

Methane-Hydrogen Diffusion Flames: Rate-Ratio Asymptotics

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Abstract. The influence of hydrogen in the methane diffusion flames is analysed. The flame structure is described asymptotically by considering a chemical kinetic mechanism made up of four global steps. The first step simulates the radicals, mainly the H-radical, attacking the fuel to form H₂ and CO. The second step is the water-gas shift reaction which was assumed in equilibrium except in a thin layer adjacent to the layer where the fuel is attacked. The third step corresponds to the recombination reaction of the H-radical. The fourth step represents the oxidation of the H₂ and formation of the H-radical. The results pointed to a maximum burning efficiency of the hydrogen enriched methane diffusion flame for mixtures diluted with nitrogen.

keywords: bicomponent diffusion flame, rate-ratio asymptotics, hydrogen-methane flame structure

1. Introduction

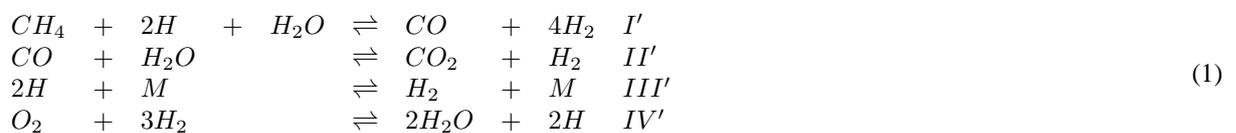
The influence of the hydrogen on burning of fuel mixtures has been studied for a long time (Scholte and Vaags, 1959b; Scholte and Vaags, 1959c; Scholte and Vaags, 1959a), but recently received more attention due to the rigorous restrictions on the emissions into the ambient (Cheng and Oppenheim, 1984; Milton and Keck, 1984; Sher and Refael, 1988; Refael and Sher, 1989; Bell and Gupta, 1997; Jackson et al., 2003). However little attention has been spent on the burning of those mixtures in diffusion flames. This work, that is an extension of previous works (Hamins and Seshadri, 1984a; Hamins and Seshadri, 1984b; Fachini, 2004b; Fachini, 2004c; Fachini, 2004a), addresses asymptotically the problem of the burning of hydrocarbon and hydrogen mixture in diffusion flames

The ratio-rate asymptotics will be used in this work to analyse the hydrocarbon-hydrogen diffusion flames. This asymptotics deals with a reduced four-steps chemical-kinetic mechanism that describes the generation and consumption of seven species. These four reactions proceed inside a thin zone, which is composed by three layers. In each layer one or two reactions take place, a feature that simplifies the analysis inside the layer. Detail of this asymptotic method can be found elsewhere (Seshadri and Williams, 1994; Seshadri, 1996).

The presence of hydrogen, that is one of the intermediate species generated by the fuel oxidation, in the fuel mixture changes the characteristic of the layer where H₂ is consumed. As a results, the flame extinction conditions are modified. The flame becomes more stable because there is an increase in the H₂ consumption and a decrease in the oxygen leakage.

2. Reduced Mechanism

The oxidation of Methane is described by the following four-step chemical-kinetic mechanism



Global reaction I' is chain-breaking and represents the reactions between the fuel and the radicals which form CO and H₂. Global reaction II' represents the oxidation of CO to form the final product, CO₂. Global reaction III' represents the three-body recombination steps and is also responsible for a major fraction of heat released in the flame. Global reaction IV' represents the reaction of O₂ with radicals and the formation of H₂O; it comprises the chain-branching steps.

The global reactions I' to IV' were determined from the simplified chemical-kinetic mechanism for methane shown in Seshadri and Williams, 1994. In addition, the principal reaction rates for the these global reactions are given in terms of the elementary reactions (Table 1) according to

$$\begin{array}{lcl}
 w'_{I'} & = & k_{11f} C_F C_H \\
 w'_{II'} & = & k_{9f} C_{CO} C_{OH} - k_{9b} C_{CO_2} C_H \\
 w'_{III'} & = & k_5 C_H C_{O_2} C_M \\
 w'_{IV'} & = & k_{1f} C_{O_2} C_H - k_{1b} C_{OH} C_O
 \end{array} \quad (2)$$

in which C_i is the molar concentration of species i . The reaction rate coefficients k_i of the elementary reactions are calculated using the expression $k_i = B_i T^{\alpha_i} \exp[-E_i/(RT)]$, in which T denotes the temperature, \bar{R} is the universal gas constant. The chemical kinetic parameters B_i , α_i and E_i are the frequency factor, the temperature exponent, and the activation energy of the elementary reaction i . The concentration of the third body C_M , appearing in reaction III' is expressed by the relation

$$C_M = \frac{p\bar{W}}{RT} \sum_{i=1}^n \frac{\eta_i Y_i}{W_i} \quad (3)$$

in which p denotes the pressure, \bar{W} is the average molecular weight and Y_i , W_i and η_i represent the mass fraction, the molecular weight and the chaperon efficiency of species i .

Table 1: The main reactions of the chemical kinetic mechanism for methane oxidation^a.

Number	Reaction	B_i	α_i	E_i
1f	$O_2 + H \rightarrow OH + O$	2.000×10^{14}	0.00	70.338
1b	$OH + O \rightarrow O_2 + H$	1.575×10^{13}	0.00	2.888
2f	$H_2 + O \rightarrow OH + H$	1.800×10^{10}	1.00	36.952
2b	$OH + H \rightarrow H_2 + O$	8.000×10^9	1.00	28.302
3f	$H_2 + OH \rightarrow H_2O + H$	1.170×10^9	1.30	15.181
3b	$H_2O + H \rightarrow H_2 + OH$	5.090×10^9	1.30	77.824
4f	$OH + OH \rightarrow H_2O + O$	6.000×10^8	1.30	0
4b	$H_2O + O \rightarrow OH + OH$	5.900×10^9	1.30	71.297
5	$H + O_2 + M \rightarrow HO_2 + M$	2.300×10^{18}	-0.80	0
9f	$CO + OH \rightarrow CO_2 + H$	4.400×10^6	1.50	-3.100
9b	$CO_2 + H \rightarrow CO + OH$	4.960×10^8	1.50	89.710
11f	$CH_4 + H \rightarrow H_2 + CH_3$	2.200×10^4	3.00	36.600
11b	$H_2 + CH_3 \rightarrow CH_4 + H$	8.830×10^2	3.00	33.530

^a Seshadri and Peters, 1988.

In order to simplify the analysis, it is considered that the radicals O and OH are in steady-state. In addition, by considering the reactions 2 and 3 in partial equilibrium, the radicals O and OH can be expressed as following

$$C_{OH} = \frac{C_{H_2O} C_H}{K_3 C_{H_2}}, \quad C_O = \frac{C_{H_2O} C_H^2}{K_2 K_3 C_{H_2}^2} \quad (4)$$

By using Eq. (4) to eliminate C_{OH} and C_O from Eq. (2), the reaction rates $w_{i'}$ can be expressed as following

$$\begin{aligned} w'_{I'} &= k_{11f} C_F C_H \\ w'_{II'} &= k_{9f} \frac{C_{H_2O} C_H}{K_3 C_{H_2}} \left(C_{CO} - \frac{K_3 C_{CO_2}}{K_9 C_{H_2O}} C_{H_2} \right) \\ w'_{III'} &= k_5 C_H C_{O_2} C_M \\ w'_{IV'} &= k_{1f} C_{O_2} C_H \left(1 - \frac{C_{H_2O}^2 C_H^2}{K_1 K_2 K_3^2 C_{H_2}^3 C_{O_2}} \right) \end{aligned} \quad (5)$$

3. Asymptotic Analysis

The asymptotic procedure uses the discrepancies in the length and time scales of the processes outside and inside of the flame to simplify and, then, analyse the flame structure problem. By taking processes with the same either time scale or length scale, the asymptotic procedure isolates the most important processes in each different zones. Solved the particular problem of each zone and matched solution with the other solutions of the other zones, the whole problem is determined.

Asymptotically, the flow field can be divided in two zones. One of them is characterized by the inert state of the reactions, named as outer zone, whose characteristic length is imposed by the boundary conditions. The other zone, named inner zone, is characterized by the reactiviness of the flow. The inner zone can be considered as a infinitely thin region when observed by the characteristic outer zone length. As a result, the heat and mass fluxes (the derivatives of the temperature and reactants mass fractions) present a jump across the inner zone.

The inner zone is localized in the flow field around the flame. By observing the reaction rates Eq. (5) inside the flame and imposing that the reaction II is not in partial equilibrium except in a thin layer, it is possible to suggest that the inner

zone can be divided in three layers. In the oxidation layer the CO and H_2 oxidation occurs and this layer is the thickest layer because the reaction rate is the slowest. In the fuel consumption layer the fuel is attacked by the H-radical and due to characteristic of this reaction I , the inner layer is the thinnest layer. Between these two layer is the non-equilibrium layer, where reaction II , the water shift reaction, controls the consumption of CO and formation of H_2 .

3.1. Outer Zone

Diffusion flames are established inside mixing layers formed by a fuel jet discharged in an oxidant ambient, vaporized fuels in oxidant ambient and two opposing impinging jets. The combustion conditions, oxygen flux and fuels fluxes to the flame, determine the position of the flame inside the mixing layer. As a result of the flame position, the heat transfer from the flame to the gases in the oxygen and fuels sides is imposed. Furthermore, the mass transfer and the reaction rate set the internal structure and the extinction condition of the flame. When the flame is close to one border of the mixing layer, practically all heat transfer occurs to that side and the other side of the flame can be assumed in equilibrium condition. In some configurations, the position of the flame inside the mixing layer dictates the strain rate on the flame. Therefore, the position of the flame inside the mixing dictates the extinction condition and flame structure.

The analysis of the flame structure does not depend on the geometrical configuration of the flow field. Only the flow field properties at the flame have to be specified in order to describe asymptotically the flame structure.

The nondimensional properties of the flow field at the flame, needed to perform the flame structure analysis, are:

$$\begin{aligned} \text{At } z = z_f, \quad \theta = \theta_f, \quad d_{\theta}^- = \left. \frac{d\theta}{dz} \right|_{z=z_f^-}, \quad d_{\theta}^+ = - \left. \frac{d\theta}{dz} \right|_{z=z_f^+}, \\ d_{O_2} = - \left. \frac{dX_{O_2}}{dz} \right|_{z=z_f^-}, \quad d_F = \left. \frac{dX_{CH_4}}{dz} \right|_{z=z_f^+}, \quad d_{H_2} = \left. \frac{dX_{H_2}}{dz} \right|_{z=z_f^+}. \end{aligned} \quad (6)$$

In the equations above, z is the nondimensional flame position ($z = z'/L$), where z' is a coordinate perpendicular to the flame and L is a characteristic length of the outer zone, $\theta = T/T_2$ is nondimensional flame temperature and d_i are the heat flux from the flame and the oxygen and hydrogen and methane mass fluxes to the flame ($X_i \equiv Y_i W_{N_2}/W_i$), where Y_i is the mass fraction of species i , and W_i is the molecular weight of species i , respectively. The subscript 2 means the property at the fuel stream boundary, and the subscript 1 means the property in the oxidant stream boundary.

The multicomponent fuel diffusion flame analysis presented in this work will be proceeded by having no restriction neither on the Lewis number nor on the heat transfer from the flame.

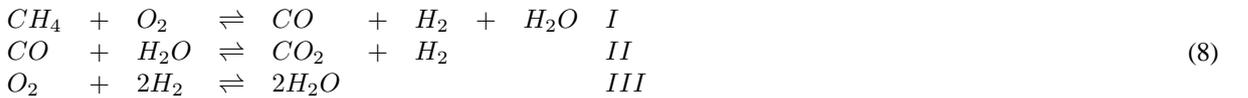
4. Inner Zone

It is presumed, analogously to previous analyses (Seshadri and Peters, 1988; Card and Williams, 1992a; Card and Williams, 1992b; Fachini and Seshadri, 2003) that the H-radical is in steady-state. Under this condition, the H-radical concentration can be calculated by the equation $w_I + w_{III} - w_{IV} = 0$, that leads to

$$X_H = \frac{K_1^{1/2} K_2^{1/2} K_3 X_{H_2}^{3/2} X_{O_2}^{1/2}}{X_{H_2O}} \left(1 - \frac{k_{11f} X_{CH_4}}{2k_{1f} X_{O_2}} - \frac{k_{5f} C_M}{k_{1f}} \right)^{1/2} \quad (7)$$

where $C_i = X_i(\rho/W_{N_2})$ ($X_i \equiv Y_i W_{N_2}/W_i$).

By making use of the steady-state condition for the H-radical, the chemical-kinetic mechanism has three global reactions as follows:



Based on the outer characteristic time (L^2/D_{θ}), the nondimensional rates for these global reactions are

$$\begin{aligned} w_I &= Ak_{11f} X_F X_H \\ w_{II} &= Ak_{9f} \frac{X_{H_2O} X_H}{K_3 X_{H_2}} \left(\frac{X_{CO}}{Le_{CO}} - \beta \frac{X_{H_2}}{Le_{H_2}} \right) \\ w_{III} &= Ak_5 C_M X_H X_{O_2} \end{aligned} \quad (9)$$

where $\beta \equiv (L_{H_2} K_3 X_{CO_2}) / (L_{CO} K_9 X_{H_2O})$, $A = (L^2/D_{\theta}) \cdot (\rho^2/W_{N_2})$, $D_{\theta} \equiv \lambda / (\rho c_p)$ is the thermal diffusivity (ρ is the density, c_p is the specific heat at constant pressure and λ is the thermal conductivity).

By writing the conservation equations in terms of the mixture fraction (Peters, 1984) or by taking the high order of magnitude processes around the flame, the following system of diffusive-reactive equations is found

$$\frac{d}{dx} \left(\frac{\rho D_{CH_4}}{\rho_0 D_{CH_4,2}} \frac{d X_{CH_4}}{dx} \frac{1}{L_{CH_4}} \right) = w_I \quad (10)$$

$$\frac{d}{dx} \left(\frac{\rho D_{O_2}}{\rho_0 D_{O_2,2}} \frac{d X_{O_2}}{dx Le_{O_2}} \right) = w_I + w_{III} \quad (11)$$

$$\frac{d}{dx} \left(\frac{\rho D_{CO}}{\rho_0 D_{CO,2}} \frac{d X_{CO}}{dx Le_{CO}} \right) = -w_I + w_{II} \quad (12)$$

$$\frac{d}{dx} \left(\frac{\rho D_{H_2}}{\rho_0 D_{H_2,2}} \frac{d X_{H_2}}{dx Le_{H_2}} \right) = -w_I - w_{II} + 2w_{III} \quad (13)$$

$$\frac{d}{dx} \left(\frac{\rho D_{H_2O}}{\rho_0 D_{H_2O,2}} \frac{d X_{H_2O}}{dx Le_{H_2O}} \right) = -w_I + w_{II} - 2w_{III} \quad (14)$$

$$\frac{d}{dx} \left(\frac{\rho D_{CO_2}}{\rho_0 D_{CO_2,2}} \frac{d X_{CO_2}}{dx Le_{CO_2}} \right) = -w_{II} \quad (15)$$

$$\frac{d}{dx} \left(\frac{\lambda}{\lambda_2} \frac{d \theta}{dx q} \right) = -q_I w_I - q_{II} w_{II} - q_{III} w_{III} \quad (16)$$

where D_i means the diffusion coefficient of species i , q is the heat release in the overall reaction $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ and q_i represents the ratio of the heat release by reaction i to the overall heat release.

The transport coefficients are represented only as a function of temperature according to $(\rho D_i)/(\rho D_{i,1}) = \lambda/\lambda_2 = \theta^m$. Since Eqs. (10) to (15) are valid around the flame, it is a good approximation to have $(\rho D_i)/(\rho D_{i,2}) = \lambda/\lambda_2 = \theta_f^m$.

Based on the previous analyses (Seshadri and Peters, 1988), to describe appropriately the three layers that form the flame, the expansion of the dependent and independent variables has to follow as

$$\begin{aligned} X_F/Le_F &= \varepsilon A_F^{(1)} x_F^{(1)} + \nu A_F^{(2)} x_F^{(2)} + \delta A_F^{(3)} x_F^{(3)} + o(\delta) \\ X_{O_2}/Le_{O_2} &= \varepsilon A_{O_2}^{(1)} x_{O_2}^{(1)} + \nu A_{O_2}^{(2)} x_{O_2}^{(2)} + \delta A_{O_2}^{(3)} x_{O_2}^{(3)} + o(\delta) \\ X_{CO}/Le_{CO} &= \varepsilon A_{CO}^{(1)} x_{CO}^{(1)} + \nu A_{CO}^{(2)} x_{CO}^{(2)} + \delta A_{CO}^{(3)} x_{CO}^{(3)} + o(\delta) \\ X_{H_2}/Le_{H_2} &= \varepsilon A_{H_2}^{(1)} x_{H_2}^{(1)} + \nu A_{H_2}^{(2)} x_{H_2}^{(2)} + \delta A_{H_2}^{(3)} x_{H_2}^{(3)} + o(\delta) \\ X_{H_2O}/Le_{H_2O} &= \varepsilon A_{H_2O}^{(1)} x_{H_2O}^{(1)} + \nu A_{H_2O}^{(2)} x_{H_2O}^{(2)} + \delta A_{H_2O}^{(3)} x_{H_2O}^{(3)} + o(\delta) \\ X_{CO_2}/Le_{CO_2} &= \varepsilon A_{CO_2}^{(1)} x_{CO_2}^{(1)} + \nu A_{CO_2}^{(2)} x_{CO_2}^{(2)} + \delta A_{CO_2}^{(3)} x_{CO_2}^{(3)} + o(\delta) \\ \theta_f/q - \theta/q &= \varepsilon A_\theta^{(1)} x_\theta^{(1)} + \nu A_\theta^{(2)} x_\theta^{(2)} + \delta A_\theta^{(3)} x_\theta^{(3)} + o(\delta) \\ z - z_f &= \varepsilon A_z^{(1)} \eta + \nu A_z^{(2)} \zeta + \delta A_z^{(3)} \xi + o(\delta) \end{aligned} \quad (17)$$

A simple asymptotic model based on the reaction rate ratios assumes that the flame is composed by three layers. The thickest layer is where the oxidation of CO and H_2 occurs, thereby named oxidation layer. In this layer it is considered that reactions I and II do not affect significantly the concentrations of CO and H_2 , except in a very thin layer, placed at $z = z_0$, as seen in Fig. 1b. Figure 1c shows schematically details of that layer where the reaction II is in non-equilibrium, named as non-equilibrium layer. Compared to the characteristic length of the oxidation layer ε , the non-equilibrium layer is a infinitely thin zone. Consequently, the fluxes of the species through it are discontinuous. The jump conditions on the fluxes are used to make the transition of the solution from $z = z_0^-$ to $z = z_0^+$, but they are also employed as boundary conditions for the problem in the non-equilibrium layer.

In the same way these two layers relate to themselves, the non-equilibrium layer relates to a very thin layer where the fuel is consumed, named fuel consumption layer. Figure 1d depicts schematically the details of this layer. In the characteristic length of the non-equilibrium layer ν , the consumption layer is infinitely thin, thus through it ($z = z_0$) the fluxes are discontinuous. Only the reaction I is important inside the fuel consumption layer. The jump condition through the thin consumption layer, placed at $z = z_0$, is used in the solution of the non-equilibrium layer and at same time as boundary conditions for the problem of the fuel consumption layer.

Once all jump conditions are satisfied by the solution of the four layers (outer layer, oxidation layer, non-equilibrium layer and fuel consumption layer) the flame structure becomes specified and the extinction condition is determined.

Despite the jump conditions are representative only in the local variables of each layer, they will be presented in this section with the outer zone variables with the aim of initiating the presentation of the asymptotic procedure.

In the *oxidation layer*, the solution of the diffusive-reactive equations must be matched with the outer structure solutions, Eqs. (6). The jump condition caused by reaction I and II can be determined by imposing $w_{III} = 0$ in Eqs. (10) to (16) and combining them to find $d^2(\Delta_{st,1} X_F/L_F + X_{H_2} + X_{CO})/dz^2 = 0$. By imposing the equilibrium condition in the reaction II , that leads to ($X_{CO} = \beta X_{H_2}$), integrating once around $z = z_f$ and applying Eqs.(6), it is possible to find

$$\left(\frac{d X_{H_2}}{dz Le_{H_2}} \Big|_{z_{0+}} - \frac{d X_{H_2}}{dz Le_{H_2}} \Big|_{z_{0-}} \right) = \frac{1}{\beta} \left(\frac{d X_{CO}}{dz Le_{CO}} \Big|_{z_{0+}} - \frac{d X_{CO}}{dz Le_{CO}} \Big|_{z_{0-}} \right) = -\frac{\Delta_{st,1}}{1 + \beta} \frac{d_F}{L_F} \quad (18)$$

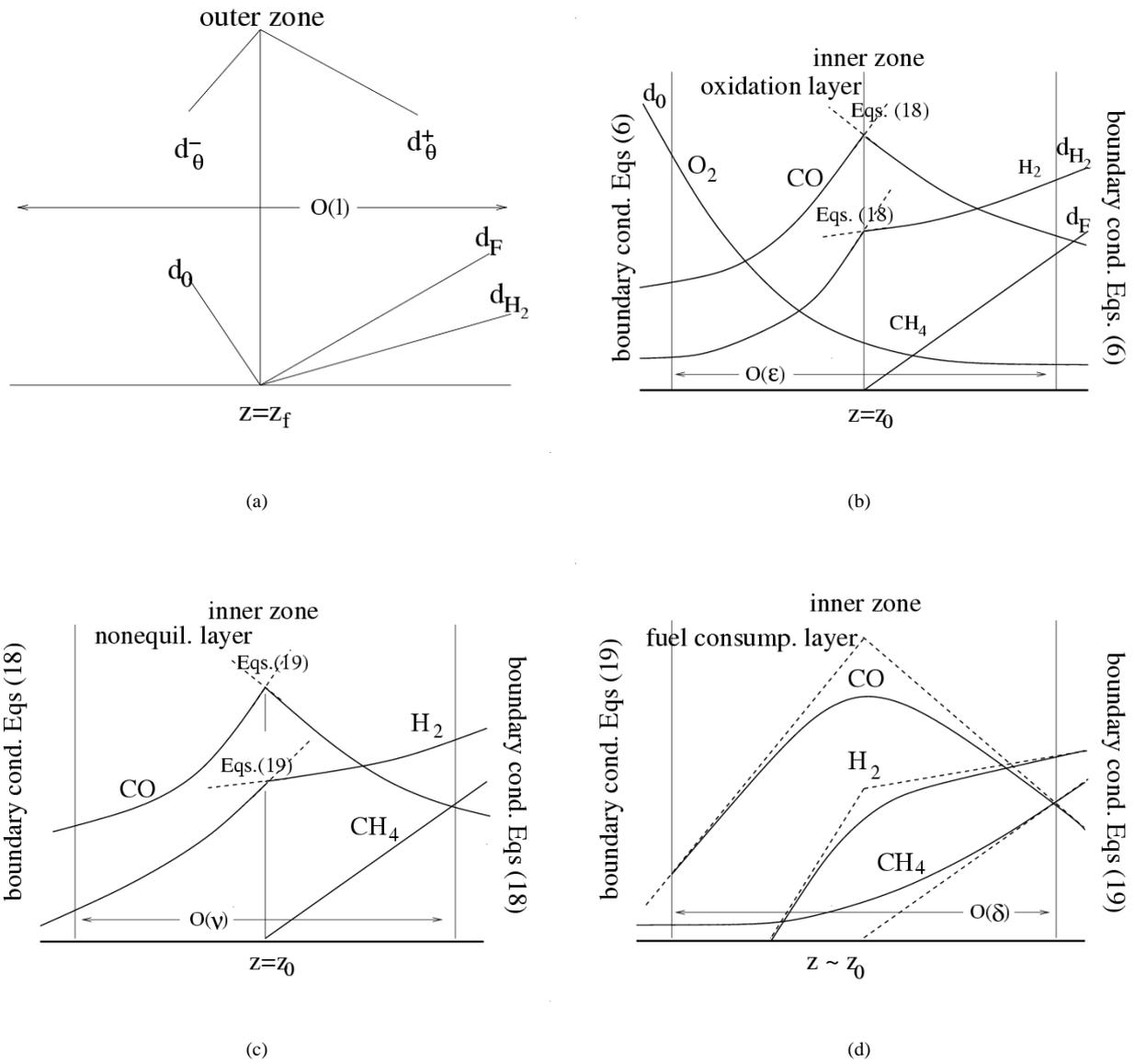


Figure 1: Schematic pictures for the boundary conditions in the outer and inner zones. The inner zone is composed by three layers. The oxidation layer (b) is where the CO and H_2 are consumed. The non-equilibrium layer (c) is where the reaction II is in non-equilibrium. The fuel layer (d) is where the fuel is consumed. The characteristic lengths of the outer zone, the oxidant layer, non-equilibrium layer and fuel layer are l , ϵ , η and δ . The condition $\delta \ll \eta \ll \epsilon \ll l$ is satisfied.

where $\Delta_{st,1}$ is the sum of the stoichiometric coefficients of the species CO and H_2 related to the reactions I in the flame zone where reactions I and II predominate over reaction III . The value of the $\Delta_{st,1}$ for methane is $\Delta_{st,1} = 2$.

In the *non-equilibrium layer*, where the reaction II is non-equilibrium, reactions I and II are important to determine the variation of the species concentrations. However, the reaction I has a significant contribution only in the fuel consumption layer. The jump in the first derivative of the species CO and H_2 can be specified considering $w_{II} = w_{III} = 0$ inside the fuel consumption layer. By combining Eqs. (10) to (16) with the condition $w_{II} = w_{III} = 0$ to find relations among the species, $d^2(\Delta_{st,2}X_F/L_F + X_{H_2}/L_{H_2})/dz^2 = d^2(\Delta_{st,3}X_{CO}/L_F + X_{H_2}/L_{H_2})/dz^2 = 0$, integrating once these equations and applying the conditions Eq.(6), the following jump conditions are found:

$$\frac{1}{\Delta_{st,2}} \left(\frac{d}{dz} \frac{X_{H_2}}{Le_{H_2}} \Big|_{z_{0+}} - \frac{d}{dz} \frac{X_{H_2}}{Le_{H_2}} \Big|_{z_{0-}} \right) = \frac{1}{\Delta_{st,3}} \left(\frac{d}{dz} \frac{X_{CO}}{Le_{CO}} \Big|_{z_{0+}} - \frac{d}{dz} \frac{X_{CO}}{Le_{CO}} \Big|_{z_{0-}} \right) = -\frac{d_F}{L_F} \quad (19)$$

where $\Delta_{st,2}$ and $\Delta_{st,3}$ are the stoichiometric coefficients for the species H_2 and CO , respectively, related to the reaction I . For the methane, $\Delta_{st,2} = 1$ and $\Delta_{st,3} = 1$

According to previous rate-ratio asymptotics (Seshadri, 1996), the position of the inner layer $z = z_0$ is in the fuel side of the stoichiometric position $z = z_f$, thus $z_0 > z_f$.

4.1. Oxidation Layer

As previously mentioned, reactions I and II are much faster than reaction III , thus the layers where they occur are infinitely thin. As a consequence, (Seshadri and Peters, 1988; Card and Williams, 1992a; Card and Williams, 1992b) the concentration of the main fuel, methane, is negligible compared with the concentration of the other species. Another consequence is the partial equilibrium of the reaction II in the oxidation layer, that leads to

$$X_{CO}/Le_{CO} = \beta X_{H_2}/Le_{H_2} \quad (20)$$

By introducing $w_I = w_{II} = 0$ and Eq.(17) into the Eqs. (10) to (16), the following equations are found

$$x_{O_2}^{(1)} = (d_{O_2}/Le_{O_2})(ax_{H_2}^{(1)}/2 - \eta) \quad (21)$$

$$-\theta^{(1)} + q_{III}ad_{O_2}x_{H_2}^{(1)}/2Le_{O_2} = d_{\theta}^- \eta/q \quad (22)$$

$$\frac{d^2}{d\eta^2} x_{H_2}^{(1)} = x_{H_2}^{(1)3/2} \left(ax_{H_2}^{(1)}/2 - \eta \right)^{3/2} \quad (23)$$

where it was imposed $A_z^{(1)} = A_{O_2}^{(1)} = A_{\theta}^{(1)} = 1$, $A_{H_2}^{(1)} = ad_{O_2}/Le_{O_2}$ and $A_{CO}^{(1)} = \beta ad_{O_2}/Le_{O_2}$. The definition of a is

$$a \equiv \frac{1}{n_{H_2}} \left[\frac{1 + (\Delta_{st,1}/(1 + \beta))(d_F Le_{H_2})/(d_{H_2} Le_F)}{1 + (n_F/n_{H_2})(d_F Le_{H_2})/(d_{H_2} Le_F)} \right]$$

n_F and n_{H_2} are defined according to the outer zone stoichiometric relation $d_{O_2}/Le_{O_2} = n_{H_2}d_{H_2}/Le_{H_2} + n_F d_F/Le_F$ where $n_{H_2} = 1/2$ and n_F are the stoichiometric coefficients of the global reactions $F + n_F O_2 \rightarrow P_1$ and $H_2 + n_{H_2} O_2 \rightarrow P_2$. For methane, as the main fuel in the mixture, $n_F = 2$. The a expression denominator represents the flux of oxygen to the flame if the global reaction is considered to be the chemical kinetic mechanism. Since the numerator is similar to the denominator, it is possible to extend the physical meaning of the denominator to the numerator. Thus, the numerator can be thought to be the oxygen flux to the flame if the three reactions, Eq. (8), is the chemical kinetic mechanism that represent the oxidation of the mixture $H_2 + F$.

Equations (21) to (23) must satisfy the boundary conditions

$$dx_{H_2}^{(1)}/d\eta = x_{H_2}^{(1)} = dx_{O_2}^{(1)}/d\eta + d_{O_2}/Le_{O_2} = d\theta^{(1)}/d\eta + d_{\theta}^-/q = 0 \quad \text{as } \eta \rightarrow -\infty \quad (24)$$

to match with the outer zone solution in the oxidant side of the flame. In the fuel side of the flame, the inner zone has a border at $\eta = \eta^0$ that is the same border for the oxidation layer. At $\eta = \eta^0$, Eq.(23) matches with the condition

$$dx_{H_2}^{(1)}/d\eta = 1 \quad \text{at } \eta = \eta^0 \quad (25)$$

In the oxidation layer, the condition

$$\varepsilon^4 D_{III} = 1 \quad (26)$$

was imposed and

$$D_{III} \equiv \left[\frac{L^2 \rho_2^2}{D_{\theta,2} W_{N_2}} \right] \left[\frac{k_5 C_M K_1^{1/2} K_2^{-1/2} K_3 A_{H_2}^{(1)1/2} Le_{H_2}^{3/2} Le_{O_2}^{3/2}}{\theta_f^{m+2} X_{H_2 O, f}} \left(\frac{d_{O_2}}{L_{O_2}} \right)^{3/2} \right] \quad (27)$$

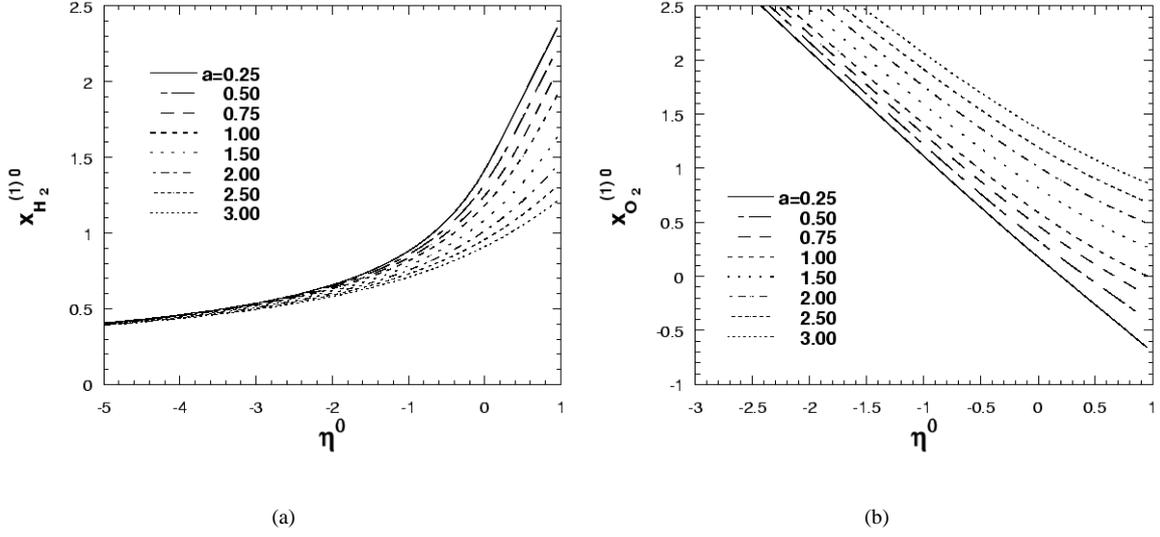


Figure 2: The hydrogen concentration $x_{H_2}^{(1)0}$ and oxygen concentration $x_{O_2}^{(1)0}$ at the border of the flame $\eta = \eta^0$. The plots are obtained by proper value of the parameter a .

The modified Damköhler number D_{II} is determined for the temperature θ^0 defined as

$$\theta^0 = \theta_f - \varepsilon(q_{III} a d_{O_2} x_{H_2}^{(1)0} / 2Le_{O_2} - d_{\theta}^- \eta^0 / q)$$

The figure (2) shows the concentrations of hydrogen and oxygen, $x_{H_2}^{(1)0} = x_{H_2}^{(1)}(\eta^0)$ and $x_{O_2}^{(1)0} = x_{O_2}^{(1)}(\eta^0)$, for some values of the parameter a . It is apparent from this figure that $x_{O_2}^{(1)0}$ curves for $a < 1$ cross the limit of zero oxygen concentration, an unreal result. This means that the flame can not be sustained as presented in this work. Also, insufficient oxygen may indicate pollutant formation.

4.2. Non-equilibrium Layer

In the non-equilibrium layer, reaction II is not in partial equilibrium. The location of this layer is around the place $z^0 = z_f + \varepsilon\eta^0$. The variation of the order ν around z^f causes variations in the properties X_{H_2} , X_{O_2} , X_{CO} of the order ν . To perform the analysis of this layer (Seshadri and Peters, 1988; Card and Williams, 1992b; Card and Williams, 1992a; Fachini and Seshadri, 2003), $A_z^{(2)} = (1 + \beta)/(1 - \beta)$ and $A_{H_2}^{(2)} = A_{CO}^{(2)} = 1$ are introduced in Eq. (17).

By substituting (17) into the system of equations (12) to (13), imposing w_I and w_{III} negligibly small and keeping the terms of the order of ν , the conservation equation for the CO and H_2O species are found,

$$-\frac{d^2 x_{H_2}^{(2)}}{d\zeta^2} = \frac{d^2 x_{CO}^{(2)}}{d\zeta^2} = \frac{x_{CO}^{(2)} - \beta x_{H_2}^{(2)}}{1 + \beta} \quad (28)$$

where was imposed that

$$\nu^2(1 + \beta)^3 D_{II} / (1 - \beta) = 1 \quad (29)$$

and the definition of D_{II} is

$$D_{II} = \frac{L^2 \rho_2^2}{D_{\theta,2} W_{N_2}} \frac{k_{9f} K_1^{-0.5} K_2^{-0.5} X_{H_2}^{0.5} X_{O_2}^{0.5} Le_{CO}}{\theta^{m+2}} \quad (30)$$

The boundary condition correspondent to $\zeta \rightarrow -\infty$ is a result of the match of the solution of this layer with the oxidation layer solution represented by Eq. (18). By introducing (17) into Eq. (18) and collecting terms of the order of ν , the conditions are found

$$\frac{dx_{H_2}^{(2)}}{d\zeta} - \frac{1 + \beta}{1 - \beta} \frac{d_{O_2} a}{Le_{O_2}} = \frac{dx_{CO}^{(2)}}{d\zeta} - \Delta_{st,1} \frac{\beta}{1 - \beta} \frac{d_F}{Le_F} = 0 \quad \text{for } \zeta \rightarrow -\infty \quad (31)$$

The boundary condition correspondent to $\zeta = 0$ comes from the match of the solution of this layer with that from the fuel consumption layer. This is accomplished by satisfying Eq. (19). Thus, by introducing (17) into Eq. (19) and collecting the terms of the order of ν ,

$$\frac{dx_{H_2}^{(2)}}{d\zeta} - \frac{1 + \beta}{1 - \beta} \frac{d_{O_2} a}{Le_{O_2}} = \frac{dx_{CO}^{(2)}}{d\zeta} - \Delta_{st,3} \frac{1 + \beta}{1 - \beta} \frac{d_F}{Le_F} = 0 \quad \text{at } \zeta = 0 \quad (32)$$

Note that in the determination of the boundary conditions Eqs. (31) and (32), the condition $dX_{H_2}/dz = d_{H_2}$ was imposed at $z = z_0^+ + \nu\eta^{0+}$ (or $\zeta = 0^+$). In addition, in the determination of the boundary conditions Eqs. (31) and (32), the condition $dX_{CO}/dz = 0$ was imposed at $z = z_0^+ + \nu\eta^{0+}$ or (or $\zeta = 0^+$), according to (Seshadri, 1996).

The solutions of Eqs. (28), under the constraints established by the boundary conditions Eqs. (31) to (32), lead to

$$\frac{X_{H_2}^0}{Le_{H_2}} = \varepsilon \frac{ad_{O_2}}{Le_{O_2}} x_{H_2}^{(1)} - \nu \frac{1}{1-\beta} \frac{d_F}{Le_F} \quad (33)$$

For the methane oxidation given by Eq. (8), $\Delta_{st,1} = 2$ and $\Delta_{st,2} = 1$.

4.3. Fuel Consumption Layer

To follow the variation of the fuel concentration inside the fuel consumption layer, the expansion given by Eq. (17) at $z = z_f + \varepsilon\eta^0$ and Eq. (7) are introduced into Eq. (10). By collecting the terms of the order of δ , the equation that controls the fuel consumption is found,

$$\frac{d^2}{d\xi^2} x_F^{(3)} = D_I \delta^2 x_F^{(3)} (1 - x_F^{(3)})^{1/2} \quad (34)$$

in which it was imposed

$$\delta = \frac{2k_{1f} X_{O_2}^0}{k_I L_F A_F^{(3)}} \quad (35)$$

and defined D_I as

$$D_I = \frac{L^2 \rho_2^2}{D_{\theta,2} W_{N_2}} \frac{k_I K_1^{0\ 1/2} K_2^{0\ 1/2} K_3^0 X_{H_2}^{0\ 3/2} X_{O_2}^{0\ 1/2}}{\theta^{0\ m+2} X_{H_2O}^0} Le_F \quad (36)$$

The boundary conditions for Eq. (34) come from the match with the solution of the non-equilibrium layer and with the outer solution ($A_F^{(3)} = d_F/Le_F$) respectively,

$$\frac{dx_F^{(3)}}{d\xi} = x_F^{(3)} = 0 \quad \text{as } \xi \rightarrow -\infty, \quad \frac{dx_F^{(3)}}{d\xi} = x_F^{(3)} = 1 \quad \text{at } \xi = \xi^0 \quad (37)$$

By integrating Eq.(34) and applying Eqs. (37), the value of the $D_I \delta^2$ leads to

$$D_I \delta^2 = 15/8 \quad (38)$$

5. Results and Conclusions

From Eqs. (17), (21), (26), (27), (33) and (38), a relation evolving θ^0 , $x_{H_2}^{(1)0}$ and η^0 is found,

$$\frac{k_{1f}^0{}^2 Le_{O_2}}{k_{11f}^0 k_{5f}^0 C_M^0 Le_F} (x_{H_2}^{(1)0})^4 \left[1 - \frac{\nu}{\varepsilon} \frac{1}{(1-\beta)ax_{H_2}^{(1)0}} \frac{Le_{O_2} d_F}{Le_F d_{O_2}} \right]^{3/2} \left[1 - \frac{2\eta^0}{ax_{H_2}^{(1)0}} \right]^{5/2} = \frac{15}{2^{3/2} a^{7/2}} \left(\frac{Le_{O_2} d_F}{Le_F d_{O_2}} \right)^2 \quad (39)$$

and it will be used to determine the extinction condition.

The flow configuration adopted in this work is that imposed by the two counterflowing streams towards a stagnation plane. The fuel stream is made up by a mixture of methane, hydrogen and nitrogen and the oxidant stream is made up by air. The details of this configuration can be found elsewhere (Seshadri and Williams, 1978).

In the counterflow configuration, the characteristic length $L \equiv lPe^{1/2}$, where $lPe^{-1/2}$ is the characteristic length of the viscous layer in the outer zone and $Pe = Lv_2/\lambda_2 = Lv_2/D_{\theta,2}$ is the Peclet number. v_2 is the gas velocity at the fuel nozzle.

The results presented in this section are based on calculations performed for fixed values of $l = 0.02m$, $\rho_1 v_1 = \rho_2 v_2$, $v_2 = 2(m/s)$, $m = 0.5$, $T_1 = T_2 = 390K$, $c_p = 1200J/(Kg.K)$ and $\lambda_2 = 0.035(J/m.K.s)$. The Lewis numbers are $Le_F = 0.60$, $Le_{H_2} = 0.30$, $Le_{O_2} = 1.11$, $Le_{CO} = 1.10$, $Le_{CO_2} = 1.39$, $Le_{H_2O} = 0.85$

Solving simultaneously Eqs. (22), (23) and (39), the unknown properties of the problem (η^0 , $x_{H_2}^{(1)0}$ and θ^0) are determined. As revealed in figure (3), the combustion of undiluted mixture of hydrogen and methane does not produce the maximum temperature. The maximum efficiency occurs for the mixture $Y_{H_2} = 0.03$, $Y_{CH_4} \sim 0.40$ and $Y_{N_2} = 0.57$. The temperature in that condition is $\theta^0 \sim 6.8$; note that for $Y_{H_2} = 0.05$, that temperature is found for $Y_{CH_4} \sim 0.80$. Therefore, once determined the combustion chamber temperature operation to accomplish the pollutant emission requirements, the concentration of methane and hydrogen can be searched to attain good ignitability of the mixture and maximum efficiency (minimum methane consumption).

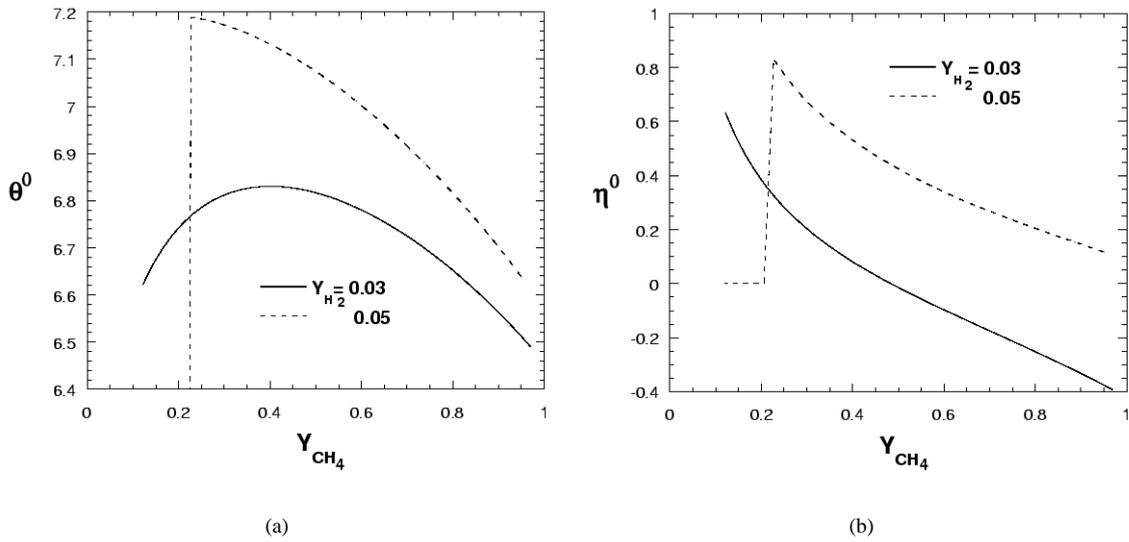


Figure 3: Flame temperature θ^0 and position of the flame border η^0 are presented as a function of the methane mass fraction.

Calculations were done for lower hydrogen mass fraction ($Y_{H_2} = 0.01, 0.02$), but the problem does not present solution for these hydrogen concentrations in the mixture. This may be an indication of the use of a wrong strategy to study the flame structure for these hydrogen concentrations.

Increasing the hydrogen mass fraction in the mixture ($Y_{H_2} = 0.03, 0.05$), the border of the flame η^0 moves to the fuel side of the flame $\eta^0 > 0$. This result is understood taking into account that the hydrogen reaction needs less oxygen than that one of the methane, thus the flame does not move to the oxygen side where the oxygen concentration is larger.

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References

- Bell, S. and Gupta, M., 1997, Extension of the Lean Operating Limit for Natural Gas Fueling of a Sparked Ignited Engine Using Hydrogen Blending, "Combust. Sci. Technol.", Vol. 123, pp. 23–48.
- Card, J. and Williams, F., 1992a, Asymptotic Analysis of the Structure and Extinction of Spherically Symmetrical n-Heptane Diffusion Flames, "Combust. Sci. Technol.", Vol. 84, pp. 91–119.
- Card, J. and Williams, F., 1992b, Asymptotic Analysis with Reduced Chemistry for the Burning of n-Heptane Droplets, "Combust. Flame", Vol. 91, pp. 187–199.
- Cheng, R. and Oppenheim, A., 1984, Autoignition in Methane Hydrogen Mixtures, "Combust. Flame", Vol. 58, pp. 125–139.
- Fachini, F., 2004a, Multicomponent Fuel Diffusion Flames: Flame Structure for Coupled Diffusion-Flame and Premixed-Flame Burning Regimes, "submitted to publication", Vol. .
- Fachini, F. F., 2004b, Multicomponent Fuel Diffusion Flames: A General Shvab-Zel'dovich Formulation, "under consideration for publication", Vol. .
- Fachini, F. F., 2004c, Multicomponent Fuel Diffusion Flames: Flame Structure for a Single Diffusion-Flame Burning Regime, "under consideration for publication", Vol. .
- Fachini, F. F. and Seshadri, K., 2003, Rate-Ratio Asymptotic Analysis of Nonpremixed n-Heptane Flames, "Combust. Sci. Technol.", Vol. 175, pp. 125–155.
- Hamins, A. and Seshadri, K., 1984a, Prediction of Overall Chemical Kinetic Rate Parameters near Extinction for Diffusion Flame Burning Multicomponent Fuels, "Combust. Sci. Technol.", Vol. 38, pp. 89–103.

- Hamins, A. and Seshadri, K., 1984b, Structure of Counterflow Diffusion Flames Burning Multicomponent Fuels, "Proc. Combust. Instit.", Vol. 20, pp. 1905–1913.
- Jackson, G. S., Sai, R., Plaia, J. M., Boggs, C. M., and Kiger, K. T., 2003, Influence of H₂ on the Response of Lean Premixed CH₄ Flames to High Strained Flow, "Combust. Flame", Vol. 132, pp. 503–511.
- Milton, B. E. and Keck, J. C., 1984, Laminar Burning Velocities in Stoichiometric Hydrogen and Hydrogen Hydrocarbon-Gas Mixtures, "Combust. Flame", Vol. 58, pp. 13–22.
- Peters, N., 1984, Laminar Diffusion Flamelet Models in Non-Premixed Turbulent Combustion, "Prog. Energy Combust. Sci.", Vol. 10, pp. 319–339.
- Refael, S. and Sher, E., 1989, Reaction-Kinetic of Hydrogen-Enriched Methane Air and Propane Air Flames, "Combust. Flame", Vol. 78, pp. 326–338.
- Scholte, T. G. and Vaags, P. B., 1959a, Burning Velocities of Mixtures of Hydrogen, Carbon Monoxide and Methane with Air, "Combust. Flame", Vol. 3, pp. 511–524.
- Scholte, T. G. and Vaags, P. B., 1959b, The Burning Velocity of Hydrogen-Air and Mixtures of Some Hydrocarbons with Air, "Combust. Flame", Vol. 3, pp. 495–501.
- Scholte, T. G. and Vaags, P. B., 1959c, The Influence of Small Quantities of Hydrogen and Hydrogen Compounds on the Burning Velocity of Carbon Monoxide-Air Flames, "Combust. Flame", Vol. 3, pp. 503–510.
- Seshadri, K., 1996, Multistep Asymptotic Analyses of Flame Structure, "Proc. Combust. Instit.", Vol. 26, pp. 831–846.
- Seshadri, K. and Peters, N., 1988, Asymptotic Structure and Extinction of Methane-Air Diffusion Flames, "Combust. Flame", Vol. 73, pp. 23–44.
- Seshadri, K. and Williams, F., 1978, Laminar Flow Between Parallel Plates with Injection of a Reactant at a High Reynolds Number, "Int. J. Heat Mass Transfer", Vol. 21, pp. 251–253.
- Seshadri, K. and Williams, F. A., 1994, "Reduced Chemical Systems and Their Application in Turbulent Combustion", Turbulent Reactive Flows, ed P. Libby and F.A. Williams, Academic Press, San Diego, CA.
- Sher, E. and Refael, S., 1988, A Simplified Reaction Scheme for the Combustion of Hydrogen Enriched Methane Air Flame, "Combust. Sci. Technol.", Vol. 59, pp. 371–389.