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Flammability Limits and NO_X formation of Reformate Gas Enriched Lean Counterflow CH_4/Air Premixed Flames

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Introduction

Lean premixed combustion is one of the most promising concepts for substantial reduction in fuel consumption and the emissions of greenhouse gases and pollutants. It involves operation with excess air-fuel ratios to substantially reduce the flame temperature. At these low temperatures and excess air-fuel 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.

Unfortunately lean premixed combustion has some intrinsic weaknesses. One of the weaknesses is that at excessive air-fuel ratios, the lean-flammability limit is approached and the flame becomes less stable. A strategy to overcome this weakness is to adopt fuel enrichment, i.e. adding a small amount of other component to the fuel to enhance the flame stability, while maintaining the advantages of lean combustion. Our previous study [1] has shown that hydrogen enrichment can significantly improve the flammability limit and reduce NO formation in counterflow CH_4/air premixed flames by allowing a combustor to operate under leaner condition.

One way to obtain hydrogen is the reforming of hydrocarbon fuels. However, the reformate gas contains not only hydrogen, but also carbon monoxide and some minor components. It is of practical 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 NO_X formation characteristics in reformate gas enriched lean CH_4/air premixed flames. Detailed chemistry and complex thermal and transport properties were used. The reformate gases were assumed to be the products of partial oxidation of methane. The effect of reformate gas addition on the flammability limits and NO_X formation will be discussed.

Numerical Model

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

The simulations assumed the stagnation point flow approximation. The governing equations can be found elsewhere [2]. The potential boundary conditions were used. Upwind and center difference schemes were respectively employed for the convective and diffusion terms in all the governing equations. Adaptive refinement of meshes was done. The arc-length continuation method [3] was adopted to obtain the extinction limits. The pressure and the fresh mixture temperature were 1 atm and 300 K, respectively.

A previous investigation [4], using an improved radiation model, in which the radiation reabsorption was taken into account, showed that the reabsorption has little influence on the extinction limits and temperatures of lean counterflow CH_4/air premixed flames. To simplify the calculation, the optically thin radiation model [1] was used in this paper.

The chemical reaction mechanism used is GRI-Mech 3.0 [5]. The thermal and transport properties were obtained by using the database of GRI-Mech 3.0 and the algorithms given in [6,7].

Results and Discussion

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 methane. Two reformate gases were examined. One is the product of partial oxidation of methane by oxygen, and the other is the product of partial oxidation of methane by air. The two reformate gases differ in the content of nitrogen. The former (reformate gas 1) does not contain nitrogen, while the latter (reformate gas 2) does. The partial oxidation was assumed to follow the reaction: $2CH_4 + O_2 + \gamma N_2 = 2CO + 4H_2 + \gamma N_2$, where γ equals 0 for the first case and 3.76 for the second. In the following discussion, α_{rg} is the volume fraction of reformate gas in the fuel mixture, i.e. $\alpha_{rg} = V_{rg}/(V_{rg} + V_{CH_4})$, where V_{rg} and V_{CH_4} are the volume flow rates of reformate gas and methane, respectively. The variable ϕ represents the equivalence ratio. For the sake of comparison, the performances of pure hydrogen enrichment will also be presented.

Since the objective of this paper is to study the effect of fuel enrichment in lean premixed flames, the equivalence ratio investigated was limited to less than 0.8.

Extinction Limits

A counterflow premixed flame can be extinguished by an extra high or low stretch rate [1]. At an extra high stretch rate, the flame is extinguished due to the shortened residence time. Figure 1 shows the effect of fuel enrichment on the stretch extinction limit for the flames with equivalence ratio of 0.6. The flames of other equivalence ratios have the similar phenomenon. It is demonstrated that similar to the addition of hydrogen [1], the addition of a reformate gas monotonously increases the stretch extinction limit. However, the effect of a reformate gas addition is not as effective as that of the pure hydrogen addition in increasing the stretch extinction limit. This is because hydrogen is one of the main components of a reformate gas, but a reformate gas also contains carbon monoxide. The addition of carbon monoxide enhances the combustion intensity of a CH_4/air premixed flame due to the reaction $CO + OH = H + CO_2$. However, the effect of its addition is not as effective as that of the hydrogen addition. In addition to hydrogen and carbon monoxide, reformate gas 2 contains nitrogen that is basically an inert species for primary combustion reactions. These lead to that the addition of either hydrogen or a reformate gas increases the stretch extinction limit of a CH_4/air premixed flame. The effect of hydrogen addition is most significant, while that of reformate gas 2 addition is least.

Figure 2 displays the variation of radiation extinction limit with the addition of a reformate gas or pure hydrogen for the flame with equivalence ratio of 0.43. Similarly, it is noted that the addition of a reformate gas or pure hydrogen causes a monotonous decrease of radiation extinction limit for CH_4/air premixed flame.

If all the stretch and radiation extinction limits and the corresponding equivalence ratios are plotted in a stretch rate – equivalence ratio plane, a C-shaped curve is formed for a constant reformate gas enrichment fraction [1]. 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 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 counterflow lean premixed flame. As an example, the C-shaped curves for the pure CH_4/air flame and those flames with 40% reformate gas addition are shown in Fig. 3. It is observed that the increase of stretch extinction limits and the decrease of radiation extinction limits lead to the wider flammable region and lower lean flammability limit when a reformate gas or hydrogen is added, with the addition of hydrogen being most effective and that of reformate gas 2 being least. The lean flammability limit of pure CH_4/air premixed flame is 0.420, while this value is extended to 0.335, 0.353 and 0.380, respectively, when 40% hydrogen, reformate gas 1 or 2 is added.

Therefore we can conclude that fuel enrichment by hydrogen or a reformate gas can improve the combustion stability and extend the lean flammability limit, although the effect of different reformate gas addition varies. This is a significant advantage of fuel enrichment technology. It allows a combustor to operate under leaner conditions, and thus reduce the emission of green house gases. For example, the stretch extinction limits of the 40% reformate gas 1 enriched flame with the equivalence ratio of 0.65 and the 40% reformate gas 2 enriched flame with the equivalence ratio of 0.68 are the same as that of the pure CH_4/air premixed flame with the equivalence ratio of 0.80, as shown in Fig.3. This indicates that if a combustor has to run at an equivalence ratio greater than or equal to 0.80 due to the high stretch rate (turbulent intensity) using pure CH_4/air premixed flame, it is allowed to run at an equivalence ratio of as low as 0.65 or 0.68, when 40% reformate gas 1 or 2 is added.

NO_X Formation

Figure 4 displays the variation of NO emission index with the addition of a reformate gas at the equivalence ratio of 0.6. The flames of other equivalence ratios have the similar phenomenon. The emission index in this paper is based on the consumption of oxygen, i.e. EI_{NO} = the ratio of the formed NO mass to the consumed molecular oxygen mass, rather than the conventional definition based on the consumption of fuel. The reason is that hydrogen and carbon monoxide, the two main components of a reformate gas, are not only the parent fuels, but also intermediate species. It clearly shows that the NO emission index monotonously increases with the addition of a reformate gas at a constant equivalence ratio and stretch rate. Although not shown, the variations of the peak NO mole fractions with the increase of a reformate gas addition have been verified to have a similar trend to the emission index.

Three factors may cause the increase of NO formation at a constant equivalence ratio, when a reformate gas is added. Firstly, the temperature increases when a reformate gas is added to a CH_4/air flame. The increase of flame temperature leads to the higher formation rate of NO. However, it should be pointed out that the temperature increase does not necessarily happen for the addition of reformate gas 2 if there were no the effects of the next two factors, because the reaction heat of reformate gas 2 combustion is actually lower than that of pure CH_4/air combustion. Secondly, the addition of a reformate gas to a CH_4/air mixture increases the concentrations of some radicals, such as H and O. The higher concentrations of these radicals

cause the higher NO formation through almost all the four routes, i.e. thermal, prompt, NNH and N_2O intermediate. The effect of hydrogen addition has been discussed previously [1]. The addition of carbon monoxide leads to the high concentrations of these radicals mainly due to the chain carrier reaction $OH + CO = H + CO_2$. Thirdly, the addition of a reformate gas intensifies the preferential diffusion effect, which increases the reaction rates and temperature in the reaction zone. Therefore the addition of a reformate gas to a CH_4/air flame increases the NO formation at a given equivalence ratio.

The above conclusion does not mean that reformate gas enrichment has a disadvantage in terms of NO formation. As indicated before, the addition of a reformate gas allows a combustor to operate at a lower equivalence ratio than that a pure CH_4/air flame has to run at. Fig. 5 shows the NO emission indices for flames with equivalence ratio varying from 0.5 to 0.8 and 40% reformate gas addition. It is seen that the decrease in equivalence ratio significantly reduces the formation of NO. Since the addition of 40% reformate gas 1 or 2 allows a combustor's operation equivalence ratio to be lowered from 0.8 to 0.65 or 0.68, as shown in Fig. 3, the NO emission index can be reduced from 0.1115 to 0.0338 or 0.0390. This is a significant advantage of fuel enrichment technology.

Figure 6 shows the NO_2 emission indices of flames with equivalence ratio varying from 0.5 to 0.8 and 40% reformate gas addition. It is noted that the addition of a reformate gas suppresses the formation of NO_2. This effect becomes more significant with the decrease of equivalence ratio. The addition of reformate gas 1 is more effective than that of reformate gas 2. A sensitivity analysis indicates that the main NO_2 formation and destruction reactions are $HO_2 + NO = NO_2 + OH$ and $NO_2 + H = NO + OH$, respectively. The activation energy of the former is negative, and the latter is positive. With the addition of a reformate gas, the formation reaction rate changes slowly due to the simultaneous increase of NO concentration and flame temperature. However, the destruction reaction rate of NO_2 quickly increases when a reformate gas is added, because of the enhanced production of radical H. Owing to the more hydrogen content, the addition of reformate gas 1 is more effective than that of reformate gas 2.

With the decrease of equivalence ratio, the formation of NO_2 first slightly reduces, and then increases, at a constant fraction of reformate gas. The first decrease in NO_2 formation is caused by the reduction in NO concentration, when equivalence ratio is decreased. However, with the further decrease in equivalence ratio, the formation reaction rate of NO_2 reduces very slowly, but the destruction reaction rate is greatly suppressed, because of the reduced flame temperature.

The N_2O emission indices of flames with equivalence ratio varying from 0.5 to 0.8 and 40% reformate gas addition are shown in Fig. 7. It is found that except at an ultra low equivalence ratio, the addition of a reformate gas reduces the formation of N_2O at a constant equivalence ratio. The most significant formation and destruction reactions of N_2O are $N_2O\ (+M) = N_2 + O\ (+M)$ and $N_2O + H = N_2 + OH$, respectively. At a constant equivalence ratio, the addition of a reformate gas causes the concentration of radical H to increase quickly, which leads to the higher N_2O destruction reaction rate and thus lower the net N_2O formation.

The formation of N_2O increases with the decrease in equivalence ratio for a given fraction of reformate gas. This is an undesirable side effect of the lean premixed combustion technology. It should be noted that this side effect is moderated by the addition of a reformate gas. This is another advantage of fuel enrichment combustion technology.

Conclusions

The extinction and NO_X formation characteristics in reformate gas enriched CH_4/air lean premixed flames have been numerically investigated by detailed chemistry and complex thermal and transport properties. The effects of two reformate gases additions were studied.

The results indicate that although a reformate gas from partial oxidation contains other components in addition to hydrogen, its addition can still significantly enlarge the flammable region and lower the flammability limit of lean CH_4/air premixed flame. As a result, the reformate gas enrichment technology allows a combustor to operate under leaner condition, and therefore significantly reduces the formation of NO. Besides, the addition of a reformate gas can moderate the side effect of the relatively higher NO_2 and N_2O formation under leaner condition. The effect of reformate gas 1 is more significant than that of reformate gas 2 due to its more hydrogen content.

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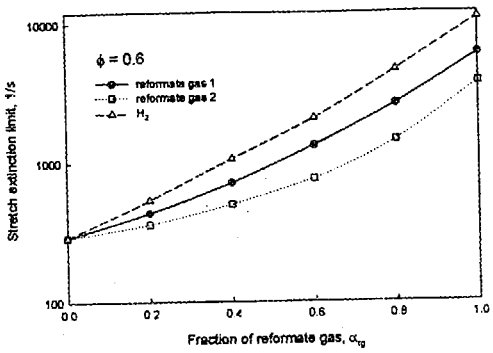

Fig. 1 Effect of fuel enrichment on stretch extinction limit.

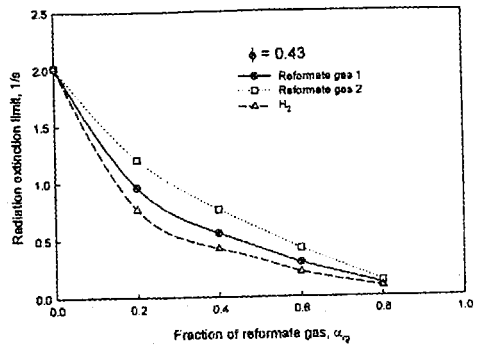

Fig. 2 Effect of fuel enrichment on radiation extinction limit.

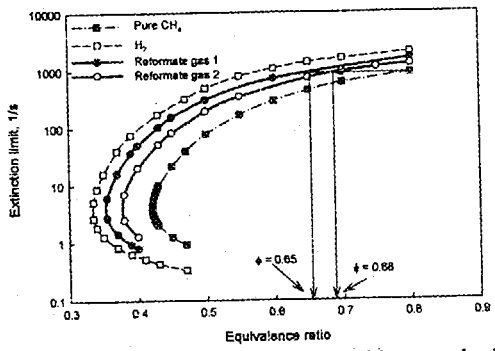

Fig. 3 C-shaped curves of flames without and with 40% reformate gas enrichment.

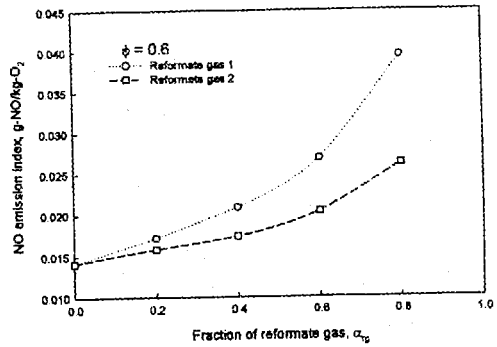

Fig. 4 Effect of reformate gas addition on NO formation.

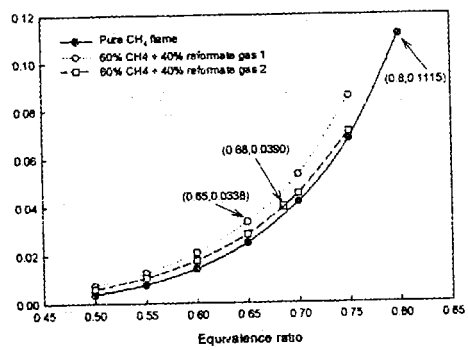

Fig. 5 Effect of equivalence ratio on NO formation.

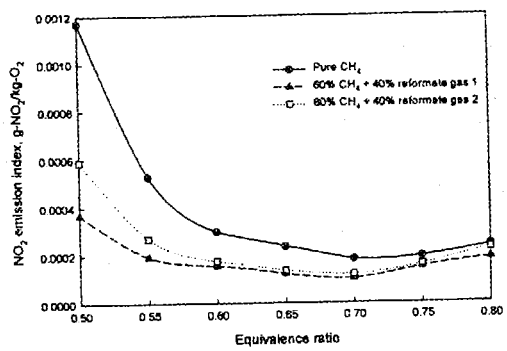

Fig. 6 Emission index of NO_2.

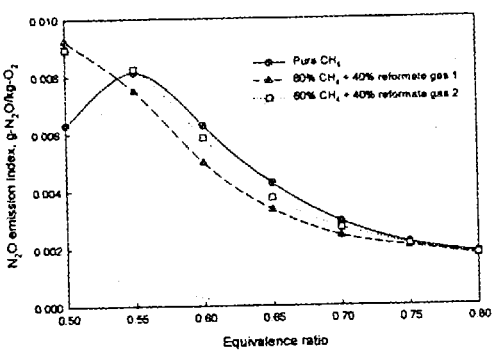

Fig. 7 Emission index of N_2O.