Effects of dilution on the extinction characteristics of strained lean premixed flames assisted by catalytic reaction

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Abstract

As a fundamental study relevant to micro-combustor application, the effects of mixture dilution on the lean extinction characteristics is studied for a stagnation-point flow system with a methane/air mixture over a platinum surface. For steady conditions, the level of flammability extension by surface reaction depends strongly on the mixture dilution, such that the benefit of catalyst-assisted lean combustion can be fully realized only with a diluted system. As for the effects of surface heat loss, while it lowers the overall flammability of the system, it was found that the level of flammability extension by surface reactions is rather insensitive to the surface thermal conditions. These observations are explained by consideration of characteristic time scales calculated from the fuel consumption rate. The extinction response to oscillatory strain rate also shows consistent behavior. Unsteady extinction behavior in response to equivalence ratio fluctuations showed an expected trend overall. It is also found that the benefit of flammability extension by catalytic reaction can become greater as the level of unsteadiness increases.

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Keywords: Extinction; Catalytic combustion; Stagnation-point flow

1. Introduction

Development of micro-power-generation systems with a dimension ranging from a few centimeters to a fraction of a millimeter has recently attracted strong research interests in favor of their high energy density and portability. For this type of combustors, high combustion temperature is undesirable since it adversely affect the mechanical and chemical structures of the interior parts. This problem can be alleviated by achieving low-temperature combustion using lean reactant mixtures. Another benefit of lean combustion is lower pollutant emission such as NOx or soot. However, low temperature combustion is more difficult to achieve in micro-combustors because their high surface-to-volume ratio causes a large heat loss compare to macro-scale combustors. A feasible approach to overcome this difficulty is to employ surface reaction using a catalytic material to assist stable combustion. It is, therefore, of fundamental importance to assess the extent of flammability enhancement due to the surface reaction, especially under lean mixture conditions.

Flammability extension by catalytic reaction has been studied in various configurations. Park et al. [1] performed a numerical study of hydrogen/air stagnation-point flow model with a platinum catalyst, and showed that catalytic reaction can extend both lean and rich flammability limits.

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Seo et al. [2] experimentally investigated a channel flow combustor with a palladium catalyst to determine the minimum surface temperature for sustained combustion. They reported an interesting observation that, when the liquefied natural gas–air ratio was 4.25%, the minimum preheat temperature at which the flame extincts was lower than the preheat temperature of surface extinction. When the fuel–air ratio was 3.86% or less, the preheat temperature for flame extinction was higher than that of surface extinction. These results suggest that successful application of catalyst-assisted micro-combustion depends on parametric conditions of the combustion systems.

Another issue of fundamental interest is the effect of unsteadiness. Due to the small dimension, a micro-combustor is subject to larger variability in operating conditions because there are large uncertainties and technical difficulties in maintaining the constant inlet parameter conditions such as the flow rate, composition, and surface heat loss in small scale devices. It has also been understood that flames near extinction conditions are in general more sensitive to external perturbations [3], which can sometimes lead to combustion instability. Therefore, the flammability extension by catalytic reactions must be carefully examined under unsteady conditions. A number of studies exist on the response of strained flames to unsteady strain rate [3–8] and composition fluctuations [9,10]. In this study, these issues are investigated in a system with homogeneous/heterogeneous reactions. In particular, the concept of the dynamic flammability limit [10] and its extension due to catalytic reactions are explored.

Therefore, the objective of the present study is to conduct numerical simulations of a stagnation-point flow system with a methane–air mixture over a platinum surface. The effects of mixture dilution and surface thermal conditions on the lean extinction limit are examined for a steady system. Subsequently, flame behavior in response to unsteady strain rate and equivalence ratio is investigated in the context of the flammability extension by catalytic reaction.

2. Model description

As shown in Fig. 1, the computational configuration is a stagnation-point flow where a mixture of methane and oxidizer is injected onto a platinum surface, forming a flame either in the flow field or on the catalytic surface. One-dimensional similarity formulation is derived with full consideration of detailed surface [11] and gas-phase [12] chemical kinetic models. The adopted surface mechanism has been validated for ignition behavior in both rich and lean conditions, and extinction under lean cases [11,13]. Due to the lack of thermodynamic data for surface species, however, there may be some inconsistencies when the mechanism is used outside the conditions at which it was designed and tested. Since the present study explores mostly lean to near-stoichiometric conditions, the qualitative behavior and major findings of the study are expected to be valid.

As in our previous study [14], both steady and unsteady computations are performed by a modified version of OPUS [15] to incorporate solid wall and surface chemistry. A fixed zonal grid refinement is applied to provide sufficient resolution in the reaction zone near the solid surface. For all calculations, the inlet gas temperature and pressure is fixed at 300 K and 1 atm, respectively. The distance between the inlet and the catalytic surface is L = 0.5 cm.

One of the main issues in this study is the effects of dilution on the separation of characteristic time scales for gas-phase and surface reactions. For this purpose, additional nitrogen is mixed into the air, measured by its mole fraction. For example, 10% nitrogen addition indicates that 0.1 mole nitrogen is added to 1 mole of air.

To study unsteady flame response, the reactant composition and flow strain rate are varied in time according to the following equations:

$$ U_x(t) = U_x(0) [1 - B (1 - \cos(2\pi ft))] , \quad (1) $$

$$ X_{CH_4}(t) = X_{CH_4}(0) [1 - A (1 - \cos(2\pi ft))] , \quad (2) $$

where $U_x$ is the axial velocity at the nozzle exit and $X$ is the mole fraction. The strain rate is then defined as the nominal velocity gradient, $S = U_x / (2L)$, due to the difficulty in defining the actual velocity gradient when the reaction occurs on the surface [14].

3. Results and discussion

3.1. Steady response: effects of dilution

A baseline study of the flame structure and species profiles in response to the addition of the surface reaction has been investigated in our previous
In this paper, the steady flame behavior subjected to reactant mixture dilution is first investigated, as an attempt to assess the effect of surface chemistry on extending the lean extinction limit at various level of gas mixture dilution. In general, it is anticipated that dilution lowers temperature and hence the reaction rate, such that the flame extinction occurs at a higher equivalence ratio. It is of interest to examine whether this effect applies to both homogeneous and heterogeneous reactions at a comparable level.

Figure 2 shows the maximum reaction zone temperature as a function of the mixture equivalence ratio for various nitrogen dilution levels, each case with and without surface reaction. For all the calculations, the strain rate was fixed at 277 s\(^{-1}\) and the surface was considered adiabatic. The results for all cases show that the maximum temperature decreases as the equivalence ratio is reduced, eventually reaching the lean extinction limit. For the results with surface reactions, it is clearly seen that an increased amount of dilution lowers the reactivity such that extinction occurs at a higher equivalence ratio. An important observation here is that the disparity between the lean extinction limit of homogeneous and heterogeneous combustion becomes larger as the level of dilution is increased. For example, in 0% dilution case the extinction limit for the homogeneous reaction is lower than that for the heterogeneous case. With 13% dilution, however, the heterogeneous combustion shows a much wider flammable range of the equivalence ratio. This implies that the sensitivity in the reduction of the characteristic reaction time scales to the mixture dilution is different between homogeneous and heterogeneous combustion processes. Therefore, it is expected that the benefit of flammability limit extension by catalytic reaction is greater as the reactant mixture is more diluted. This behavior was found to be qualitatively consistent for other values of the strain rate.

More extensive calculations were performed to determine the extinction limit extension over a range of nitrogen dilution. In addition to the adiabatic wall considered in the above, we have also considered the cases where the catalytic surface is subjected to heat loss or heat addition. Heat loss from the surface is modeled by a general form: \[ q = h(T_{surf} - T_0) \], where \( T_0 \) is the ambient temperature set at 300 K, and \( h \) is the effective heat transfer coefficient accounting for the associated conductive and conductive modes. In this study, \( h = 4 \text{ W/m}^2\text{K} \) is used. For the heated surface case, a net power of \( 10^4 \text{ W/m}^2 \) is supplied to the substrate.

Figure 3 is plot of lean extinction limits as a function of the nitrogen dilution for various thermal conditions on the surface. For all surface conditions with zero dilution, it is interesting to note that catalytic reaction results in higher lean extinction limit. In other words, catalytic reaction actually leads to a narrower flammable range. The benefit of flammability extension by surface chemistry occurs only with nitrogen dilution of approximately 5% and above, and the level of extension continues to increase as the level of dilution increases. This behavior is attributed to the fact that, at such lean conditions, the addition of catalytic surface scavenges radicals generated from the gas-phase reactions, hence attenuating the overall reactivity of the system. This results provide an important practical implication that the use of surface reaction in a lean premixed micro-

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Fig. 2. Maximum temperature as a function of the equivalence ratio for various levels of nitrogen dilution for adiabatic surface. Lines without symbols: without surface reactions. Lines with symbols: with surface reactions.

Fig. 3. Lean extinction limits as a function of the nitrogen dilution for various surface thermal conditions, for \( S = 277 \text{ s}^{-1} \). Lines without symbols: without surface reactions. Lines with symbols: with surface reactions.
The effect of nitrogen dilution is primarily to lower the flame temperature and thereby lengthening the characteristic chemical time scales relative to the characteristic flow residence time. It is apparent that this effect is more pronounced in the gas-phase than on the surface. To verify this observation, the characteristic chemical time scales for the gas-phase and surface chemistry, $\tau_g$ and $\tau_s$, respectively, are defined based on the primary fuel consumption as [14]

\[
\tau_g = \frac{X_{CH_4}}{\dot{ω}_{CH_4} R^0 T}, \quad (3)
\]

\[
\tau_s = \frac{X_{CH_4} \Gamma}{\dot{s}_{CH_4}}, \quad (4)
\]

where the units are in seconds, $X_{CH_4}$ is mole fraction of methane at the nozzle exit, $R^0$ is the universal gas constant, and $\Gamma$ is site density of the surface species. In determining the reaction rate, $\dot{s}_{CH_4}$, for the surface reactions is evaluated at the catalytic surface, while for the gas-phase reactions the spatial maximum value of $\dot{ω}_{CH_4}$ is used. Note that $\dot{ω}_{CH_4}$ in Eq. (3) and $\dot{s}_{CH_4}$ in Eq. (4) have different units [14]. The characteristic times are evaluated at a fixed strain rate of $S = 277\, s^{-1}$ for the steady initial conditions shown in Fig. 4.

The results for the three dilution cases considered in Fig. 2 are summarized in Table 1. It is found that the gas-phase reaction time scales increases with dilution by several factors, while the surface reaction time scale remains almost the same. This confirms that the gas-phase reaction is more sensitive to dilution than surface reaction.

### 3.2. Unsteady response to oscillatory strain rate

The effect of dilution on the chemical time scales has an additional implication in unsteady flame response. As reported in a number of previous studies [6,3,16], flames subjected to unsteady flow perturbation behave as a low-pass filter; the flame response becomes attenuated as the frequency of the external perturbation increases. In this case, the cut-off frequency beyond which the flame no longer responds to unsteady fluctuation depends on the characteristic time scale of the relevant chemical reactions.

The above consideration is extended to a system in the presence of heterogeneous combustion. A steady flame is now subjected to an oscillatory strain rate by imposing a sinusoidal velocity fluctuation as given by Eq. (1) for various frequencies. For these calculations, the equivalence ratio is fixed at $\phi = 0.8 (A = 0)$, and the initial strain rate is fixed at $S(0) = 277\, s^{-1}$ with $B = 0.1$. The surface is considered adiabatic so that the maximum temperature always occurs at the surface for both catalytic or non-catalytic cases. To show the effect of dilution clearly, the 0% dilution case is compared to the 18% dilution case, which was the maximum value before extinction.

Figure 4 shows the amplitude of the maximum temperature oscillation, $\Delta T$, in response to the unsteady strain rate as a function of frequency. For each case, $\Delta T$ is normalized by the quasi-steady value ($f \rightarrow 0$). As the frequency of oscillation is increased, the flame temperature response for various conditions become attenuated at different cut-off frequencies. For either case of dilution, surface reactions have shorter characteristic time scales, such that the response is less attenuated.

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3.3. Dynamic flammability limit

To further examine the effects of dilution on unsteady flame characteristics, we now study the unsteady flame response to oscillatory equivalence ratio as given by Eq. (2). The main interest is to identify the extension of lean flammable limit for a given strain rate as a function of frequency, following the concept of the dynamic flammability limit, which is defined as the minimum instantaneous equivalence ratio during the oscillation without extinction, introduced by Sankaran and Im [10]. For each frequency, $f$, we can determine the maximum allowable amplitude of oscillation, $A$, beyond which the flame extinguishes. This implies that the dynamic flammability limit is a function of frequency for the given strain rate, surface thermal condition, and the initial equivalence ratio. We attempt to conduct an analysis to a system in the presence of heterogeneous combustion, with an emphasis on the effects of nitrogen dilution, heat loss, and the frequency of the equivalence ratio oscillation.

The flame responses with and without catalytic reaction are compared under three cases: (a) 0% dilution without heat loss, (b) 13% dilution without heat loss, and (c) 13% dilution with heat loss. Following Eq. (2), the initial condition, $X_{CH_4}(0)$, as been set such that the equivalence ratio, $\phi = 2X_{CH_4}(0)/X_{O_2}(0)$, is 0.68, 0.76, and 0.80 for cases (a) to (c), respectively. For all cases, the strain rate is set to $277 \text{s}^{-1}$.

Figures 5a–c show the limit-cycle behavior of the maximum flame response for various frequencies of oscillation in $\phi_{\text{flame}}$, which is determined at the upstream flame base at $T = 302 \text{K}$. Since the amplitude of $\phi_{\text{flame}}$ was taken to be the maximum without quenching the flame, the minimum equivalence ratio reached during the limit cycle is considered the dynamic flammability limit for a given frequency condition. Comparing Figs. 5a and b, it is clear that the diluted case shows a greater extension of the lean flammability limit by adding the surface reaction; not only is the steady flammability limit further extended to a leaner condition, but the additional unsteady extension for the same frequency is also greater with surface reaction. This is attributed to the fact that the surface reaction is faster and thus can respond to the imposed oscillation more rapidly. Moreover, the surface reaction case undergoes a larger excursion in the flame strength, hence there is a larger amount of excess enthalpy during a cycle to
sustain combustion at leaner conditions. Similar behavior is also observed in Fig. 5c in the presence of heat loss, although the overall flammability limits are relatively higher than those in (b). As discussed in Fig. 3, the amount of flammability extension due to surface reaction is found to be rather insensitive to the surface thermal condition even considering unsteady situations.

To summarize the unsteady characteristics, it is of interest to compare the dynamic flammability extension between the cases with and without surface reaction, denoted by $\Delta \phi_s$ and $\Delta \phi_g$, respectively. Here, $\Delta \phi$ is defined as the maximum flammability extension compared to the steady limit for a given frequency. Figure 6 shows the difference, $\Delta \phi_s - \Delta \phi_g$, as a function of frequency for the three cases shown in Fig. 5. Note that the increase in the curve with frequency indicates that the additional dynamic flammability extension due to surface reaction becomes greater as frequency increases. In other words, the benefit of surface reaction in extending flammability is greater for a larger level of unsteadiness. For 0% dilution, the curves fall into an negative region for frequencies above 200 Hz due to the fact that surface reaction acts negatively on the system flammability. However, there is a reversal in the curve at low frequencies below 200 Hz resulting in flammability enhancement by surface reaction even with 0% dilution. Therefore, the benefit of catalytic flammability extension is found to be greater with dilution, while the difference between the cases with and without heat loss appears to be insignificant.

4. Conclusions

In this paper, steady and unsteady extinction characteristics of a stagnation-point flow combus-

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