Effects of platinum stagnation surface on the lean extinction limits of premixed methane/air flames at moderate surface temperatures

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1. Introduction

Catalysts are playing increasingly important roles in modern combustion systems particularly in the power generation sector. A number of review papers are available on the subject of catalytically-aided combustion in various engineering applications [1–4]. Catalytic materials are used to improve combustion stability over a wider range of fuel–air ratios, thereby allowing fuel lean, low temperature and staged (i.e. rich and lean burn zones) combustion strategies. For example, the combined effects of locally lean equivalence ratios, lower combustion temperatures and catalytic reaction can significantly reduce NOx emissions [5,6]. Recent research has demonstrated the effects of catalysts at pressures relevant to boiler and gas turbines [7–9]. Further work has explored the exciting opportunity to enable zero emissions strategies (e.g. highly dilute oxygen-fired combustion [10]) through the application of catalytically-aided combustion with high levels of dilution with exhaust gases [11,12].

Catalytically-assisted combustion has also been applied to increase the stable range of micro-scale combustion devices [13–15]. Although combustion of hydrocarbon fuels is an attractive means for power generation in compact devices in favor of the high energy densities, the large surface-to-volume ratios associated with a small device dimension can lead to excessive heat loss, making sustained gas-phase combustion a challenge. Catalytic reactions have the potential to enhance reactions at lower temperatures and extend the range of the allowable fuel–air composition for stable combustion [16,17]. It remains to be seen, however, whether the augmented reactivity by the catalytic surface can actually lead to the desired flammability limit extension when there is direct coupling between the homogeneous and heterogeneous reactions using practical fuels and device operating conditions.

The objective of this study is therefore to understand and assess the extent of the catalytic impact on homogeneous combustion in a flame-catalyst system. A stagnation-point flow reactor is adopted as a model configuration, because it allows systematic control of the characteristic flow time scales by varying the nozzle inflow velocity independently from the chemical time scales [18]. The system is also amenable to a one-dimensional modeling by the similarity approximation of the flow field. This configuration has served as a canonical geometry to develop reaction mechanisms and to investigate the catalytic effects on combustion characteristics. The stagnation flow reactor has also been used in studies of catalyst oxidation and ignition phenomena [18–26]. For example, investigations of catalytic light-off and homogeneous ignition phenomena of methane have been performed by Williams et al. [21], Vlachos et al. [23] and Veser and Schmidt [24], and fuel conversion efficiencies of methane–air mixtures over platinum in a stagnation flow have been conducted by Dupont et al. [25].

There are several ways that a catalyst can be incorporated in combustion processes. The simplest application is to operate the catalyst at a low temperature where gas-phase reactions are insignificant, and in such a way that complete fuel oxidation takes place. In this case the heat release due to the catalytic reaction is
harnessed. It is also possible to couple a catalyst with gas-phase combustion. Reacting part of the fuel air mixture prior to a gas phase combustor can heat the incoming reactant flow as well as partially decompose the fuel to alter the combustion characteristics of the fuel in the downstream gas phase reactor. Lastly, a catalyst can be located within a gas phase combustor where the catalyst interacts with gas-phase combustion directly. When directly coupling gas phase and catalytic reactions it is useful to quantitatively determine the significance of gas-phase reactions as opposed to surface reactions. For example, McDaniel et al. [27] separated homogeneous and heterogeneous chemistry effects and identified the initiation of a self-sustaining high heat release rate catalytic reaction as “light-off”, and the initiation of a self-sustaining gas-phase reaction “ignition”. The present study uses the methane–air/platinum system due to the importance of methane in natural gas fired systems and because the relevant kinetics for homogeneous and heterogeneous reactions for CH$_4$/N$_2$/O$_2$/Pt are relatively well understood; enabling comparison between experimental and computational results. Moreover, recent computational studies by Li and Im [16,17] on a methane–platinum stagnation-point flow system reported that the lean flammability limit can be extended when the characteristic time scale of the catalytic reactions is sufficiently shorter than that of the homogeneous reactions, as was the case when the reactant mixture was diluted by inert gases. The general conclusion was the catalytic extension of flammability can be more significant as the ratio of the catalytic to homogeneous reactions time scales becomes smaller. Such conditions are met if: (a) the reactant mixture is diluted, (b) the strain rate for the gas-phase flame is increased, or (c) the catalytic surface temperature is increased. The main goal of this study is to assess if a significant level of catalytic flammability extension is attainable, using common fuels and at moderate combustor temperatures (less than 750 K) and atmospheric pressures, using these guidelines.

In the present study, the stagnation plane is either a low surface reactivity/control case or catalytic using a platinum-coated surface, so the effects of surface reactions can be assessed relative to the baseline results of the control surface. For each reactant flow rate condition, the equivalence ratio of the fuel air mixture is decreased until flame extinction occurs. The lean extinction limits and stagnation surface temperatures are recorded. Complementary modeling efforts are employed using the heat transfer and flow boundary conditions of the experiments. Through the combined experimental and computational parametric studies, a feasible range of operating conditions for catalytic flammability extension is identified.

2. Experimental method

A schematic of the experimental apparatus is shown in Fig. 1 and is described in detail in Wiswall et al. [28]. Briefly, premixed methane and air impinge on the stagnation plane to achieve stagnation-point flow. A co-flow of nitrogen around the reactant mixture prevents entrainment of atmospheric air. The dimensions of the fuel/air tube are 9.08 mm inner diameter with a 0.265 mm wall thickness. The co-flow tube is 17.3 mm inner diameter. The length of the co-flow tube is 130 mm. Type 304 stainless steel is used for all tubing.

Figure 2 is a schematic of the stagnation plane and the support. The support for the stagnation plane is 304 stainless steel and is 100 mm × 110 mm square and 12.5 mm thick. The stagnation plane is a 0.5 mm thick silicon wafer (coated or uncoated) with a diameter of 100 mm which is positioned 45 mm above the nozzle exit. The silicon wafer is mounted on the supporting stainless steel plate using a vacuum. Three 0.2 mm diameter K-type thermocouples (Omega Engineering Inc.) are simultaneously used to measure the stagnation plane temperature, $T_p$. The thermocouples are placed at three locations radially outward from the centerline of the flow (see Fig. 2). The thermocouple beads are in physical contact with the back surface of the silicon wafer, and the measured temperature is reported as the stagnation plane temperature. The temperature on the back surface of the steel support plate, $T_s$, is measured using thermocouples cemented at three radial positions corresponding to the three locations of the stagnation plane measurements. The temperature difference between the wafer and the back surface of the support is used to determine the heat flux through the catalyst support. The thermocouple voltages are measured using a multi-meter (Fluke 45) and recorded by a data acquisition system (Labview 8) at a rate of 2.5 Hz.

The impinging velocity of the reactant flow was measured using 2-D particle imaging velocimetry (PIV). Both the flow gradient in the radial direction, and the deceleration of the centerline velocity impinging on the stagnation plane, were measured. Figure 3 shows a cross section of the flow impinging on the stagnation plane and the zone where the PIV measurements were performed.
The reactant mixture equivalence ratio ($\phi$) is determined by the volumetric flow rate measurements of air ($Q_{\text{air}}$) and methane ($Q_{\text{fuel}}$):

$$\phi = \frac{Q_{\text{fuel}}}{Q_{\text{air}} stoch}.$$  

(1)

The nozzle exit velocity, $V$, is also determined by the volumetric flow rate measurements of air and methane, and is the calculated centerline velocity of the flow exiting the nozzle assuming fully developed parabolic flow within the nozzle. The air and methane flow rates are independently controlled to produce the desired values of $\phi$ and $V$, which are the input parameters of the study. The dependent variables are the lean extinction limit, $\phi_{\text{ext}}$, the stagnation plane temperature, $T_p$, and the backside support plate temperature, $T_b$. The uncertainty of the flow meters is two standard deviations of five repeated calibrations, giving a 95% confidence level. The estimated measurement uncertainties are less than ±4% for $\phi$ and $V$, and ±15 K for temperature. The uncertainty in the lean extinction limit arises from both the measurement uncertainty in the reactant fuel air mixture and the repeatability of the lean extinction limit. Details of the experimental uncertainty of the lean extinction limit can be found in Wiswall et al. [28]. The uncertainty in the lean extinction limit arises from both the measurement uncertainty in the reactant fuel air mixture and the repeatability of the lean extinction limit. To measure the lean extinction limit, the average nozzle exit velocity and the nitrogen mole fraction in the oxidizer were held constant while $\phi$ was decreased until extinction occurred. The lean extinction limit was defined as the average between the lowest measured $\phi$ yielding a stable flame and the slightly lower $\phi$ yielding an unstable condition. The resolution of controlling $\phi$ in the experimental setup was 0.008.

For the catalyst experiments, platinum-coated silicon wafers were used. The platinum was deposited on a silicon wafer by physical vapor deposition. To achieve a stable deposition of platinum, a 30 nm layer of titanium was first deposited on the silicon followed by deposition of a 100 nm layer of platinum. A bare silicon wafer was used for the control case and was confirmed to have no discernable catalytic activity at the conditions studied.

3. Experimental and modeling procedures

After establishing the desired flow rates, the methane–air flame is ignited using a propane–air torch. The plate is allowed to reach steady state conditions for a period of 90 min. The nozzle flow velocity, equivalence ratio and steady state temperatures are then recorded. The premixed flames typically exhibit a flat disk region approximately 1 cm in diameter (see Fig. 4). The equivalence ratio is decreased while keeping the nozzle flow velocity constant and the system is again allowed to reach steady state. This procedure is repeated until the flame extinguishes. Figure 5 shows the results from a typical experiment for a particular nozzle flow velocity. The vertical line on the figure represents the extinction limit, which is reported as the average of the minimum $\phi$ where a stable flame could be established and the next lower increment in $\phi$ for which the flame extinguished. For the parametric conditions studied, gas-phase flame extinction immediately leads to the termination of the total chemical reactivity of the system; no sustained surface-only reaction mode was observed.

As noted earlier, lean extinction limits were determined experimentally and computationally. A computational model of a one-dimensional stagnation-point flow configuration with detailed gas phase and surface reaction mechanisms was adopted. Details of the computational method are described in Li and Im [16]. The gas-phase reaction mechanism of GRI-Mech 3.0 [29] was used for the methane/air gas-phase chemistry and the surface mechanism of Deutschmann et al. [30] was used for the platinum interactions. The surface and gas-phase mechanisms were used without modification, including a constant surface site density of $2.72 \times 10^{-4}$ mol/cm$^2$ as in the original surface mechanism. For the computational studies, the lean extinction limit was determined to be the minimum equivalence ratio at which a stable steady flame solution was found.

Two additional efforts were made for consistent comparison of the experimental and simulation results in this study. First, the axial velocity profiles along the centerline of the axisymmetric flow were matched between experiment and computation. The
centerline velocity profile was experimentally measured using particle image velocimetry and normalized by the average nozzle exit velocity, which was determined from the measured volumetric flow rate divided by the nozzle area. The symbols in Figs. 6 and 7 show the measured axial velocities along the centerline for conditions with a flame present and without. For both cases, the measured profiles exhibit a large region of nearly constant velocity close to the nozzle exit. This behavior contrasts computational results in which the axial velocity immediately decreases after the flow exits the nozzle. Therefore, the effective nozzle distance was determined from the experimental data as the distance from the stagnation plane to the location where the velocity has decreased 5% from the velocity at the nozzle exit. The effective nozzle distance is then used as the computational domain size, along with the prescribed nozzle exit velocity provided by the experimental data. This computational approach yields strain rates comparable to the experiments near the stagnation surface and the flame zone.

Next, the effects of heat transfer at the catalytic surface were matched. This was a nontrivial task as the important modes of heat transfer (conduction, convection, and radiation) depend significantly on the flow conditions as well as the material properties, which were difficult to determine in some cases (e.g., the emissivities of the platinum and silicon surfaces as functions of temperature). As a compromise, the following method was used. For the simulations, the thermal boundary condition of the stagnation surface was matched to the measured experimental values by assuming a backside plate temperature and plate thickness fixed at 300 K and 1 cm, respectively. An effective conductivity, $k_{eff}$, was determined for each experimental condition such that the computed stagnation surface temperature matched the measured stagnation surface temperature. Using this approach, the different modes of heat transfer as well as the possible variations in the backside plate temperature were all captured in $k_{eff}$. Considering that the heat transfer properties depend significantly on the surface temperature (for conduction and radiation) and nozzle exit velocity (for convection), the following linear correlation was developed:

$$k_{eff} = (a_1 V + b_1) T_s + (a_2 V + b_2)$$

and the four constants were determined by fitting all experimental data at all strain rate and equivalence ratio conditions under study. It was necessary to derive a distinct curve fit for the silicon and catalytic surface conditions because the surface radiative properties differ significantly. The resulting constants are $a_1 = -0.2625$, $b_1 = 0.2038$, $a_2 = 144.1$, and $b_2 = -108.4$ for the silicon surface and $a_1 = -0.2702$, $b_1 = 0.2176$, $a_2 = 147.4$, and $b_2 = -116.9$ for the platinum surface. The units of $k_{eff}$, $V$ and $T_s$ are W/m K, m/s and K. Note that the expression for $k_{eff}$ was developed as a means to match the experimental and computational thermal boundary conditions and as a consequence can be applied with high confidence only within the range of the experimental calibration.

In general, the values for $k_{eff}$ do not span a large range ($k_{eff} = 4.4–5.6$ W/m K for the control surface and $k_{eff} = 4.0–5.2$ W/m K for the platinum surface); however, some trends are observed. For a given strain rate condition, $k_{eff}$ tends to increase with surface temperature, implying increasing radiation heat loss. Furthermore, $k_{eff}$ decreases as $V$ increases, indicating there is higher heat transfer to the stagnation surface as the reactant flow rate increases. This trend is attributed the flame moving closer to the stagnation surface, thus increasing the radiation and convection to the surface, which is discussed further below. The correlations for $k_{eff}$ are used in the computational simulations presented in the subsequent sections.

4. Results and discussion

The stagnation surface temperatures were measured for five nozzle exit velocities for the stable flame conditions prior to extinction at $\phi_{ext}$. Figures 8 and 9 present the results for $T_s$ as a function of equivalence ratio for the control and platinum-coated surfaces, respectively. At flow velocities larger than 90 cm/s, stable flame conditions could not be achieved. At velocities lower than 57 cm/s, the flame stabilized on the burner nozzle at some of the equivalence ratios of interest. For both control and catalytic surface conditions, the overall trend is that $T_s$ increases with increasing $\phi$ and flow velocity, and that the lean extinction limit increases with flow velocity. The increasing value for $T_s$ with increasing $\phi$ is expected considering the flame temperature is higher for a higher value of $\phi$. Furthermore, $T_s$ increases with increasing flow velocity because the flame stabilizes closer to the plate, thereby losing a larger amount of heat to the stagnation surface. In other words, as the nozzle exit velocity increases, the flame intensity is weakened by the increased heat loss and the reduced flow residence time to complete reaction, such that extinction is expected at a higher chemical intensity in the flame.

Figure 10 compares the experimental results for $T_s$ for the control and the catalytic surfaces at the lean extinction limit for the range of nozzle exit velocities. The data show the surface temperature at extinction is larger for the platinum-coated stagnation
surface. On the other hand, Fig. 11 shows that the lean extinction limit itself is not significantly affected by the presence of the catalyst surface, where the small differences in the catalyst and control surface data are within the experimental uncertainties.

The experimental results are compared with the computational results for $T_s$ in Fig. 12 and for $\phi_{\text{ext}}$ in Fig. 13. The data show the use of the effective heat conductivity and effective nozzle distance in the model yields good quantitative and qualitative agreement with the experimental data. The results indicate the flame extinction behavior is predominantly controlled by the strain-induced gas-phase flame extinction at the combined conditions of critical equivalence ratio and velocity. The surface temperature at this condition may differ by a few tens of degrees, but this is not sufficient to induce a significant level of catalytic activity to promote sustained gas-phase combustion.

The experimental and computational results in this study suggest catalytically-assisted flammability extension is unlikely in methane–air–platinum combustion devices operating at similar flow and heat loss conditions. Because platinum has been demonstrated as effective at sustaining catalytic reaction of methane at temperatures $>1000$ K [21,24], substantially higher surface

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Fig. 8. Experimental results for the stagnation surface temperature versus $\phi$ for constant nozzle exit velocities for the control stagnation surface. For clarity, the representative uncertainties are shown by the error bars on the largest values for $\phi$.

Fig. 9. Experimental results for the stagnation surface temperature versus $\phi$ for constant nozzle exit velocities for the platinum-coated stagnation surface. For clarity, the representative uncertainties are shown by the error bars on the largest values for $\phi$.

Fig. 10. Experimental results for the stagnation surface temperature at the lean extinction limit for different nozzle exit velocities. The filled symbols are platinum catalyst data and the open symbols are control surface data.

Fig. 11. Experimental results for the lean extinction limit as a function of the nozzle exit velocity. The filled symbols represent the platinum catalyst stagnation surface and the open symbols represent the control stagnation surface.

Fig. 12. Comparison of experimental and numerical results for the stagnation surface temperature at extinction as a function of the nozzle exit velocity. Open and closed symbols denote the control and platinum surface conditions, respectively.
temperatures than those studies here may sufficiently enhance the catalytic activity of the methane–air/platinum system to extend the lean flammability limits. Alternatively, conditions which weaken the gas-phase flame may be more sensitive to the presence of the platinum surface. For example, Li and Im [17] reported a noticeable level of catalytic flammability extension in the presence of mixture dilution.

To assess the effects of mixture dilution at the conditions in the present experiments, additional simulations were conducted. Adopting the $k_{eff}$ correlation and using comparable nozzle exit velocities to the experiments, various levels of nitrogen dilution in the fuel/air mixture were evaluated and the resulting impact on $\phi_{ext}$ was quantified. For the range of the velocities considered in the present experiment (57–90 cm/s), catalytic extension of the lean flammability limit was not obtained at any level of nitrogen dilution. Calculations were also conducted at higher strain rates and for adiabatic surface conditions. Figure 14 shows the computational results for the flammability limit as a function of the nitrogen dilution for nozzle exit velocities of 74 cm/s and 139 cm/s. Only for the 139 cm/s case, with limited flow residence time, were we able to obtain a narrow range of high levels of dilution where the presence of catalytic reaction lowered $\phi_{ext}$ and hence promoted sustained combustion. At lower levels of dilution, the catalyst suppresses reaction and increases the value of the lean extinction limit. Also included in Fig. 14 are the computational results for surface conditions where heat loss has been considered by applying the correlations for $k_{eff}$. Although the reactant flow rates are outside the range of the calibration for $k_{eff}$, the qualitative trends for heat loss can be compared to the adiabatic case. There is a slight benefit to the conditions when heat losses are present in terms of a lower value of nitrogen dilution at the cross-over point where the catalyst starts to extend the lean flammability limits. However, the overall lean extinction limits are higher compared to the adiabatic case, which is expected when surface heat loss is present.

5. Concluding remarks

The experimental results of this study demonstrate a range of conditions where the lean flammability limits for methane–air combustion are not sensitive to platinum. A slight increase in the surface temperature at the extinction limit was observed for the platinum surface. This effect is attributed to differences in the heat transfer properties of the stagnation surface, in particular the difference in emissivity between platinum and silicon. The results demonstrate the lean extinction limit of this methane–air–platinum reactor is dominated by gas phase extinction for the conditions studied. Therefore, it is concluded that catalytic flammability extension by platinum may not be feasible for small scale methane–air combustion systems subjected to a significant level of heat loss. To make the approach viable, the device may need to minimize surface heat loss in combination with sufficient dilution of the fuel/air mixture to achieve low-temperature combustion. Some recent designs of heat-recuperating micro-combustors [31] may indeed be able to exploit this limit. Alternatively, the surface reactions of some higher hydrocarbon fuels on platinum have much higher reactivity at lower temperatures. Our recent study [28] reported that surface-only reactions were obtained for the same stagnation-point flow reactor with propane as the gaseous fuel; thereby the potential benefit of catalytic materials was demonstrated. Further investigations are needed in order to identify feasible design and operating conditions applicable to practical compact catalyst-assisted combustion systems, particularly those using methane.

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