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Extinction limits and structure of counterflow nonpremixed H₂O-laden CH₄/air flames

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Abstract

In order to better understand combustion processes when large amounts of water (H₂O) naturally incorporate into the fuel stream, e.g., the combustion of methane (CH₄) hydrates and H₂O/fuel emulsions, the extinction limits and structure of counterflow nonpremixed flames of mixtures of H₂O vapor and CH₄ and air were identified experimentally and computationally. With H₂O vapor addition, the maximum flame temperature was experimentally determined, while the flame structure and extinction limits were computed using a detailed kinetic mechanism. Predicted and measured tendencies of the maximum flame temperature for various conditions exhibit encouraging agreement and thus justify using the computational results to analyze the detailed flame structure and determine the extinction limits. The extinction limits (in terms of the H₂O to CH₄ molar ratio) are reduced with increasing strain rates, implying that flames can sustain more H₂O vapor at low strain rates. Thus, the maximum flame temperature at the extinction limits increases with increasing strain rates because there is less H₂O to act as a thermal sink. The observed flammable range of the H₂O to CH₄ molar ratio is comparable to that found in self-

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sustained combustion of CH₄ hydrates. The chemical effects of H₂O addition on flame structure are insignificant.

Keywords: Water-laden flames; Nonpremixed methane/air flames; Counterflow flames; Extinction limits; Methane hydrates

1. Introduction

Recently there is increasing interest in methane (CH₄) hydrate combustion due to the large energy resource that methane hydrates represent, as well as their potential environmental impact [1]. Burning methane hydrates involves a combustion process where a large amount of water (H₂O) is naturally incorporated into the fuel stream since hydrates consist of 86% water and 14% methane by mole fraction [2,3]. Despite this extremely high water content, qualitative experiments show that the fuel gas released from hydrates can sustain a flame (though not all of the water evaporates) [4]. Although it is well recognized that gas hydrates present remarkable challenges in both energy and environmental applications [1], their combustion behavior has not been studied extensively, and in particular the range of water vapor to methane molar ratio where a flame can be sustained has not been identified. While not at quite the extreme levels of water addition as hydrate flames, other examples of water-laden fuel nonpremixed flames also occur. In the combustion of water/fuel emulsions high amounts of water are added to liquid spray fuels to mitigate nitrogen oxides (NO_x) production. The rapidly rising fuel plume above LNG pool fires has been shown to incorporate large amounts of water on the fuel side of the flame, and some gel fuels have relatively high water content as part of their structure.

Motivated by the above water-added combustion processes, where water is incorporated on the fuel side of nonpremixed flames that are observed in nature and combustion devices, we examine the effects of water addition on the fundamental combustion characteristics of a counterflow flame. The desire to understand the interaction between water and flame is not new [5–10], but our focus is on fuel-side water, and very large levels of water addition. Since a turbulent nonpremixed flame can be considered as an ensemble of strained, laminar, one-dimensional flamelets which can be represented by a counterflow nonpremixed flame configuration [11], many fundamental studies of water-laden nonpremixed flames have been conducted using the counterflow configuration. The previous studies have focused mainly on fire suppression applications since water mists can be considered as a nontoxic, non-corrosive suppressant with zero ozone depletion and global warming risks, due to its significant cooling capacity and diluting effects of reactants in both liquid and vapor phases, reducing the adiabatic flame temperature [5–8]. These prior studies usually provide information such as limits of water mist concentration below which flames cannot be self-sustained, or droplet size and mist loading density for the best suppression performance to show that water mist is a potential candidate for replacing Halon 1301 suppressant [5–7]. The extinction and structure of air-side water-laden flames for various strain rates were experimentally investigated as well [8]. As mentioned earlier, environmental concerns have also motivated studies of water-laden flames. For example, Park et al. [9] have used water emulsified diesel to reduce NO_x and soot by reducing flame temperature in internal combustion engines, though a recent study shows that carbon monoxide (CO) emissions are not affected by water [10]. Because most previous studies, focusing on fire suppression and premixed engine applications, have considered liquid water introduced into the air stream of the counterflow flame burner, our study, which is to examine in part the combustion

properties of fuel/water mixtures emanating from methane hydrates, introduces the water vapor into a heated fuel stream through the bottom nozzle of the counterflow flame burner.

In view of the above considerations, we aim to study experimentally and computationally the extinction and structure of water-laden nonpremixed methane/air flames under conditions that are close to those observed in methane hydrate as this is the most extreme example of natural fuel/water mixture combustion. The counterflow burner configuration will be used since previous studies have shown it suitable for studying extinction limits and flame structure for various strain rates. Different from the previous studies, however, prevaporized water is injected into a heated methane stream issuing from the bottom nozzle, as mentioned earlier. The detailed flame structure and extinction limits (in terms of the water to methane molar ratio) were computed using a recent detailed kinetic mechanism, while the maximum flame temperature was experimentally determined to justify using the present computational results through comparison with predicted temperature. Radiative heat loss effects of water-laden methane/air flames were also included in the computations.

2. Experimental and computational methods

The counterflow nonpremixed flame was adopted as the model flame for the present investigation. The counterflow nonpremixed flame configuration represents a strained, laminar, one-dimensional flamelet, and its dynamics are well studied and defined.

Fig. 1a shows a diagram of the present experimental apparatus, which consists of a counterflow burner having a pair of main stainless steel tubes (nozzles), each surrounded with a concentric tube to provide sheath coflow of nitrogen (N_2) which prevents burning of fuel with the ambient air, a fuel (CH_4), air and N_2 supply system, a water supply system with an electric

furnace for vaporizing water and mixing it with CH_4 , thermocouples for measuring the temperature at various points on the burner and the distribution in the flame. A digital camera (Nikon D70) records flame images to measure the visible flame position and appearance.

Fig. 1 Schematics of experimental apparatus (a) and counterflow nonpremixed flame (b). (web color only; 2-column fitting)

Fuel with water vapor and air are issued respectively from the bottom and top nozzles with the inner diameter $d = 19.0$ mm and the nozzle separation distance $L = 12.7$ mm. For obtaining stabilized, uniform flow at the nozzle exit, the flows issue through stainless steel beads with an average particle diameter of 2.61 mm and three layers of stainless steel honeycombs. A stainless steel screen covers each nozzle exit. The upper and lower inner tubes are aligned so that their centerline is along the same axis. The burner is placed inside a semi-closed, Plexiglas chamber to isolate the flame from laboratory drafts. Fuel with water vapor mixes with air near a stagnation plane between the nozzles. A spark-igniter initiates the laminar, flat nonpremixed flame. Fig. 2 shows typical counterflow flame images. To prevent burning of fuel with the ambient air, the N_2 coflow dilutes the products and prevents heating the upper nozzle. The

coflow injection velocity u_c is adjusted to be the same as the respective fuel and air injection velocities u_F and u_o . Note, however, that the fuel-side co-flow velocity does not include the additional velocity produced when water vapor is added. Commercial mass flow controllers (Cole Parmer: 1–100 L/min) with accuracy $\pm 0.2\%$ of full scale deliver CH_4 (purity $> 99.999\%$) and air (21% oxygen (O_2)/79% N_2 in volume, purity $> 99.9\%$). The mass-flow controllers are calibrated using a bubble meter. Coflowing N_2 is supplied using rotameters (Aalborg: 0–150 L/min) with accuracy $\pm 1.0\%$ of full scale which are also calibrated using the bubble meter. Deionized liquid water (purity $> 99.9999\%$) is supplied into the fuel stream using a syringe pump (New Era: 0–30 cc) with a volumetric accuracy of $\pm 1.0\%$. The pump is PC controlled to deliver liquid at preselected times and rates and it is calibrated by collecting liquid for timed intervals. Water and fuel mixtures run through an electric furnace (maximum heating temperature of 1373 K). The lower (fuel) nozzle is electrically heated using a heating band and is thermally insulated. The upper (air) nozzle is cooled using a water-cooling coil. Micropositioning stage-mounted B-type thermocouples (bead diameter of $200 \pm 20 \mu\text{m}$; accuracy $\pm 0.25\%$) are used to identify the maximum flame temperature. Tension is added to the bead in order to prevent sagging when thermocouples are inserted into the flame. To confirm that water is prevaporized prior to injection at the fuel nozzle exit, temperatures at the electric furnace entrance and exit and the fuel nozzle exit are monitored using K-type thermocouples (bead diameter of $250 \pm 20 \mu\text{m}$; accuracy $\pm 0.05\%$).

Fig. 2 Photographs of counterflow nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames of $R_{\text{H}_2\text{O}/\text{CH}_4} = 0$ (a), 0.3 (b) and 0.9 (c): $\dot{V}_F = 2.4 \text{ L/min}$ and $\dot{V}_O = 4.4 \text{ L/min}$. (web color only; single column fitting)

For all experiments of water-laden CH₄/air nonpremixed flames, the strain rate a , i.e., u_F and u_O , is set to a fixed value and then the H₂O to CH₄ molar ratio $R_{\text{H}_2\text{O}/\text{CH}_4}$ is increased up to the extinction limit. In the present study, the strain rate is defined as [12]:

$$a = \frac{-2u_O}{L} \left[1 - \frac{u_F}{u_O} \left(\frac{\rho_F}{\rho_O} \right)^{\frac{1}{2}} \right] \quad (1)$$

where ρ is the density and the subscripts F and O denote fuel and oxidizer (air), respectively. With this definition the effective fuel density changes slightly with water addition, but with the small molar mass difference between methane and water, this effect is very small. For various a and $R_{\text{H}_2\text{O}/\text{CH}_4}$ conditions the maximum flame temperature (T_{max}) is measured. Final results are obtained by averaging measurements of 4 to 6 tests at each condition. Experimental uncertainties (95% confidence) for u , T and $R_{\text{H}_2\text{O}/\text{CH}_4}$ were less than 5%. Direct measurements showed that the fuel nozzle exit temperature is closer to $T_F = 550 \pm 3$ K and the air nozzle exit temperature $T_O = 440 \pm 3$ K. Thus, computations were carried out for these conditions. Atmospheric pressure (NP) was maintained throughout for $a = 115\text{--}164 \text{ s}^{-1}$ ($u = 0.33\text{--}0.78 \text{ m/s}$) and $R_{\text{H}_2\text{O}/\text{CH}_4} = 0\text{--}1.4$.

Computational methods are similar to past work [13], except for the detailed reaction mechanism. The method will be described only briefly; see [13–15] for more details. Fig. 1b schematically shows a counterflow, axisymmetric nonpremixed flame stabilized near the stagnation plane of two opposing jet flows. Assuming that the radial velocity varies linearly in the radial direction, the two-dimensional flow analysis can be simplified and the fluid properties become functions of only the axial direction x . The resulting equations are the same as those in [13]: e.g., the equation of energy conservation,

$$\rho u \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left(\lambda \frac{dT}{dx} \right) + \frac{\rho}{c_p} \sum_{k=1}^K c_{p_k} Y_k V_k \frac{dT}{dx} + \frac{1}{c_p} \sum_{k=1}^K h_k \dot{w}_k - \frac{\dot{q}_r}{c_p} = 0 \quad (2)$$

The notation of the equation is: c_p as the specific heat at constant pressure; λ is the thermal conductivity; c_{pk} is the specific heat at constant pressure of species k , $k = 1, \dots, K$; Y_k is the mass fraction of species k ; V_k is the diffusion velocity; h_k is the specific enthalpy of species k ; $\dot{w}_k$ is the mass-rate of production of species k ; and $\dot{q}_r$ is the radiative heat loss rate. The boundary conditions for the fuel and oxidizer streams at the nozzles are those from the measurements, as mentioned earlier.

In order to obtain the radiative loss term in Eq. (2), radiative transport including both emission and absorption is computed using the statistical narrow-band model with an exponential-tailed inverse line strength distribution [16]. The radiative transfer equations are solved using the discrete ordinate method and S6 quadrature scheme with parameters taken from literature values [17] without modification.

The counterflow nonpremixed flames are simulated using a code revised from the program OPPDIF developed by Lutz et al. [18]. The governing equations coupled with the equations of the statistical narrow-band radiation model are solved with the finite difference method. The code allows for multi-component diffusion, thermal diffusion, variable thermochemical properties, and variable transport properties. The CHEMKIN package [19–21] is used as a preprocessor to find the thermochemical and transport properties for the code. All the calculations are carried out with the detailed $\text{CH}_4/\text{O}_2/\text{N}_2$ mechanism of Smith et al. [22], involving 53 species and 325 reversible reactions.

3. Results and discussion

3.1. Flame morphology

Fig. 2 shows photographic images of counterflow nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames with $R_{\text{H}_2\text{O}/\text{CH}_4} = 0$ (a), 0.3 (b) and 0.9 (c): the volumetric flow rate of CH_4 $\dot{V}_F = 2.4$ L/min and the volumetric flow rate of air $\dot{V}_O = 4.4$ L/min. They show the appearance of conventional counterflow nonpremixed flames. All the flames with and without water vapor addition are located on the fuel side of the symmetric plane between two nozzles. For no (Fig. 2a) and low (Fig. 2b) water-laden conditions, the flame consists of a blue zone and a yellow luminous zone at the flame wings (edges) which is separated from the blue zone by a thin dark zone. With water addition, however, the blue zone is extended, while the yellow luminous zone is reduced. The blue zone is observed on the air side of the flame, while the luminous zone is observed on the fuel side. In the blue zone the peak flame temperature is observed and thus primary combustion reactions occur. In the yellow zone, soot precursors may be formed; however, their concentration does not seem to be high enough for nucleation to occur because of the oxidative attack by OH radicals on them [23]. Measurable size soot particles do not seem to be formed since a darker luminous (e.g., orange) zone is not observed. The origin of the thin dark zone is not clear, though it may be generated due to the mixing of fuel and air with coflowing N_2 and thereby cooling and diluting effects. With more enhanced water addition (Fig. 2c), the yellow luminous zone disappears. This observation may support that OH radicals attack and oxidize soot precursors, e.g., acetylene (C_2H_2), in the yellow zone, since the increased amount of H_2O vapor can provide more OH to the heated pre-flame zone. However, it should be noted that a preliminary spectroscopic investigation of the luminous zone showing the presence of sodium (from water and/or impurities inside the burner and on the nozzle exit mesh) indicates that further

considerations are necessary to determine if this yellow luminous zone is observed just due to soot particles. A relationship between the added amount of H_2O vapor and the predicted concentration of C_2H_2 will be discussed in Section 3.3.

3.2. Extinction limits

Effects of water vapor addition on the flame temperature and extinction limits (in terms of $R_{\text{H}_2\text{O}/\text{CH}_4}$) of nonpremixed CH_4/air flames were experimentally and computationally examined to gain a better understanding of the impact that water addition has on the flame reaction zone and the involved thermal and chemical processes. Comparison of the predicted extinction limits with the results from burning methane hydrates may help understand how much water in methane hydrates evaporates and is involved to combustion.

The maximum flame temperature was experimentally determined to justify using the present computational results to analyze the detailed flame structure and determine the extinction limits through comparison with predicted temperature. In order to measure the maximum flame temperature a stabilized flame is obtained first by spark-igniting the $\text{H}_2\text{O}-\text{CH}_4$ -air mixture near a stagnation plane between fuel and air nozzles that is established by injecting H_2O -laden CH_4 and air to desired flow rates, and then coflowing N_2 is issued with the injection velocity u_c that is adjusted to be the same as u_F and u_o . With gradual water addition test conditions are changed. At each test condition the maximum flame temperature has been measured. Fig. 3 shows the measured and predicted $T_{\max}$ as a function of $R_{\text{H}_2\text{O}/\text{CH}_4}$ for nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames of $a = 115\text{--}164 \text{ s}^{-1}$ (increasing with increasing $R_{\text{H}_2\text{O}/\text{CH}_4}$; $\dot{V}_F = 3.0 \text{ L/min}$ and $\dot{V}_O = 6.0 \text{ L/min}$) at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$. The figure shows clearly that $T_{\max}$ monotonously decreases with increasing $R_{\text{H}_2\text{O}/\text{CH}_4}$ and a . This tendency is expected, of course, since the water acts as a fuel

diluent as well as a thermal sink. The precise conditions of the measurements and computations do not match because, as described earlier, the experimental coflow condition and nozzle temperatures are difficult to maintain constant. Nevertheless, predicted and measured tendencies of the maximum flame temperature exhibit encouraging agreement with quantitative discrepancies among the predictions and measurements within 5% and thus justify using the computational results to analyze the detailed flame structure and determine the extinction limits. Although it is small, the source of this discrepancy seems to be the convective and conductive heat losses that were not computationally considered, but the effects would be remarkable in the experiment. In fact, computations considering convective and conductive heat losses, which were preliminarily conducted by adding the convective and conductive heat loss term in Eq. (2) and introducing the concept of an effective heat-loss coefficient, indicated a good quantitative agreement with experiments in general. However, a qualitatively opposite tendency, i.e., an increase in flame temperature with increasing strain rate at the same level of water addition, was observed. This result was almost certainly due to the heat transfer, where with fixed heat transfer coefficient, the lower strain rate flames lose more heat to the burner. Meanwhile, the experimental heat transfer situation is more complex. Thus, it was very difficult to estimate the amount of conductive and convective heat losses since they are generally affected by the nozzle materials, the fluid composition, the flow properties such as velocity and viscosity, and temperature. These preliminary computations including the conductive and convective heat losses via a constant effective heat-loss coefficient indicated that these losses are obviously the source of the discrepancy between computation and experiment, but a precise modeling of the experimental heat transfer situation is beyond the scope of this study. Thus, only the radiation heat losses were considered in the present investigation.

Fig. 3 Measured and predicted maximum flame temperature as function of $R_{\text{H}_2\text{O}/\text{CH}_4}$ for nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames of $a = 115\text{--}164 \text{ s}^{-1}$ (increasing with increasing $R_{\text{H}_2\text{O}/\text{CH}_4}$; $\dot{V}_F = 3.0 \text{ L/min}$ and $\dot{V}_O = 6.0 \text{ L/min}$) at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$. Predictions based on kinetics of Smith et al. [22]. (single column fitting)

Effects of water vapor addition and strain rate on the temperature profile of nonpremixed CH_4/air flames are given in Fig. 4, which shows the distribution of temperature for pure CH_4/air ($R_{\text{H}_2\text{O}/\text{CH}_4} = 0$) and water-added CH_4/air ($R_{\text{H}_2\text{O}/\text{CH}_4} = 0.5\text{--}1.4$) flames of $a = 115\text{--}164 \text{ s}^{-1}$ (increasing with increasing $R_{\text{H}_2\text{O}/\text{CH}_4}$; $\dot{V}_F = 3.0 \text{ L/min}$ and $\dot{V}_O = 6.0 \text{ L/min}$) at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$. The figure also exhibits the tendency observed in Fig. 3 that T_{max} , i.e., peak temperature, decreases with increasing $R_{\text{H}_2\text{O}/\text{CH}_4}$ and a due to water as a fuel diluent and a thermal sink. With water addition and increasing a , the flame thickness decreases and flame moves towards the oxidizer(air) side due to the enhanced exit velocities at the nozzles and the increased momentum of the water-laden jet.

Fig. 4 Predicted effects of H_2O addition and a on temperature profiles of nonpremixed CH_4/air flames of $a = 115\text{--}164 \text{ s}^{-1}$ (increasing with increasing $R_{\text{H}_2\text{O}/\text{CH}_4}$; $\dot{V}_F = 3.0 \text{ L/min}$ and $\dot{V}_O = 6.0 \text{ L/min}$) at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$. Predictions based on kinetics of Smith et al. [22]. (single column fitting)

Fig. 5 shows the computed T_{max} as a function of $R_{\text{H}_2\text{O}/\text{CH}_4}$ for nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames of $a = 50, 100, 300$ and 500 s^{-1} at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$, including the extinction limits. The figure shows an approximately linear decrease in flame temperature with water addition except near extinction, which is expected since the water acts as a fuel diluent. A decrease in flame temperature with increasing strain rate at the same level of water addition is also observed due to the cooling effects of enhanced strain rate. However, the most important observation is that these flames can carry very high levels of water (up to and beyond water to methane molar ratios of 4.0), indicating the range comparable to the results found in the combustion of methane hydrates: 0.1–3.7 [4]. A reduction of the extinction limits, i.e., a reduction in the amount of water that can be carried by the fuel without extinguishing the flame, with increasing strain rate is observed, which implies that more water vapor can be added at low strain rates while less water vapor can be added at high strain rates. Thus, the maximum flame

temperature at the extinction limits increases with increasing strain rates because there is less water to act as a thermal sink.

Fig. 5 Predicted $T_{\max}$ as function of $R_{\text{H}_2\text{O}/\text{CH}_4}$ for nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames of $a = 50\text{--}500$ s^{-1} at NP, $T_F = 550$ K and $T_O = 440$ K. Based on kinetics of Smith et al. [22]. (single column fitting)

Fig. 6 shows the predicted $T_{\max}$ as a function of a for nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames of $R_{\text{H}_2\text{O}/\text{CH}_4} = 0\text{--}2.5$ at NP, $T_F = 550$ K and $T_O = 440$ K. The figure also exhibits an approximately liner decrease in flame temperature with increasing a except near extinction. Of course, this tendency is observed due to the cooling effects of enhanced a . A decrease in flame temperature with water addition at the same level of a is again observed since the water acts as a fuel diluent as well as a thermal sink. As aforementioned, the most important observation in Figs. 5 and 6 is that the range of water to methane molar ratio is comparable to the results found in the combustion of methane hydrates. Thus, we expect that the present results using counterflow nonpremixed water-laden CH_4/air flames can provide more insight into the thermal and chemical processes which may occur in the combustion of methane hydrates.

Fig. 6 Predicted $T_{\max}$ as function of a for nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames of $R_{\text{H}_2\text{O}/\text{CH}_4} = 0\text{--}2.5$ at NP, $T_F = 550$ K and $T_O = 440$ K. Based on kinetics of Smith et al. [22]. (single column fitting)

3.3. Flame structure

In order to gain a better understanding of the thermal and chemical processes that may be involved when large amounts of water is added to CH_4/air flames, we use the computations to examine the detailed flame structure. As discussed in Section 3.2, reasonable agreement between predicted and measured $T_{\max}$ as a function of $R_{\text{H}_2\text{O}/\text{CH}_4}$ for the present nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames justifies using the present computational results to analyze the detailed flame structure.

Effects of water vapor addition on the structure of nonpremixed CH_4/air flames at NP are given in Fig. 7, which shows the distribution of temperature and species mole fractions for pure CH_4/air ($R_{\text{H}_2\text{O}/\text{CH}_4} = 0$) and H_2O -added CH_4/air ($R_{\text{H}_2\text{O}/\text{CH}_4} = 2.0$) flames of $a = 50$ s^{-1} at NP, $T_F = 550$ K and $T_O = 440$ K. It should be noted that for these computations fuel is injected at the same velocity as the air ($u_F = u_O$). Both the flames are located near the symmetric plane between the nozzles. Also, the results indicate that the flames are located on the air (oxygen) side of the stagnation plane more. This is a result of the stoichiometry for the reaction between the CH_4 (and

H₂O vapor) and air [13]. It should be noted that the stagnation plane is not symmetric for the nozzles and moves towards the fuel side since the H₂O-CH₄ mixture lighter than air is injected at the same velocity as the air. With H₂O addition, $T_{\max}$ drops around 260 K and the flame thickness somewhat decreases. The decreased temperature causes radical concentrations, particularly the light radical H, in the reaction zone of the H₂O-added flame to decrease compared with the pure CH₄ flame, decreasing the reactivity for the H₂O-added flame.

Fig. 7 Predicted effects of H₂O addition on structure of low-stretched nonpremixed CH₄/air flame at NP, $T_F = 550$ K and $T_O = 440$ K ($a = 50$ s⁻¹). Based on kinetics of Smith et al. [22]. (single column fitting)

Fig. 8 Predicted effects of H₂O addition on structure of high-stretched nonpremixed CH₄/air flame at NP, $T_F = 550$ K and $T_O = 440$ K ($a = 300$ s⁻¹). Based on kinetics of Smith et al. [22]. (single column fitting)

Fig. 8 shows structure for high-stretched pure CH₄/air ($R_{H_2O/CH_4} = 0$) and H₂O-added CH₄/air ($R_{H_2O/CH_4} = 2.0$) flames of $a = 300$ s⁻¹ at NP, $T_F = 550$ K and $T_O = 440$ K. Similar to the relatively low-stretched flames in Fig. 7, T_{max} drops around 370 K and the flame thickness somewhat decreases with H₂O addition. Again, the decreased temperature causes H concentration to decrease. Both the flames with and without H₂O addition are still located on the air side of the stagnation plane due to the stoichiometry for the reaction between the H₂O-CH₄ mixture and air. With increasing a , however, the flame position becomes closer to the stagnation plane and the flame thickness decreases due to the enhanced exit velocities at the nozzles, compared with the low-stretched flames in Fig. 7. It is also of interest to note that the peak value for H increases with increasing a . Such an increase would seem to imply a corresponding

increase in the reaction intensity which does not appear to be physical, especially in view of the fact that $T_{\max}$ decreases with increasing a . This result is caused by the fact that H produced on the fuel side cannot be completely consumed on the oxygen side because of the strong temperature dependence of the $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ reaction and the reduced flame temperature at high a , and hence the unreacted H is accumulated [13].

Effects of H_2O addition can be categorized into thermal and chemical effects. The thermal effects are due to the relative reduction of CH_4 concentration with H_2O (as an inert diluent) addition, while the chemical effects are due to the replacement of reactive CH_4 by nonfuel H_2O . In the present investigation, an imaginary inert gas X, which has the same thermodynamic and transport properties as those of H_2O but does not participate in reaction, is introduced to extract the pure thermal effects of H_2O addition. Fig. 9 shows the thermal and chemical effects of water vapor addition on the structure of a nonpremixed CH_4/air flame of $a = 50 \text{ s}^{-1}$ at NP, $T_{\text{F}} = 550 \text{ K}$ and $T_{\text{O}} = 440 \text{ K}$. Due to relative reduction of supplied CH_4 with H_2O addition, the flame temperature decreases for both $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ and $\text{X}/\text{CH}_4/\text{air}$ flames, compared with pure CH_4/air flames. However, both the $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ and $\text{X}/\text{CH}_4/\text{air}$ flames show almost the same structure except for some minor species, though the distribution of H_2O mole fraction is different because X is introduced. A similar tendency was observed for most $R_{\text{H}_2\text{O}/\text{CH}_4}$, though a small (but still ignorable) change is observed for relatively high a near the extinction limit. This implies that the chemical effects of H_2O addition are negligible and thus the thermal process (i.e., cooling and diluting effects) is mainly involved when H_2O is added to CH_4/air flames.

Fig. 9 Predicted thermal and chemical effects of H₂O addition on structure of nonpremixed CH₄/air flame of $a = 50 \text{ s}^{-1}$ at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$. Based on kinetics of Smith et al. [22]. (single column fitting)

In Section 3.1 (Fig. 2) we have observed that with enhanced water addition the yellow luminous zone in the nonpremixed H₂O/CH₄/air flames disappears. This observation may support that OH radicals attack and oxidize soot precursors, e.g., C₂H₂, in the yellow zone, since the increased amount of H₂O vapor can provide more OH to the heated pre-flame zone [23]. Thus, effects of H₂O addition on C₂H₂ concentration of nonpremixed CH₄/air flame were computationally considered. A relationship between the added amount of H₂O vapor and the predicted concentration of C₂H₂ is briefly examined since any soot formation mechanism has not been considered in the present reaction mechanism, which is beyond the scope of this study. Fig. 10 shows the effects of H₂O addition on C₂H₂ mole fraction of low-stretched nonpremixed CH₄/air flame of $a = 50 \text{ s}^{-1}$ at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$. As expected, with enhanced water

addition the mole fraction of C_2H_2 decreases. Also, as shown in Fig. 7, with water addition more OH radicals are found in the fuel side (in terms of the location where the peak T is observed), though with increasing R_{H_2O/CH_4} the peak concentration of OH in the flame decreases due to the reduced burning intensity. This tendency is confirmed from Fig. 11, which shows the effects of water addition on OH production rate of the same flames as shown in Fig. 10. These observations support that with enhanced water addition the yellow luminous zone in the nonpremixed H_2O/CH_4 /air flames disappears since more OH radicals in the fuel side due to the increased amount of H_2O vapor oxidize soot precursors such as C_2H_2 in the yellow zone. Meanwhile, earlier experimental studies of nonpremixed flames with fuel dilution to control flame temperature showed less sooting tendency at lower flame temperature because soot forms on the fuel-rich side of stoichiometry where no O_2 is present and hence, no soot oxidation process occurs [24]. This can also partially explain the present less sooting tendency with increasing R_{H_2O/CH_4} because flame temperature decreases with increasing R_{H_2O/CH_4} , though the effects of the enhanced OH radicals with increasing R_{H_2O/CH_4} seem to be more dominant. Figs. 12 and 12 that show the effects of H_2O addition on C_2H_2 mole fraction and OH production rate of high-stretched nonpremixed CH_4 /air flame of $a = 300 \text{ s}^{-1}$ at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$ also indicate the same tendencies as those in Figs. 10 and 11.

Fig. 10 Predicted effects of H₂O addition on C₂H₂ mole fraction of low-stretched nonpremixed CH₄/air flame at NP, $T_F = 550$ K and $T_O = 440$ K ($a = 50$ s⁻¹). Based on kinetics of Smith et al. [22]. (single column fitting)

Fig. 11 Predicted effects of H₂O addition on OH production rate of low-stretched nonpremixed CH₄/air flame at NP, $T_F = 550$ K and $T_O = 440$ K ($a = 50$ s⁻¹). Based on kinetics of Smith et al. [22]. (single column fitting)

Fig. 12 Predicted effects of H₂O addition on C₂H₂ mole fraction of high-stretched nonpremixed CH₄/air flame at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$ ($a = 300 \text{ s}^{-1}$). Based on kinetics of Smith et al. [22]. (single column fitting)

Fig. 13 Predicted effects of H₂O addition on OH production rate of high-stretched nonpremixed CH₄/air flame at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$ ($a = 300 \text{ s}^{-1}$). Based on kinetics of Smith et al. [22]. (single column fitting)

As a final item of investigation, the effects of water vapor addition on flame position were examined. There are various ways to determine the flame position x_F . In the present study, the locations of $T_{\max}$, the maximum heat-release rate and the maximum OH concentration are

computationally predicted. As aforementioned, it was experimentally observed that all the flames with and without water vapor addition are located on the fuel side of the symmetric plane between two nozzles (Fig. 2). Also, the computational results under u_F and u_O condition indicated that the flames are located on the air (oxygen) side of the stagnation plane more as a result of the stoichiometry for the reaction between the CH_4 (and H_2O vapor) and air [13]. The stagnation plane is not symmetric for the nozzles and moves towards the fuel side since the H_2O - CH_4 mixture lighter than air is injected at the same velocity as the air; however, with increasing a the flame position becomes closer to the stagnation plane and the flame thickness decreases due to the enhanced exit velocities at the nozzles, compared with the low-stretched flames. For a fixed a , it was observed that $T_{\max}$ -based x_F decreases with increasing $R_{\text{H}_2\text{O}/\text{CH}_4}$, i.e., flames shift towards the fuel side nozzle with water addition (Figs. 7 and 8), though it is unremarkable for high-stretched flames. This implies that the effects of increased momentum of the water-laden jet on x_F are less dominant compared with the effects of the stoichiometry for the reaction between the water-laden CH_4 and air that are expected to shift x_F towards the fuel side nozzle due to the relatively reduced mole fraction of CH_4 in the fuel stream with water addition. Fig. 14 shows the predicted x_F that are based on the locations of the maximum heat-release rate and the maximum OH concentration as a function of $R_{\text{H}_2\text{O}/\text{CH}_4}$ for nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames of $a = 50$ and 300 s^{-1} at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$, clearly indicating this tendency. However, unremarkable changes of x_F as a function of $R_{\text{H}_2\text{O}/\text{CH}_4}$ indicate the net effect of water addition on the flame position is not significant.

Fig. 14 Predicted flame position as function of $R_{\text{H}_2\text{O}/\text{CH}_4}$ for nonpremixed $\text{H}_2\text{O}/\text{CH}_4/\text{air}$ flames of $a = 50$ and 300 s^{-1} at NP, $T_F = 550 \text{ K}$ and $T_O = 440 \text{ K}$. Based on kinetics of Smith et al. [22]. (single column fitting)

4. Conclusions

The extinction and structure of counterflow nonpremixed water-vapor-laden methane/air flames were experimentally and computationally studied to better understand combustion processes when a large amount of water is naturally incorporated into the fuel stream. Predicted and measured tendencies of the maximum flame temperature exhibit encouraging agreement and thus justify using the computational results to analyze the detailed flame structure and determine the extinction limits. For a fixed strain rate, the maximum flame temperature decreases with water addition due to the cooling and dilution effects but flames can sustain water beyond molar ratios of 4. Also, the extinction limits (in terms of the water to methane molar ratio) are reduced with increasing strain rates, implying that more (less) water vapor can be added at low (high) strain rates. The present predicted maximum amount of water that flames can sustain is comparable to the maximum amount of water vapor observed in the combustion of methane hydrates, indicating that the present flame configuration provides some insight into the thermal and chemical

processes that occur in these highly humidified flames. Predictions assuming added water vapor inert indicate that the chemical effects of water addition on flame structure are negligible and thus the thermal process (i.e., cooling and diluting effects) is mainly involved when water is added to methane/air flames. Also, it is observed that flames shift towards the fuel side nozzle with water addition though it is not significant, indicating that the effects of increased momentum of the water-laden jet on the flame position are less dominant compared with the effects of the stoichiometry for the reaction between the water-laden methane and air. With enhanced water addition the yellow luminous zone in the nonpremixed water-vapor-laden methane/air flames disappears since more hydroxyl radicals in the fuel side due to the increased amount of water vapor oxidize soot precursors such as acetylene in the yellow zone.

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