The effect of reformate gas enrichment on extinction limits and NOX formation in counterflow CH4/air premixed flames

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Abstract

The reformate gas enriched counterflow lean premixed CH4/air flames were studied by numerical simulation in this paper. The reformate gas was assumed to be the product of partial oxidation of methane by air, and it consists of H2, CO and N2. Detailed chemistry and complex thermal and transport properties were employed. The results indicate that the addition of the reformate gas enlarges the flammable region, and extends the lean flammability limit of counterflow CH4/air premixed combustion. When the reformate gas is added, the formation of NO is reduced in a near-stoichiometric flame, and increased in an ultra-lean flame at a constant equivalence ratio. The more significant advantage of the reformate gas enriched lean premixed combustion is that it greatly reduces the formation of NO by allowing a combustor to operate at leaner condition without any effect on flammable range. Further, the addition of the reformate gas decreases the formation of NO2 and N2O at a constant equivalence ratio.

Keywords: Lean premixed combustion; Fuel enrichment; NOX; Extinction limit; Reformate gas

1. Introduction

Lean premixed combustion is a promising concept for substantial reduction in fuel consumption and emissions of greenhouse gases and pollutants. It involves operation at lower equivalence ratios to reduce flame temperatures. At these lower temperatures and equivalence ratios, NO formation from thermal and prompt routes can be effectively suppressed. Emission of soot, the predominant source of particulate matter and a major global warming contributor, can also be essentially eliminated in these flames.

However, lean premixed combustion has some intrinsic weaknesses. One of the weaknesses is that at a lower equivalence ratio, the lean flammability limit is approached and flames become less stable. A strategy to overcome this weakness is to adopt fuel enrichment, i.e., adding a small amount of other fuel, to extend the flammability limit and improve the flame stability, while maintaining the advantages of lean premixed combustion. Our previous study [1] has shown that hydrogen enrichment can extend the flammability limit and reduce NO formation in counterflow...
CH/air premixed flames by allowing a combustor to operate at leaner condition.

Hydrogen can be produced by reforming hydrocarbon fuels. The product of fuel reforming, known as reformate gas, contains not only hydrogen, but also carbon monoxide and some other components, depending on the method of reforming. Instead of hydrogen, if the reformate gas of a hydrocarbon fuel can be directly used as the enrichment component, the fuel enrichment combustion technology will be more practical and economical.

The extinction characteristics of stretched premixed flames have been extensively studied for different fuels [2–6]. Similarly, many researchers have investigated the formation of NOX in various flames [7–12]. The influence of hydrogen addition on flame extinction and NOX formation in CH/a air premixed flames has also been studied in [1,13–15]. However, only one study [14] has been reported on the effect of the addition of carbon monoxide, another main component of a reformate gas, on extinction limits in lean premixed flames. If partial oxidation method is employed for reforming, the reformate gas usually contains certain amount of nitrogen that also affects the extinction and NOX formation. Besides, no study has presented any details of NOX formation under reformate gas enrichment condition. Therefore, it is of great interest to understand the combustion and pollutant formation characteristics of reformate gas enriched lean premixed flames.

The purpose of this paper is to numerically investigate the extinction and NOX formation characteristics in reformate gas enriched lean CH/a air premixed flames. The reformate gas was assumed to contain H2, CO and N2. The effect of reformate gas addition on extinction limits and NOX formation is analyzed and discussed.

2. Numerical model

The flame configuration studied is an axisymmetric counterflow laminar flame, stabilized near the stagnation plane of two opposed-jets.

The governing equations can be found elsewhere [16]. The calculations were carried out with a code used previously [1,4–6]. Upwind and center difference schemes were used for the convective and diffusion terms, respectively, in all the governing equations. Adaptive refinement of meshes was done to obtain grid independent result. The arc-length continuation method [16] was employed to get extinction limits. The pressure and the fresh mixture temperature are, respectively, 1 atm and 300 K.

Two different free stream conditions—potential and plug flow—were alternately used in the literature for counterflow flame simulation. They produce similar qualitative results [17]. As a pure numerical study, the potential boundary condition was used in this paper.

The optically thin radiation model [3] was used to save the computational cost, since the reabsorption has little influence on extinction limits and temperatures in most lean CH/a air premixed flames [18]. The reaction mechanism used is GRI-Mech 3.0 [19]—an optimized mechanism for methane combustion. The thermal and transport properties were obtained by using the database of GRI-Mech 3.0 and the algorithms given in [20,21].

3. Results and discussion

The reformate gas was assumed to be the product of partial oxidation of methane by air via the reaction

\[
2\text{CH}_4 + \frac{79}{21}\text{N}_2 = 2\text{CO} + 4\text{H}_2 + \frac{79}{21}\text{N}_2
\]

Therefore, the volume composition of the reformate gas is \((42\text{CO} + 84\text{H}_2 + 79\text{N}_2)/205\).

The fraction of the added reformate gas is defined as \(\alpha_{rg} = V_{rg}/(V_{rg} + V_{CH4})\), with \(V_{rg}\) and \(V_{CH4}\) are, respectively, the volume flow rates of the reformate gas and methane. The complete combustion of the fuel mixture goes via the reaction

\[
(1 - \alpha_{rg})\text{CH}_4 + \alpha_{rg}\left(\frac{42}{205}\text{CO} + \frac{84}{205}\text{H}_2 + \frac{79}{205}\text{N}_2\right) + \left(2 - 2\alpha_{rg} + \frac{63\alpha_{rg}}{205}\right)\text{O}_2 = \left(1 - \alpha_{rg} + \frac{42\alpha_{rg}}{205}\right)\text{CO}_2 + \left(2 - 2\alpha_{rg} + \frac{84\alpha_{rg}}{205}\right)\text{H}_2\text{O} + \frac{79\alpha_{rg}}{205}\text{N}_2
\]

Nitrogen in this reaction is from the fuel reforming, while that contained in air does not explicitly appear here, since it does not affect the calculation of fuel–oxidant ratio. Therefore, the stoichiometric fuel–oxidant ratio in a reformate gas enriched mixture is:

\[
(F/O)_{st} = (1 - \alpha_{rg} + 126\alpha_{rg}/205)/(2 - 2\alpha_{rg} + 63\alpha_{rg}/205)
\]

The equivalence ratio is defined as the ratio of actual fuel–oxidant ratio to the stoichiometric value, i.e.,

\[
\phi = (F/O)/(F/O)_{st}
\]

In all the figures, the quantity \(a\) represents stretch rate.

3.1. Extinction limits

It has been well known that at a constant equivalence ratio, a counterflow premixed flame is extinguished by a high stretch rate due to the shortened residence time. This high stretch rate
is called stretch extinction limit. On the other side, for an ultra-lean counterflow premixed flame, a low stretch rate also results in the flame extinction because of radiation heat loss. The low stretch rate at extinction is named as radiation extinction limit. If all these stretch and radiation extinction limits are plotted versus equivalence ratio, a C-shaped curve can be obtained. The upper branch of the curve is the stretch extinction limit branch, and the lower branch is the radiation extinction limit branch. The two branches merge at a critical equivalence ratio, which is the lean flammability limit [4].

The flammability limit is extended to leaner side, that of pure CH₄/air at equivalence ratio of 0.9. The extinction limit of the 40% reformate gas enriched CH₄/air premixed flame is extended from 0.42 to 0.38 or 0.2. The stretch region of CH₄/air premixed flame is enlarged and reduces the radiation extinction limit at a constant equivalence ratio. The flammable region is called stretch extinction limit. On the other side, for an ultra-lean counterflow premixed flame, a low stretch rate also results in the flame extinction because of radiation heat loss. The low stretch rate at extinction is named as radiation extinction limit. If all these stretch and radiation extinction limits are plotted versus equivalence ratio, a C-shaped curve can be obtained. The upper branch of the curve is the stretch extinction limit branch, and the lower branch is the radiation extinction limit branch. The two branches merge at a critical equivalence ratio, which is the lean flammability limit [4]. The region bounded by this C-shaped curve is the flammable region. Figure 1 displays the C-shaped curves for pure CH₄/air flame, 40% reformate gas enriched CH₄/air flame and pure reformate gas/air flame. For comparison, the C-shaped curves of 40% H₂ and 40% CO enriched CH₄/air premixed flames are also shown in Fig. 1. The definition of the added H₂ and CO fractions is similar to that of the reformate gas.

It is observed that the addition of the reformate gas increases the stretch extinction limit and reduces the radiation extinction limit at a constant equivalence ratio. As a result, the flammable region of CH₄/air premixed flame is enlarged and the flammability limit is extended to leaner side, due to the addition of the reformate gas. The effect of the reformate gas addition is enhanced with the increase in the fraction of the reformate gas. When 40% reformate gas is added, or all the fuel is replaced by the reformate gas, the flammability limit of CH₄/air premixed flame is extended from 0.42 to 0.38 or 0.2. The stretch extinction limit of the 40% reformate gas enriched flame at equivalence ratio of 0.73 is the same as that of pure CH₄/air at equivalence ratio of 0.9. This means that the addition of 40% reformate gas allows the operation equivalence ratio of a combustor to be moved from 0.9 to 0.73 without any effect on flammable range. Therefore, similar to the addition of hydrogen [1], the addition of the reformate gas can significantly improve the flame stability of lean premixed CH₄/air combustion.

Compared to the addition of H₂ and CO, the effect of the reformate gas addition is less effective than that of H₂ addition, but more significant than that of CO addition. This is because the reformate gas is a mixture of H₂, CO and N₂. Our previous study [1] has shown that the addition of H₂ can significantly enlarge the flammable region of CH₄/air premixed flame. The addition of CO also enhances the combustion intensity of a CH₄/air premixed flame due to the reaction CO + OH = H + CO₂ and the rise in temperature. However, the effect of CO addition is not as effective as that of H₂ addition. In addition, the reformate gas also contains nitrogen that is basically an inert species for primary combustion reactions. Thus the addition of the reformate gas enlarges flammable region of CH₄/air premixed flame, but the effectiveness is between those of H₂ and CO addition.

In real applications, a reformate gas also contains small amount of CO₂ and H₂O that may slightly narrow the flammable region. However, the formation of CO₂ and H₂O in fuel reforming process increases the reformate gas temperature, which tends to enlarge the flammable region. Therefore, the existence of CO₂ and H₂O in a reformate gas should not significantly change the above conclusion.

3.2. NO formation

The distributions of NO mole fraction in two typical flames at various reformate gas fractions are shown in Fig. 2. The stretch rate of these two flames is the same, 30 s⁻¹, and the equivalence ratios are, respectively, 0.9 and 0.65. These two equivalence ratios were selected because the former represents a near stoichiometric value, whereas the latter is an ultra-lean one. The effects of stretch rate and equivalence ratio will be discussed later. The dash-dot curve in this figure, which is almost the same as the solid one, will be explained below.

It is observed that the addition of the reformate gas enlarges the NO distribution region for both equivalence ratios. This is because the addition of the reformate gas increases the flame speed, leading to a longer distance between the primary reaction zone and the stagnation plane at a constant stretch rate. However, the peak NO mole fraction is reduced in the flame with equivalence ratio of 0.9, while it is increased in the flame of equivalence ratio 0.65, when the reformate gas is added.

To check further the effect of the reformate gas addition on NO formation, we analyze the mechanism of NO formation now. In a hydrocarbon flame, NO can be formed through the thermal, the prompt, the N₂O and the NNH intermediate routes [1,7–9,12]. In our previous study [1], a
method, in which the initial reactions converting molecular nitrogen to atomic nitrogen and species containing nitrogen element were gradually switched off, was employed to identify the relative contributions of different NO routes. Some researchers argued that due to the complexity of NO formation, the initial reactions of the four routes might not be independent. To verify our approach, in addition to the simulations using the full Gri-Mech 3.0 reaction scheme, we did four extra calculations for the two pure CH\textsubscript{4}/air flames with equivalence ratios 0.9 and 0.65. The reaction scheme in each of these four extra simulations only contains the initial reactions converting molecular nitrogen from one route. The NO mole fraction obtained by summing the NO from these four extra simulations is also shown in Fig. 2. No discernible difference can be observed between the curves obtained from the full Gri-Mech 3.0 chemistry (solid line) and the summation (dash-dot line) of the four extra simulations. The flames of other equivalence ratios have similar result. This suggests that any interactions among the four NO formation routes are negligible in a lean premixed flame. The method used in [1] does properly identify the relative contributions of the four routes, and thereby was used again in this paper.

Figure 3 illustrates the variations of NO emission indices from different routes. The definition of NO emission index is the ratio of total formed NO to total heat release in a flame. It first shows that the addition of the reformate gas decreases the formation of NO (full NO) in the flame with equivalence ratio of 0.9, whereas the reformate gas addition increases NO in the flame with equivalence ratio of 0.65. Further, the addition of the reformate gas reduces the contribution of the prompt route in each flame. This is because the addition of the reformate gas decreases the concentration of radical CH, which is the most important radical to initiate NO formation through the prompt route.

For the contribution of the thermal route, the contradictory phenomena are observed for the two equivalence ratio flames. The addition of the reformate gas reduces the contribution of the thermal route in the flame with equivalence ratio of 0.9, but slightly increases that in the flame with equivalence ratio of 0.65. It is caused by the different effects of the reformate gas addition on temperature for the two flames, as shown in Fig. 4. The addition of the reformate gas decreases the peak temperature in the flame of equivalence ratio 0.9, while increases that in the flame of equivalence ratio 0.65. When the reformate gas is added, the decrease in temperature of the near stoichiometric flame (\(\phi = 0.9\)) is due to the lower heat release of the reformate gas, since part of the energy is released during the reforming process. At a lower equivalence ratio, such as \(\phi = 0.65\), the air requirement of the reformate gas
The rise in the concentration of H causes the increase in the concentration of radical O, since the rate of the chain branching reaction 

\[
H + O_3 = OH + O
\]

is also intensified. As for OH, the addition of the reformate gas causes that more OH is needed to complete the reactions 

\[
OH + H_2 = H + H_2O \quad \text{and} \quad OH + CO = H + CO_2.
\]

but more OH may be produced by the reaction 

\[
H + O_3 = OH + O.
\]

As a result, the variation of OH concentration depends on the balance between these reactions. This is the reason that the concentration of OH changes very slowly or even keeps constant with the increase in the fraction of the reformate gas. The variations in the concentrations of these radicals affect the formation of NO through the N2O intermediate route.

In the N2O intermediate route, molecular nitrogen is first converted to N2O, and then the formed N2O is partly converted to NO. The most important formation and destruction reactions of N2O are, respectively, N2O (+M) = N2 + O (+M) and 

\[
N_2O + H = N_2 + OH.
\]

When the reformate gas is added, the concentrations of both H and O increase, but the increase rate of H concentration is a little higher. Consequently, the net formation rate of N2O slowly decreases, as will be discussed later. The conversion of N2O to NO are mainly through paths: N2O → NO and N2O → NH → HNO → NO. The conversion rates of these two paths slightly increase due to the rise in the concentrations of H and O, with the addition of the reformate gas. The comprehensive effects of these factors lead to that the contribution of the N2O intermediate route keeps almost constant or slightly decreases in a flame, when the reformate gas is added.

Therefore, we conclude that the addition of the reformate gas reduces the formation of NO in a near stoichiometric flame, mainly due to the decrease in the contributions of the prompt and thermal routes. However, the addition of the reformate gas increases the formation of NO in an ultra-lean premixed flame, primarily because the contribution of the NNH intermediate route is increased.

### 3.3. Effect of stretch rate

**Figure 5** shows the effect of stretch rate on NO formation in pure CH4/air and 40% reformate gas enriched CH4/air premixed flames. The maximum stretch rates investigated are close to the stretch extinction limits of pure CH4/air flames for both equivalence ratios. It is noted that at all stretch rates, the addition of the reformate gas reduces NO formation in the flame with equivalence ratio of 0.9, while increases that in the flame with equivalence ratio of 0.65. This is consistent with that previously observed for flames at stretch rate of 30 s\(^{-1}\).

With the increase of stretch rate, NO emission indices monotonically decrease for the flames of...
equivalence ratio 0.9, either with or without the reformate gas addition. However, when equivalence ratio equals 0.65, NO emission index monotonically decreases for the flame without the reformate gas addition, but first slightly increases and then decreases for the flame with 40% reformate gas addition.

The variation of stretch rate effect on NO formation in different flames is caused by the preferential diffusion of hydrogen. The Lewis number of pure CH₄/air flame is slightly less than, but close to, unity. Therefore, the increase of stretch rate reduces the formation of NO due to the decrease in flame thickness in pure CH₄/air flames. Hydrogen has significantly high diffusion coefficient. When the reformate gas is added, the preferential diffusion of hydrogen tends to cause the rise of flame temperature, as stretch rate is increased. This preferential diffusion effect becomes more significant with the decrease in equivalence ratio. When equivalence ratio equals 0.9, although the preferential diffusion slightly increases temperature in the reformate gas enriched flame, the reduction in flame thickness still causes the monotonic decrease in NO emission index, when stretch rate is increased.

However, for equivalence ratio 0.65, the preferential diffusion of hydrogen becomes so significant that the effect of temperature increase exceeds that of the reduction in flame thickness in the 40% reformate gas enriched flame. This leads to a slight rise in NO emission index, as stretch rate is increased from a low value to 200 s⁻¹. With the further increase in stretch rate, flame temperature rises slowly or even decreases, due to the shortened residence time. Together with the reduction in flame thickness, NO emission index finally decreases when stretch rate is further increased to more than 200 s⁻¹ for the 40% reformate gas enriched flame at equivalence ratio of 0.65.

Figure 6 displays the variations of NO emission indices for the flames without reformate gas addition and with 40% reformate gas addition at stretch rates of 30 and 400 s⁻¹, when equivalence ratio is changed. It is illustrated that the decrease of equivalence ratio significantly reduces the formation of NO in a flame. This is easy to understand and an advantage of lean premixed combustion.

Although the addition of the reformate gas suppresses the formation of NO at a constant equivalence ratio for a near stoichiometric flame, more significant benefit can be observed from Fig. 6. As we stated before, the addition of the reformate gas enlarges the flammable range and thus allows a combustor to operate at leaner conditions. For example, with the addition of 40% reformate gas, the equivalence ratio of a combustor can be moved from 0.9 to 0.73 without any effect on flammable range. Then it can be found from Fig. 6 that NO emission index can be reduced from 2.2E⁻⁰⁸ to 4.3E⁻⁰⁹ g-NO/J-heat release at stretch rate of 30 s⁻¹. Although the reduction in NO emission is decreased at stretch rate of 400 s⁻¹ due to the preferential diffusion of hydrogen, it is still very significant, if the equivalence ratio is moved from 0.9 to 0.73 with the addition of 40% reformate gas. Therefore, we can conclude that, like the addition of hydrogen [1], the addition of the reformate gas also significantly reduces the formation of NO by allowing a combustor to operate at leaner condition. This is the biggest advantage of the fuel enriched lean premixed combustion technology. Considering the lower cost of the reformate gas enrichment than that of hydrogen, it is more practical and economical in the application.

3.5. NO₂ formation

Figure 7 shows the variation of NO₂ emission index with the addition of the reformate gas for flames with stretch rate of 30 s⁻¹ and equivalence ratio 0.9. The change of NO₂ emission index is shown in Fig. 7.
ratios of 0.9 and 0.65. The definitions of NO₂ and N₂O emission indices are similar to that for NO.

It is found that the addition of the reformate gas monotonically decreases the formation of NO₂ for the flame of equivalence ratio 0.9. When equivalence ratio equals 0.65, the formation of NO₂ decreases until the fraction of the reformate gas 0.6 is reached. Then with the further rise of the reformate gas addition, the formation of NO₂ slightly increases.

A sensitivity analysis indicates that the main formation and destruction reactions of NO₂ are, respectively, HO₂ + NO = NO₂ + OH and NO₂ + H = NO + OH. As discussed before, the addition of the reformate gas reduces the formation of NO and increases the concentration of H for the flame of equivalence ratio 0.9. This tends to reduce the formation rate and increase the destruction rate of NO₂ when the reformate gas is added. Therefore, the addition of the reformate gas monotonically reduces the formation of NO₂ in this flame.

When equivalence ratio equals 0.65, the addition of the reformate gas increases both the formation of NO and the concentration of H, as shown in Figs. 3 and 4, leading to the increase in both formation and destruction rates of NO₂. The formation rate increase is slower than that of the destruction rate when the fraction of the reformate gas is increased from 0 to 0.6, resulting in the decrease of NO₂ formation. However, with the further addition of the reformate gas to over 0.6, the quick increase in the formation of NO causes that the NO₂ formation rate exceeds the destruction rate. Consequently, NO₂ formation slightly increases, when the fraction of the reformate gas is increased from 0.6 to 1.0.

3.6. N₂O formation

Figure 8 shows the variation of N₂O emission index for the flames with stretch rate 30 s⁻¹ and equivalence ratios of 0.9 and 0.65, when the reformate gas is added. Other flames have similar result.

It is illustrated that the addition of the reformate gas decreases the formation of N₂O for both flames. As we discussed before, the main formation and destruction reactions of N₂O are, respectively, N₂O(+M) = N₂ + O(+M) and N₂O + H = N₂ + OH. Destruction rate of N₂O becomes faster than its formation due to a faster increase in H concentration when the reformate gas is added.

It is also noted that the formation of N₂O in the flame of equivalence ratio 0.65 is greater than that in the flame of equivalence ratio 0.9. This is consistent with that observed in hydrogen enriched lean premixed flames [1]. It implies that the formation of N₂O will be an issue in ultra-lean premixed combustion technology. However, the addition of the reformate gas can reduce the formation of N₂O at a constant equivalence ratio. This is another advantage of the reformate gas enrichment combustion.

4. Conclusions

The extinction and NOₓ formation in reformate gas enriched lean premixed methane/air flames have been investigated by numerical simulation. The results indicate that the addition of the reformate gas enlarges the flammable region and extends the lean flammability limit of premixed CH₄/air flames. The addition of the reformate gas reduces the formation of NO for a near-stoichiometric flame, and increases that for an ultra-lean flame at a constant equivalence ratio. However, the addition of the reformate gas can greatly reduce the formation of NO by allowing a combustion system to operate at leaner condition without any effect on flammable range. This is a significant advantage of the reformate gas enriched combustion technology. Moreover, the addition of the reformate gas decreases the formation of NO₂ and N₂O at a constant equivalence ratio.

References