NRC Publications Archive Archives des publications du CNRC

A numerical study on the effect of CO addition on flame temperature and NO formation in counterflow CH₄/air diffusion flames

Guo, Hongsheng; Neill, W. Stuart

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

Publisher's version / Version de l'éditeur:

Proceedings of IMECE2007, pp. 1-7, 2007

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=436ce8e0-c3d9-4227-8285-06464b88f28b>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=436ce8e0-c3d9-4227-8285-06464b88f28b>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

IMECE2007-41438

A NUMERICAL STUDY ON THE EFFECT OF CO ADDITION ON FLAME TEMPERATURE AND NO FORMATION IN COUNTERFLOW CH₄/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

W. Stuart 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

ABSTRACT

A numerical study was carried out to understand the effect of carbon monoxide enrichment on flame temperature and NO formation in counterflow methane/air diffusion flames. Detailed chemistry and complex thermal and transport properties were employed. The results indicate that when carbon monoxide is added to the fuel, both flame temperature and NO formation rate are changed due to the variations in adiabatic flame temperature, fuel Lewis number and chemical reaction. The combination effects of three factors result in the different characteristics of flame temperature and NO formation at various strain rates, when carbon monoxide is added.

At a low strain rate, the addition of carbon monoxide causes a monotonic decrease in flame temperature and peak NO concentration. However, NO emission index first slightly increases, and then decreases. When the value of strain rate is moderate, the addition of carbon monoxide has negligible effect on flame temperature and leads to a slight increase in both peak NO concentration and NO emission index, until the fraction of carbon monoxide reaches about 0.7. Then with a further increase in the fraction of added carbon monoxide, all three quantities quickly decrease. When strain rate is increased to a value close to the strain extinction limit of pure methane/air diffusion flame, the addition of carbon monoxide causes increase in flame temperature and NO formation rate, until a critical carbon monoxide fraction is reached. After the critical fraction, the further addition of carbon monoxide leads to decrease in both flame temperature and NO formation rate. The paper also analyzed the variation in the mechanism of NO formation, when carbon monoxide is added.

Keywords: diffusion flame, NO_x, fuel enrichment, carbon monoxide.

INTRODUCTION

Fuel enrichment is a promising concept for reducing fuel consumption and pollutant emission from combustion systems. Usually hydrogen is selected as the additive for fuel enrichment combustion. 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_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_x formation in diffusion flames. In general, NO, the dominant component of NO_x, is mainly formed by the prompt route in a hydrocarbon diffusion flame. When an enrichment component, such as hydrogen or carbon monoxide (CO), is added to a hydrocarbon fuel, 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_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_x formation in strained nonpremixed methane and n-heptane flames at a fixed strain rate (100 s⁻¹). It was found that the addition of hydrogen has a minor effect on NO_x formation in methane (CH₄) flames and reduces the formation of NO_x in n-heptane flames. Our previous study [10] on the effect of hydrogen enrichment on NO formation in CH₄/air diffusion flames at various strain rates showed that the addition of a small amount of hydrogen has negligible effect on NO

formation at low to moderate strain rates, but significantly increases NO formation at a high strain rate.

Although hydrogen has been shown to be an effective additive for fuel enrichment technology, it is only an energy carrier. It has to be generated from other fuels or water. A widely used method to obtain hydrogen is reforming hydrocarbon fuels. However, the reformat gas contains not only hydrogen, but also carbon monoxide and some other minor components. If carbon monoxide and other components contained in reformat gas do not have any negative side effects, or even helps in terms of improving combustion efficiency and reducing pollutant emission, we can directly use reformat gas as the additive in fuel enrichment combustion technology. Therefore, it is of interest to understand the effect of carbon monoxide enrichment on combustion performance and pollutant emission.

In this paper, a detailed numerical study on the effect of carbon monoxide addition on the formation of NO in CH₄/air diffusion flames with various strain rates was conducted. The fraction of carbon monoxide changed from 0 to 0.9. The investigated strain rate covered a wide range.

NUMERICAL MODEL

Similar to in our study on hydrogen enrichment [10], an axisymmetric laminar counterflow flame configuration was employed, with fuel stream issuing from one nozzle and air from another, as shown in Fig. 1. This flame configuration was selected due to its simple geometry and the implications of the results from it for understanding real turbulent flame phenomena. The simulations assumed the stagnation point flow approximation. The governing equations can be found elsewhere [11]. The calculations were carried out with a code revised from that of Kee et al. [12]. 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 [13].

Fig. 1 Flame configuration.

The potential boundary conditions were used for free stream. The chemical reaction mechanism used is GRI-Mech 3.0 [14], which is an optimized mechanism for methane combustion, and 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 [15, 16]. The pressure and the fresh mixture temperature were 1 atm and 298 K, respectively.

RESULTS AND DISCUSSION

In all the studied flames, the fuel stream consists of methane and carbon monoxide. The fraction of carbon monoxide is defined as $\alpha_{CO} = V_{CO} / (V_{CO} + V_{CH_4})$, with V_{CO} and V_{CH_4} being, respectively, the volume flow rates of carbon monoxide and methane. The quantity a in all the figures represents strain rate. Although we are interested in fuel enrichment combustion, which only requires a small amount of enrichment additive, the fraction of carbon monoxide in this study covered a range from 0.0 to 0.9 at three typical strain rates for completeness.

Flame Temperature

When carbon monoxide is added to methane, flame structure and temperature are modified. Figure 2 shows flame temperature distributions in flames containing 0, 50, 80 and 90% carbon monoxide in fuel stream at strain rates of 10, 100 and 300 s⁻¹. The horizontal axis of Fig. 2 represents the distance from the stagnation plane. The fuel stream comes from the right side, and air from the left side. The three strain rates were selected because they represent three typical values: low, moderate and high. The higher one (300 s⁻¹) is close to the strain extinction limit for CH₄/air diffusion flame at atmosphere pressure and room temperature condition. It is observed that the addition of CO causes the move of the peak flame temperature position toward the stagnation plane at all strain rates. This is because the mass diffusion rate of carbon monoxide is lower than that of methane.

Since the adiabatic equilibrium flame temperature (called adiabatic temperature hereafter) of carbon monoxide is higher than that of methane at stoichiometric condition, it was expected that the addition of carbon monoxide to methane would increase the maximum flame temperature. However, the simulation results do not support this, as shown in Fig. 2. More detailed effect of carbon monoxide on maximum flame temperature is shown in Fig. 3. It is noted that the variation trend of peak flame temperature differs when strain rate is changed

At a low strain rate, the addition of carbon monoxide causes a monotonic decrease in the maximum flame temperature. When strain rate is increased to a moderate (100 s⁻¹) or higher value (300 s⁻¹), as carbon monoxide begins to be added to methane, the peak temperature is almost constant (at $a = 100$ s⁻¹) or slightly increases (at $a = 300$ s⁻¹). However, with further increasing the fraction of added CO, the peak temperature starts to decrease. These are due to the comprehensive effects of adiabatic temperature, fuel Lewis number, chemical reaction and residence time.

The Lewis number of fuel affects the maximum temperature of a diffusion flame. If Lewis number is defined as the ratio of thermal diffusion rate to mass diffusion rate, the peak flame temperature of a diffusion flame will be increased or decreased when Lewis number is less or greater than unity. The Lewis number of fuel is slightly less than unity for pure methane diffusion flame. When carbon monoxide is added to methane, the fuel becomes a mixture. The Lewis number of carbon monoxide is slightly great than unity, leading to the slightly greater fuel Lewis number in carbon monoxide enriched mixture than in pure methane. The increase in fuel Lewis number tends to decrease the peak flame temperature,

which is one reason for the decrease in the maximum temperature at strain rate of 10 s^{-1} , when the fraction of added CO is small. The almost constant and slight increase in maximum flame temperature at moderate and higher strain rates will be explained later.

Fig. 2 Flame temperature distribution.

To confirm the effect of fuel Lewis number, extra calculations were carried out at strain rate of 10 s^{-1} . For these calculations, the Lewis numbers of all species were artificially set as unity. The maximum flame temperatures from these extra calculations are also shown in Fig. 3. It is found that being qualitatively consistent with the variation trend of adiabatic flame temperature, peak flame temperature slightly increases, as the fraction of added carbon monoxide is increased from zero to about 0.3. Therefore, fuel Lewis number is a key factor causing the monotonic decrease in the peak flame temperature at a low strain rate. However, with further increasing the

fraction of added carbon monoxide, similar to normal calculations, peak flame temperature also starts to decrease. This is because the addition of carbon monoxide causes variation not only in fuel Lewis number, but also in chemical reactions.

Fig. 3 Variation of peak flame temperature.

Fig. 4 Variation of peak OH mole fraction.

The primary oxidation reaction of carbon monoxide is $\text{OH} + \text{CO} = \text{H} + \text{CO}_2$. When CO is added to methane, the rate of this reaction is increased, and thus more OH is needed. Meanwhile, the main chain branching reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ is also intensified because more H is formed by the previous one. The net variation of radical OH depends on the balance between the two reactions, when CO is added. Figure 4 displays the variation of maximum OH mole fraction at the three typical strain rates. It is demonstrated that at a low strain rate (10 s^{-1}), the addition of CO results in a monotonic decrease in the concentration of radical OH. This means that the addition of CO causes the reduction in the combustion intensity of methane at a low strain rate. It should be pointed out that the variation of OH concentration is also affected by the flame temperature variation resulted from Lewis number effect. Similar to Fig. 3, Fig. 4 also shows that concentrations of radical OH obtained from the extra calculations at which Lewis numbers of all species were set as unity for flames of strain rate

10 s^{-1} . The maximum OH concentration is almost constant in the extra calculations, when the fraction of added CO is less than 0.3, implying that the Lewis effect dominates at this stage. The chemical effect become more important when the fraction of CO is bigger, since a large amount of OH is need to complete the reaction $\text{OH} + \text{CO} = \text{H} + \text{CO}_2$, which results in the reduction in OH concentration and reaction intensity.

Fig. 5 NO mole fraction distribution.

With strain rate being increased to a moderate or higher value, when small amount of CO is added, the maximum flame temperature and OH concentration do not change (at a moderate strain rate) or slightly increase (at a high strain rate). This is because the residence time in these flames is not long enough to complete the combustion of methane. With the addition of a small amount of CO to methane, the combustion intensity is enhanced due to the reactions $\text{OH} + \text{CO} = \text{H} + \text{CO}_2$

and $\text{H} + \text{O}_2 = \text{OH} + \text{O}$. This enhancement of combustion intensity does not happen at a low strain rate, since the residence time is long enough to complete the combustion of methane.

However, when the fraction of added CO is increased to a larger value, both the maximum flame temperature and OH concentration also start to decrease, owing to the consumption of OH by the reaction $\text{OH} + \text{CO} = \text{H} + \text{CO}_2$. This is similar to what is observed in flames of low strain rate.

Therefore, the variation of flame temperature is caused by the combination of the effects of adiabatic temperature, fuel Lewis number, chemical reaction, and residence time. These effects will also result in the variation in NO formation, when CO is added.

NO Formation

Figure 5 gives the distribution of NO concentration at the three typical strain rates, and varying CO mole fraction with each scenario. It is noted that the effect of CO addition on NO also varies with the change in strain rate. More detailed information on NO formation is shown in Figs. 6 and 7, where NO emission index is defined as the ratio of total formed NO to total heat release.

Fig. 6 Variation of peak NO mole fraction.

Fig. 7 Variation of NO emission index.

At strain rate of 10 s^{-1} , the maximum NO concentration monotonically decreases with increasing fraction of added CO.

However, when strain rate is increased to a moderate or higher value, the maximum NO concentration first increases and then decreases. Being different, at all three strain rates, NO emission index varies in a qualitatively similar way, i.e. first increases to a critical value and then decreases, as the fraction of CO is increased. However, the increase rate of NO emission index is smaller at lower strain rates. The critical CO fraction, at which NO emission index reaches its maximum, changes at different strain rate. To explain these phenomena, we first analyze the mechanism of NO formation.

Figure 8 shows the pathway of NO formation for pure methane flame at strain rate of 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 $1.0 \times 10^{-8} \text{ mole}/(\text{cm}^2 \cdot \text{s})$ have been neglected. It is observed that most NO is formed by the reactions $\text{HNO} (+\text{H}, \text{OH}) \rightarrow \text{NO}$ and $\text{N} (+\text{OH}) \rightarrow \text{NO}$. Apparently, the reactions $\text{HNO} (+\text{H}, \text{OH}) \rightarrow \text{NO}$ belong to the prompt route, since species HNO is from the paths resulting from the reaction of molecular nitrogen with radical CH. Although the reaction $\text{N} (+\text{OH}) \rightarrow \text{NO}$, which was attributed to the thermal NO formation route in many references, contributes significantly to NO formation, it is noted that atomic nitrogen participating in this reaction comes from the paths $\text{N}_2 (+\text{CH}) \rightarrow \text{HCN} \rightarrow \text{NCO} \rightarrow \text{NH} \rightarrow \text{N}$, $\text{N}_2 (+\text{CH}) \rightarrow \text{HCN} \rightarrow \text{NH} \rightarrow \text{N}$ and $\text{N}_2 (+\text{CH}) \rightarrow \text{N}$. Therefore, the formation of atomic nitrogen is initiated by the reaction of molecular nitrogen with radical CH, which is the typical prompt route nitrogen conversion. Consequently, we conclude that prompt route dominates the formation of NO in a pure methane diffusion flame.

Fig. 8 NO formation pathway in CH_4/air at strain rate of 10 s^{-1} .

In addition to the formation of NO, NO is also consumed by reactions with some hydrocarbon radicals, such as CH_2 , CH_3 and HCCO . The consumption of NO is usually called reburning. Figure 9 displays the distribution of NO formation rate for the pure methane flame at strain rate of 10 s^{-1} . It is found that NO is formed in the peak temperature region (see Fig. 2) and consumed later when transported to stagnation plane. Although not displayed, our results show that other flames have qualitatively similar phenomenon until the fraction of CO is increased to greater than about 0.8, i.e. prompt route dominates NO formation in most of our studied flames.

Fig. 9 Distribution of NO formation rate.

Now we can explain the phenomena in Figs. 6 and 7. At strain rate of 10 s^{-1} , the monotonic decrease in peak NO concentration is because the reduction in flame temperature (as shown in Fig. 1) reduces the formation rate of NO, when CO is added. It should be pointed out, although prompt route dominates NO formation, temperature variation still modifies the rates of most reactions. However, the addition of CO moves the primary reaction zone toward the stagnation plane, which leads to the NO reburning rate also reducing. When a small amount of CO is added, the reduction in total of NO formation (positive rate in Fig. 9) near the peak flame region is less than that of NO reburning (negative in Fig. 9), resulting in the slight increase in NO emission index. With further increasing the fraction of CO, the significant reduction in NO formation rate results in the decrease in both peak NO concentration and NO emission index.

Fig. 10 Variation of peak CH concentration.

When strain rate is increased to a moderate or higher value, a small CO addition enhances the combustion intensity of methane, as mentioned before. This leads to CH radical concentration increase, as shown in Fig. 10. The increase in CH concentration and constant (at a moderate strain rate) or increase (at a higher strain rate) in flame temperature cause the rise in both maximum NO concentration and NO emission index, as a small amount of CO is added. This is the reason that

both the maximum NO concentration and NO emission index increase, when a small amount of carbon monoxide is added. As noted from Figs. 6, 7 and 10, the rise rate increases with increasing strain rate. It is because the enhancement in combustion intensity is more significant at a higher strain rate. With further increasing the fraction of added CO, the situation becomes similar to that at strain rate of 10 s^{-1} , i.e. both the maximum NO concentration and NO emission index start to decrease.

Therefore, the addition of CO to methane may modify the emission characteristics of NO. The effect changes at different strain rate. Overall, we find that the effect of CO addition on NO formation is minor at low to moderate strain rates. Although the addition of carbon monoxide causes relatively significant increase in NO formation at high strain rate flames, the absolute NO emission level is low for these flames. Giving the other advantages of CO addition in diffusion flames, like the reduction in the formation of soot, there is no significant negative side effect on combustion and pollutant emission when CO is added to a diffusion flame.

CONCLUSIONS

A detailed numerical study on the effect of carbon monoxide enrichment on flame temperature and NO formation in counterflow methane/air diffusion flames has been conducted. The results indicate that the addition of carbon monoxide to methane modifies both flame temperature and NO emission due to the variations in adiabatic flame temperature, fuel Lewis number and chemical reaction. For a low strain rate flame, the addition of carbon monoxide causes a monotonic decrease in flame temperature and peak NO mole fraction. However, NO emission index first slightly increases, and then decreases. When strain rate is increased to a moderate or higher value, the addition of small amount of CO either does not change peak flame temperature too much, or slightly increases it. Both peak NO concentration and NO emission index increases when small amount of CO is added at a moderate or higher strain rate. For all the cases studied, both peak flame temperature and NO emission rate start to decrease when additional CO is added.

REFERENCES

- [1] Jackson, G.S., Sai, R., Plaia, J.M., Boggs, C.M., Kiger, K.T., 2003, "Influence of H_2 on the response of lean premixed CH_4 flames to high strained flows", *Combust. Flame*, 132, pp.503-511.
- [2] Ren, J.Y., Qin, W., Egolfopoulos, F.N., Mak, H., Tsotsis, T.T., 2001, "Methane reforming and its potential effect on the efficiency and pollutant emissions of lean methane-air combustion", *Chemical Engineering Engineering Science*, 56, pp.1541-1549.
- [3] Guo, H., Smallwood, G.J., Liu, F., Ju, Y., Gülder, Ö.L., 2005, "The Effect of Hydrogen Addition on Flammability Limit and NO_x Emission in Ultra Lean Counterflow CH_4 /Air Premixed Flames", *Proc. Combust. Inst.*, 30, pp.303-311.
- [4] Guo, H., Smallwood, G.J., Gülder, Ö.L., 2007, "The effect of reformat gas enrichment on extinction limits and NO_x formation in counterflow CH_4 /air premixed flames", *Proc. Combust. Inst.*, 31, pp.1197-1204.
- [5] Gülder, Ö.L., Snelling, D.R., and Sawchuk, R.A., 1996, "Influence of hydrogen addition to fuel on temperature field and soot formation in diffusion flames", *Proc. Combust. Inst.*, 26, pp.2351-2358.
- [6] Guo, H., Liu, F., Smallwood, G.J., and Gülder, Ö.L., 2006, "A numerical study on the influence of hydrogen addition on soot formation in a laminar ethylene-air diffusion flame", *Combust. Flame*, 145, pp.324-338.
- [7] Ju, Y., and Niioka, T., 1994, "Reduced kinetic mechanism of ignition for nonpremixed hydrogen/air in a supersonic mixing layer", *Combust. Flame*, 99, pp.240-246.
- [8] Fotache, G.G., Kreutz, T.G., and Law, C.K., 1997, "Ignition of hydrogen-enriched methane by heated air", *Combust. Flame*, 110, pp.429-440.
- [9] Naha, S., and Aggarwal, S.K., 2004, "Fuel effects on NO_x emissions in partially premixed flames", *Combust. Flame*, 139, pp.90-105.
- [10] Guo, H., Neill, W.S., and Smallwood, G.J., "A numerical investigation of NO_x formation in counterflow CH_4/H_2 /air diffusion flames", 2006 ASME International Mechanical Engineering Congress & Exposition, paper No. IMECE2006-14458, November 5-10, 2006, Chicago, Illinois, USA.
- [11] Giovangigli, V., and Smooke, M.D., 1987, "Extinction of strained premixed laminar flames with complex chemistry", *Combust. Sci. Tech.*, Vol. 53, pp.23-49.
- [12] Kee, R.J., Grcar, J.F., Smooke, M.D., and Miller, J.A., A Fortran Program for Modelling Steady Laminar One-Dimensional Premixed Flames, Report No. SAND85-8240, Sandia National Laboratories, 1985.
- [13] Guo, H., Ju, Y., Maruta, K., Niioka, T. and Liu, F., 1997, "Radiation Extinction Limit of Counterflow Premixed Fuel-Lean Methane-Air Flame", *Combust. Flame*, 109, pp.639-646.
- [14] Gregory P. Smith, David M. Golden, Michael Frenklach, Nigel W. Moriarty, Boris Eiteneer, Mikhail Goldenberg, C. Thomas Bowman, Ronald K. Hanson, Soonho Song, William C. Gardiner, Jr., Vitali V. Lissianski, and Zhiwei Qin http://www.me.berkeley.edu/gri_mech/.
- [15] Kee, R. J., Warnatz, J., and Miller, J. A., 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.

- [16] Kee., R. J., Miller, J. A., and Jefferson, T. H., A General-Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package, Report No. SAND 80-8003, Sandia National Laboratories, 1980.