hydrogen, NO emission index is defined based on total heat release rather than fuel consumption, i.e. NO emission index equals the ratio of total formed NO to total heat release (g-NO/J-Heat). For the sake of comparison and presentation below, the variations of peak NO mole fraction (peak NO) and temperature ($T_{\text{max}}$) are also shown in Fig. 4. It is found that at a given stretch rate, although the peak flame temperature monotonically increases, the behaviors of NO emission index and peak NO mole fraction are complex, as the fraction of hydrogen is increased. Moreover, the variation trends of NO emission index and peak NO mole fraction change for different stretch rates.

![Graph of NO emission index and peak temperature]

Fig. 4 Variations of NO emission index, peak temperature and peak NO mole fraction.

![Graph of NO emission index with stretch rate]

Fig. 5 Variation of NO emission index with stretch rate at different hydrogen fractions.
At a lower or moderate stretch rate (a = 10 or 100 s\(^{-1}\)), there is a critical hydrogen fraction between 0.0 and 1.0, at which NO emission index reaches its maximum value. The value of this critical hydrogen fraction is higher when stretch rate is 100 s\(^{-1}\) than when stretch rate is 10 s\(^{-1}\). However, such a critical hydrogen fraction does not exist and NO emission index reaches the maximum at \(a_{H_2} = 1.0\), when stretch rate is 300 s\(^{-1}\). The peak NO mole fraction always reaches the maximum at \(a_{H_2} = 1.0\), regardless of the variation in stretch rate.

When stretch rate is lower (10 s\(^{-1}\)) stretch rate, at the beginning, both peak NO mole fraction and NO emission index increase with the increase in the fraction of hydrogen. The rise is more significant when stretch rate is 300 s\(^{-1}\) than when stretch rate is 100 s\(^{-1}\). Then the increase of hydrogen fraction causes a slight decrease in both the peak NO mole fraction and NO emission index. Finally with the further increase in the fraction of hydrogen, both the peak NO mole fraction and NO emission index quickly rise until the critical hydrogen fraction is reached when stretch rate is 100 s\(^{-1}\), or the pure hydrogen flame condition is reached when stretch rate is 300 s\(^{-1}\). When the fraction of hydrogen is greater than the critical value, the variations of peak NO mole fraction and NO emission index at stretch rate of 100 s\(^{-1}\) are qualitatively similar to those at stretch rate of 10 s\(^{-1}\).

Figure 5 demonstrates the variation of NO emission index at three different hydrogen fraction levels (0.0, 0.2 and 0.5), as stretch rate changes. It is further confirmed that at lower to moderate stretch rates, hydrogen enrichment has minor influence on NO formation. This qualitatively agrees with the conclusion obtained by Naha and Aggarwal [9] at a fixed stretch rate. However, the effect of hydrogen addition on NO formation becomes more significant at higher stretch rates. It should be pointed out that the lower NO formation at stretch rate of 10 s\(^{-1}\) than that at some higher stretch rates is because of radiation heat loss that increases with the decrease in stretch rate [12].

The above observed phenomena can be explained by the variations in the mechanisms of NO formation and flame structure, when hydrogen is added at different stretch rates. It is well known that NO generally can be formed by four routes in a hydrocarbon flame, i.e. the thermal, the prompt, the N\(_2\)O and the NNH intermediate routes. The thermal NO formation route is comprised of the three reactions: \(N_2 + O = N + NO\); \(N + O_2 = NO + O\); and \(N + OH = NO + H\); of which the first one is the initiation reaction that converts molecular nitrogen to NO and atomic nitrogen. The prompt NO in hydrocarbon flames is initiated by the rapid reactions of hydrocarbon radicals with molecular nitrogen, and then the formed atomic nitrogen and species containing elementary nitrogen are converted to NO. The N\(_2\)O intermediate route is initiated by the reactions: \(N_2O (+M) = N_2 + O (+M)\); \(N_2O + H = N_2 + OH\); \(N_2O + O = N_2 + O_2\); and \(N_2O + OH = N_2 + HO_2\); and then \(N_2O\) formed is partially converted to NO. In addition, NO formation can also be initiated by the reactions of molecular nitrogen with other hydrocarbon-free radicals, such as \(H, OH, H_2\) to form NNH, and NNH is later converted to NO. This last route to form NO is known as the NNH intermediate route. Figure 6 displays the pathways of NO formation in the pure CH\(_4\)/air and H\(_2\)/air diffusion flames when stretch rate equals 10 s\(^{-1}\). The thickness of each line represents the magnitude of the rate and the arrow indicates the direction of the reaction. The paths with rates less than 1.0\(\times\)10\(^4\) mole/(cm\(^2\)-s) have been neglected. The species not participating in any reaction in the H\(_2\)/air flame are still kept in Fig. 6b for comparison. It is observed that most NO is formed by the reactions HNO (+H, OH) \(\rightarrow\) NO and N (+OH) \(\rightarrow\) NO in the CH\(_4\)/air flame, and by N (+OH) \(\rightarrow\) NO and N\(_2\) (+O) \(\rightarrow\) NO in the H\(_2\)/air flame. Apparently the reactions HNO (+H, OH) \(\rightarrow\) NO in the CH\(_4\)/air flame belong to the prompt route, since species HNO is from the paths resulting from the reaction of molecular nitrogen with radical CH. Although both flames share the reaction N (+OH) \(\rightarrow\) NO, which was attributed to the thermal NO formation route in many references, it is noted that atomic nitrogen participating in this
reaction in the two flames comes from different paths. In the CH\textsubscript{4}/air flame, it is from the paths N\textsubscript{2} (+CH) → HCN → NCO → NH → N, N\textsubscript{2} (+CH) → HCN → NH → N and N\textsubscript{2} (+CH) → N. Therefore, the formation of atomic nitrogen in the CH\textsubscript{4}/air flame is initiated by the reaction of molecular nitrogen with radical CH, which is the typical prompt route nitrogen conversion. On the other hand, in the H\textsubscript{2}/air diffusion flame, the atomic nitrogen is from the path N\textsubscript{2} (+O) → N that is the thermal route. This tells us that the method to identify the mechanism of NO formation in a flame should not be based on how NO is finally formed, but on how molecular nitrogen is initially converted to atomic nitrogen or species containing element nitrogen. The paths of NO formation through the N\textsubscript{2}O and NNH intermediate routes are not shown in Fig. 6, since their rates are less than 1.0x10\textsuperscript{-8} mole/(cm\textsuperscript{2}⋅s). It is clear from Fig. 6 that the formation of NO in the CH\textsubscript{4}/air flame is mainly due to the prompt route, while in the H\textsubscript{2}/air flame is due to the thermal route. Based on above analysis and for simplification, we examine the mechanism of NO formation of other flames according to the consumption rates of molecular nitrogen by different routes, rather than the final formation of NO.

Figure 7 shows the variations of molecular nitrogen consumption rates by different routes in flames of three typical stretch rates, when the fraction of hydrogen is changed. The definition of nitrogen consumption rate is similar to that for NO emission index. Positive value means nitrogen is consumed (converted to NO or species containing elementary nitrogen), and negative value indicates that nitrogen is formed (NO or species containing elementary nitrogen is converted back to molecular nitrogen). For completeness, the nitrogen consumption rates by the N\textsubscript{2}O and NNH intermediate routes are also shown, although their contributions are very small in all the studied flames. The identification method of the nitrogen consumption by different routes can be found elsewhere [3]. It is observed that for all the pure CH\textsubscript{4}/air flames, the prompt route dominates the conversion of nitrogen. The consumption rate of nitrogen by the thermal route is actually slightly negative. It is because a large amount of atomic nitrogen is formed by the reaction N\textsubscript{2} + CH = HCN + N in a CH\textsubscript{4}/air flame, resulting in that the forward rate of the reaction NO + N = N\textsubscript{2} + O exceeds the reverse rate. Differently, the thermal route contributes most nitrogen conversion in all the H\textsubscript{2}/air diffusion flame. The combination of the variations in the nitrogen consumption rates by the thermal and prompt routes can explain most of the phenomena observed in Fig. 4, when the fraction of hydrogen is increased from 0.0 to 1.0.

When stretch rate equals 10 \textsuperscript{s\textsuperscript{-1}}, the consumption rates of nitrogen by the thermal and prompt routes respectively increases and decreases, leading to that the net (or total) nitrogen consumption rate and NO emission index keep constant, as the fraction of hydrogen is increased from 0.0 to 0.4. With the further increase of hydrogen fraction from 0.4 to the critical value (0.95), the consumption rate of nitrogen by the thermal route quickly increases, while that by the prompt route gradually decreases, resulting in that the net nitrogen consumption rate and NO emission index rapidly increase. The monotonic decrease of nitrogen consumption rate by the prompt route is because of the decrease in the concentration of CH radical, as shown in Fig. 8, as hydrogen is added. For the thermal route, when the fraction of hydrogen is increased from 0.0 to the critical value, the increase of nitrogen consumption rate is caused by the increase in flame temperature, as shown in Fig. 4. The slower increase rate of nitrogen consumption by the thermal route at lower hydrogen fraction is because the absolute temperature level is relatively lower. When the fraction of hydrogen is greater than the critical value, the decrease in nitrogen consumption rate and NO emission index is caused by the decrease in the consumption of nitrogen by the thermal route. This will be further explained later.

![Fig. 7 Nitrogen consumption rates.](image-url)
the thermal route, and the rise in the nitrogen consumption by the prompt route that generates a large amount of atomic nitrogen and thus intensifies the forward rate of the reaction $\text{NO} + \text{N} = \text{N}_2 + \text{O}$. The increase in the consumption rate of nitrogen by the prompt route is caused by the fact that a small amount of hydrogen addition intensifies the combustion of a $\text{CH}_4$/air diffusion flame if stretch rate is not very low. This effect of a small amount hydrogen addition does not happen at a lower stretch rate, such as $a = 10 \text{ s}^{-1}$, since the residence time of reactants in the reaction zone of a lower stretch rate flame is long enough to complete the combustion for a $\text{CH}_4$/air diffusion flame, and thus the addition of hydrogen only increases flame temperature and reduces the concentration of radical CH. With the fraction of hydrogen being increased to over a certain value, the concentration of radical CH starts to decrease, resulting in the reduction in the consumption rate of nitrogen by the prompt route and NO emission index when stretch rate equals 100 and 300 $\text{ s}^{-1}$. Finally, with the further increase in the fraction of hydrogen to the critical value at a stretch rate of 100 $\text{ s}^{-1}$ or to 1.0 at a stretch rate of 300 $\text{ s}^{-1}$, the nitrogen consumption rate by the thermal route and NO emission index increases again due to the significantly increased temperature.

![Fig. 8 Variation of peak CH mole fraction.](image)

Now we explain the phenomena when the fraction of hydrogen is greater than the critical value at a lower or moderate stretch rate. When the fraction of hydrogen exceeds the critical value, the increase of hydrogen fraction reduces the nitrogen consumption rate and NO emission index, while increases the peak mole fraction of NO, Figs. 4 and 7. This is because when the fraction of hydrogen is increased to a higher level, the reaction zone is moved further away from the stagnation plane, as shown in Figs. 2 and 3. The formation of NO in the primary reaction zone keeps increasing because of the rise in flame temperature, as the fraction hydrogen is increased from the critical value to 1.0 at a given stretch rate. This results in that the peak NO mole fraction keeps increasing. However, when the formed NO is transported to the region close to stagnation plane, part of NO is converted back to molecular nitrogen by the reaction $\text{NO} + \text{N} = \text{N}_2 + \text{O}$, leading to the decrease in NO emission index for flames at a lower or moderate stretch rate. However, at a higher stretch rate, this phenomenon does not happen, since the primary reaction zone is closer to stagnation plane for flames at all hydrogen addition levels.

In summary, the simulation results show that the addition of hydrogen in a $\text{CH}_4$/air diffusion flame does not have significant effect on NO formation for lower and moderate stretch rate flames, as long as the fraction of added hydrogen is not big enough to close to 1.0. Although the addition of a small amount of hydrogen increases the formation of NO in higher stretch rate flames, this increase is expected to be controlled by adding some other components, such as EGR. Giving the other advantages of hydrogen addition in diffusion flames, like the reduction in the formation of soot, we can say that we do benefit from hydrogen enrichment combustion technology for diffusion flames.

**CONCLUSIONS**

A detailed numerical study on the effect of hydrogen enrichment on flame structure and NO$_X$ formation in counterflow $\text{CH}_4$/air diffusion flames has been conducted. The result indicates that for flames with low to moderate stretch rates, with the increase of the enrichment fraction from 0 to 0.5–0.6, NO emission index keeps almost constant or only slightly increases. When the enrichment fraction is increased from 0.5–0.6 to about 0.9, NO emission index quickly increases, and finally NO formation decreases again when pure hydrogen flame condition is approached. However, for flames with higher stretch rates, with the increase of hydrogen enrichment fraction from 0 to 1.0, the formation of NO first quickly increases, then slightly decreases and finally increases again. Detailed analysis suggests that the variation of the characteristics in NO formation in stretched $\text{CH}_4$/air diffusion flames is caused by the change of flame structure and NO formation mechanism, when the enrichment fraction and stretch rate are changed.

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