Asymptotic Structure of Rich Methane-Air Flames

K. SESHADRI*
Center for Energy and Combustion Research, Department of Mechanical and Aerospace Engineering, University of California at San Diego, La Jolla, CA 92093-0411, USA

X. S. BAI
Division of Fluid Mechanics, Department of Heat and Power Engineering, Lund Institute of Technology, S 221 00 Lund, Sweden

and

H. PITSC
Center for Turbulence Research, Stanford University, Stanford, CA 94305-3030, USA

The asymptotic structure of unstrained, laminar, fuel-rich, premixed methane flame is analyzed by using a reduced chemical-kinetic mechanism made up of three global steps. Analysis is carried out for values of equivalence ratio greater than 1.3. The flame structure is presumed to comprise three zones: an inert preheat zone, a thin reaction zone, and a post-flame zone. In contrast to previous asymptotic analyses of lean flames and moderately rich flames, where the reaction zone of these flames was presumed to be made up of two layers, for rich flames analyzed here all chemical reactions are presumed to take place in one layer. The structure of the reaction zone of rich flames is obtained by integrating two second order ordinary differential equations, one giving the consumption of fuel and the other the consumption of oxygen. For values of equivalence ratio greater than 1.3, burning velocities obtained from the asymptotic analysis are found to agree reasonably well with those obtained using a chemical-kinetic mechanism made up of elementary reactions. © 2002 by The Combustion Institute

INTRODUCTION

Burning velocities of unstrained premixed methane flames obtained using chemical-kinetic mechanisms made up of elementary reactions show that for lean and near stoichiometric reactant mixtures with equivalence ratio, \( \phi \), less than 1.1, the burning velocity increases with increasing \( \phi \) [1]. For moderately rich reactant mixtures with \( \phi \) roughly between 1.1 and 1.3, the burning velocity decreases rapidly with increasing \( \phi \) [1]. For rich mixtures with \( \phi \) greater than 1.3, the burning velocity decreases slowly with increasing \( \phi \) [1]. These results were obtained using the so-called \( C_1 \)-mechanism, \( C_2 \)-mechanism, and the \( C_3 \) mechanism. In the \( C_1 \)-mechanism/\( C_2 \)-mechanism/\( C_3 \)-mechanism, elementary reactions comprising compounds made up of two/three/four or more carbon atoms are excluded. Numerical calculations carried out using chemical-kinetic mechanisms made up of elementary reactions show that the structure of lean flames, moderately rich flames, and rich flames are not the same. For this reason, previous rate-ratio asymptotic analyses of near stoichiometric and lean methane flames [2–6] were different from rate-ratio asymptotic analysis of moderately rich flames [7]. These asymptotic studies successfully predicted the increases in the value of the burning velocity with increasing \( \phi \) for near stoichiometric and lean methane flames, and the rapid decreases in the value of the burning velocity with increasing \( \phi \) for moderately rich flames. The asymptotic analysis for moderately rich flames failed to predict the slow decreases in the value of the burning velocity with increasing \( \phi \) for \( \phi > 1.3 \). Here, an asymptotic analysis is developed for obtaining the burning velocity of rich methane flames.

Previous asymptotic analyses of near stoichiometric flames, lean flames and moderately rich methane flames were carried out after introducing the approximation that the reaction zone of these flames is made up of two layers; an inner layer and an oxidation layer [2–7]. In the inner layer, methane is completely consumed and CO and \( H_2 \) are main compounds formed. In the
oxidation layer of these flames O₂, CO, and H₂ are consumed. In these previous analyses the characteristic temperature of the inner layer was presumed to be given by T° [2–7]. The inner layer temperature was obtained from a balance between chain-branching reactions and chain-breaking reactions [6]. Its value is less than the adiabatic temperature, Tb. In the oxidation layer, the temperature increases from T° to Tb [2–7]. The analysis of moderately rich flames showed that with increasing values of φ, T° approaches Tb, and the approximation that the reaction zone is made up of two layers breaks down for even higher equivalence ratio. Hence, in the present asymptotic analysis all chemical reactions are presumed to take place in one layer. The characteristic temperature of this layer is the adiabatic temperature To. Appendix A shows structures of a lean flame, a moderately rich flame, and a rich flame. These structures were calculated using the C₂-mechanism. Net rates of production of various species in these flames were obtained. They clearly show that the reaction zone of lean flames and moderately rich flames are made up of two layers, while the reaction zone of rich flames is made up of one layer.

Previous asymptotic analyses of near stoichiometric, lean, and moderately rich methane flames were carried out employing reduced chemical-kinetic mechanisms derived from the C₁-mechanism. For rich flames analyzed here, the elementary reaction CH₃ + CH₃ = C₂H₆, that leads to the C₂-chain, is found to be the principal step by which CH₃ is consumed (see Appendix A). Hence, the present asymptotic analysis is carried out employing a reduced mechanism derived from the C₂-mechanism.

REDUCED MECHANISM

The C₂-mechanism employed here is made up of reactions (1)–(61) shown in Table 1.1 of Ref. [8]. The species CH₄, O₂, C₂H₆, C₂H₅, C₂H₄, C₂H₃, C₂H₂, CH, H₂O, CO₂, CH₃, CH₂, CH, CH₂O, CHO, CO, H₂, HO₂, H₂O₂, O, and OH. This reduced five-step mechanism is written as

\[ CH₄ + H = CH₃ + H₂, \]  
\[ 2 CH₃ + O₂ = 2CO + 3 H₂, \]  
\[ CO + H₂O = CO₂ + H₂, \]  
\[ H + H + M = H₂ + M, \]  
\[ O₂ + 3H₂ = 2H + 2H₂O. \]  

Global step Ib is different from that employed in a previous study of moderately rich methane flames [7]. In this previous study the elementary reaction CH₃ + O = CH₂O + H was found to be the main path by which CH₃ is consumed, whereas in the present study the main path by which CH₃ is consumed is found to be CH₃ + CH₃ = C₂H₆ (see Appendix A). This is the reason for the difference between the global step Ib employed in the present analysis and that used in the previous analysis of moderately rich methane flames [7]. Global step Ib is deduced by beginning with the reaction, CH₃ + CH₃ = C₂H₆ and eliminating the reaction rates of the elementary steps C₂H₆ + H = C₂H₅ + H₂, C₂H₅ = C₂H₄ + H, C₂H₄ + H = C₂H₃ + H₂, C₂H₃ = C₂H₂ + H, C₂H₂ + O = CH₂ + CO, CH₂ + O₂ = CO + OH + H, OH + H = O + H₂ from the source terms of the steady state species C₂H₅, C₂H₄, C₂H₃, C₂H₂, CH₂, and O [9].

Table 1 shows the elementary reactions considered to be the major contributors to the rates of the global steps of the reduced mechanism. Symbols f and b appearing in the first column of Table 1, respectively, identify the forward and backward steps of a reversible elementary reaction n. The backward steps of reactions (34), (35), (36), and (37) are not included in the mechanism shown in Table 1.1 of Ref. [8]. Therefore, they are neglected in the asymptotic analysis. The backward steps of reactions (1), and (5) are neglected in the asymptotic analysis because numerical calculations show that their influence on burning velocities is small for 1.3 < φ < 2.5. Rate data for the elementary steps are identical to those shown in Table 1.1 of Ref. [8]. Reaction rate coefficients kₙ of the elementary reactions are calculated by using the expression
The quantities \( k_\text{c} \) and \( k_\text{d} \) are the frequency factor, the temperature exponent, and the activation energy of the elementary reaction \( n \). The concentration of the third body \( C_3 \) is calculated by using the relation \( C_3 = \left(pW/(\mathcal{R}T)\right)|\Sigma n_i\eta_i/W_i| \), where \( p \) denotes the pressure, \( W \) the molecular weight of the mixture, \( Y_1 \), \( Y_2 \), and \( \eta_i \) are respectively, the mass fraction, the molecular weight, and the chaperon efficiency of species \( i \). Chaperon efficiencies are shown in Table 1. The rates of reactions (4) and (18) are not used in the analysis.

Reaction rates of the global steps \( w_k \) in the five-step mechanism \((k = 1a-IV)\), are

\[
\begin{align*}
  w_{1a} &= -w_{34f} + w_{38f} - w_{38b}, \\
  w_{1b} &= 0.5 w_{35f} + w_{36f} + 0.5 w_{37f}, \\
  w_{1i} &= w_{18f} - w_{18b}, \\
  w_{1II} &= w_{5f} + w_{34f}, \\
  w_{1IV} &= w_{1f} - 0.5 w_{35f} + 0.5 w_{37f},
\end{align*}
\]

Here \( w_n \) is the reaction rate of elementary reaction \( n \). A number of elementary reactions in addition to those shown in Eq. 1 contribute to the rates of the global steps of the reduced mechanism. Contributions of these additional reactions are neglected because they are found to be small.

Steady-state concentration of \( O \) is required for calculating the global rates of the reduced mechanism. To make the analysis simple the elementary reactions (2) and (3) are presumed to maintain partial equilibrium. A previous study has shown that burning velocities, calculated after introducing these partial equilibrium approximations, are reasonably accurate [1]. The partial equilibrium approximations give

\[
C_O = \frac{C_{H_2}C_{O_2}^2}{K_2K_3C_{H_2}^2},
\]

where \( C_i \) is the molar concentration of species \( i \), and \( K_n \) is the equilibrium constant of the elementary step \( n \).

Steady-state approximations are introduced for \( H \) and \( CH_3 \). This gives the three-step mechanism

### Table 1

Rate data for elementary reactions employed in the asymptotic analysis

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>( B_n )</th>
<th>( \alpha_n )</th>
<th>( E_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1f</td>
<td>( O_2 + H \rightarrow OH + O )</td>
<td>2.000E + 14</td>
<td>0.00</td>
<td>70.30</td>
</tr>
<tr>
<td>f</td>
<td>( H_2 + O \rightarrow OH + H )</td>
<td>5.060E + 04</td>
<td>2.67</td>
<td>26.3</td>
</tr>
<tr>
<td>2b</td>
<td>( H + OH \rightarrow O + H_2 )</td>
<td>2.222E + 04</td>
<td>2.67</td>
<td>18.29</td>
</tr>
<tr>
<td>3f</td>
<td>( H_2 + OH \rightarrow H_2O + H )</td>
<td>1.000E + 08</td>
<td>1.60</td>
<td>13.80</td>
</tr>
<tr>
<td>3b</td>
<td>( H_2 + H_2O \rightarrow OH + H_2 )</td>
<td>4.312E + 08</td>
<td>1.60</td>
<td>76.46</td>
</tr>
<tr>
<td>4f</td>
<td>( OH + OH \rightarrow H_2O + O )</td>
<td>1.500E + 09</td>
<td>1.14</td>
<td>0.42</td>
</tr>
<tr>
<td>4b</td>
<td>( O + H_2O \rightarrow OH + OH )</td>
<td>1.473E + 10</td>
<td>1.14</td>
<td>71.09</td>
</tr>
<tr>
<td>5f*</td>
<td>( H + O_2 + M \rightarrow HO_2 + M )</td>
<td>2.300E + 18</td>
<td>-0.80</td>
<td>0.00</td>
</tr>
<tr>
<td>18f</td>
<td>( CO + OH \rightarrow CO_2 + H )</td>
<td>4.400E + 06</td>
<td>1.50</td>
<td>-3.10</td>
</tr>
<tr>
<td>18b</td>
<td>( H + CO_2 \rightarrow OH + CO )</td>
<td>4.956E + 08</td>
<td>1.50</td>
<td>89.76</td>
</tr>
<tr>
<td>34f*</td>
<td>( CH_3 + H \rightarrow CH_4 k_0 )</td>
<td>6.257E + 23</td>
<td>-1.80</td>
<td>0.00</td>
</tr>
<tr>
<td>35f</td>
<td>( CH_3 + O \rightarrow CH_3O + H )</td>
<td>2.108E + 14</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>36f*</td>
<td>( CH_3 + CH_3 \rightarrow C_2H_6 k_0 )</td>
<td>7.000E + 13</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>37f</td>
<td>( CH_3 + O_2 \rightarrow CH_3O + OH )</td>
<td>1.270E + 41</td>
<td>-7.00</td>
<td>11.56</td>
</tr>
<tr>
<td>38f</td>
<td>( CH_4 + H \rightarrow CH_3 + H_2 )</td>
<td>3.613E + 13</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>38b</td>
<td>( CH_3 + H_2 \rightarrow CH_4 + H )</td>
<td>3.400E + 11</td>
<td>0.00</td>
<td>37.40</td>
</tr>
</tbody>
</table>

Units are moles, cubic centimeters, seconds, kJoules, Kelvin.

* Third body collision efficiencies are \([M] = 6.5[CH_3] + 1.5[CO_2] + 0.75[CO] + 0.4[N_2] + 6.5[H_2O] + 0.4[O_2] + 1.0[Other].

* For reaction 34f and reaction 36f: \( k = F k_k k_0 [p/(\mathcal{R}T)]/[k_\text{c} + k_\text{d} [p/(\mathcal{R}T)] \right), \) where \( \log_{10} F = \log_{10} F_r / (1 + (\log_{10}(k_\text{c}/\mathcal{R}T)[k_\text{d}/\mathcal{R}T])^2) \right), \) \( N = 0.75 - 1.27 \log_{10} F_r \). For reaction 34f \( F_r = 0.577 \exp[-T/2370.0] \). For reaction 36f \( F_r = 0.38 \exp[-T/73.0] + 0.62 \exp[-T/1180.0] \).
\[ \text{CH}_4 + \text{O}_2 \rightleftharpoons \text{CO} + \text{H}_2 + \text{H}_2\text{O}, \quad (\text{Ia}) \]

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2, \quad (\text{II}) \]

\[ \text{O}_2 + 2\text{H}_2 \rightleftharpoons 2\text{H}_2\text{O}. \quad (\text{III}) \]

Reaction rates of the global steps \( w_k \) in the three-step mechanism \( (k = \text{Ia}^- - \text{III}^-) \), are

\[
\begin{align*}
    w_{\text{Ia}^-} & = w_{\text{Ia}} = -w_{34f} + w_{38f} - w_{38b}, \\
    w_{\text{II}^-} & = w_{\text{II}} = w_{18f} - w_{18b}, \\
    w_{\text{III}^-} & = w_{\text{III}} = w_{5f} + w_{34f}.
\end{align*}
\]

Steady-state concentrations of H and CH\(_3\) are calculated using the algebraic equations

\[
\begin{align*}
    -2w_{1f} + 2w_{5f} + w_{34f} + w_{35f} - w_{37f} & + w_{38f} - w_{38b} = 0, \\
    w_{34f} + w_{35f} + 2w_{36f} + w_{37} - w_{38f} + w_{38b} & = 0.
\end{align*}
\]

The three-step mechanism, \( k = \text{Ia}^- , \text{II}^- , \text{III}^- \), is employed in the asymptotic analysis.

**FORMULATION**

Steady propagation of a planar, laminar flame under adiabatic conditions is considered. The Mach number is presumed to be small. Mass conservation gives \( \rho v = \rho_0 s_L \), where \( \rho \) is the density, \( v \) the gas velocity, and \( s_L \) the burning velocity. Subscript \( u \) refers to the initial conditions in the unburnt reactant mixture. Lewis numbers, \( \text{Le}_i = \lambda/(\rho c_p D_i) \), for species \( i \) are assumed to be constants. Here \( \lambda \) is the thermal conductivity, \( c_p \) the mean specific heat at constant pressure, and \( D_i \) the diffusion coefficient of species \( i \). The heat capacity is presumed to be constant. Diffusion velocities of species are presumed to be given by Fick’s Law [10]. The non-dimensional species balance equations and the energy conservation equation are

\[
\begin{align*}
    \frac{dX_i}{dx} - \frac{1}{\text{Le}_i} \frac{d^2X_i}{dx^2} & = \sum_{k = \text{Ia}}^{\text{III}} (v_{i,k} \omega_k), \\
    \frac{d\tau}{dx} - \frac{d^2\tau}{dx^2} & = \sum_{k = \text{Ia}}^{\text{III}} (Q_{k} \omega_k),
\end{align*}
\]

where \( x = \int_0^x (\rho c_p/\lambda) dx' \) and \( x' \) is the spatial coordinate. The origin \( x = 0 \) is taken to coincide with the location of the inner reactive-diffusive zone. The quantity \( v_{i,k} \) is the stoichiometric coefficient of species \( i \) in the global step \( k \) of the reduced mechanism. The value of \( v_{i,k} \) is positive if species \( i \) appears on the right side of global step \( k \) and negative if it appears on the left side. The dependent variables \( X_i \) and \( \tau \) are defined as

\[
X_i = \frac{Y_i W_F}{Y_{F,u} W_i}, \quad \tau = \frac{T - T_u}{T_c - T_u}.
\]

\( X_i \) is the normalized mass fraction of species \( i \), \( \tau \) is the normalized temperature, and subscript \( F \) refers to the fuel. \( Y_{F,u} \) is the initial value of \( Y_F \) in the unburnt reactant mixture, \( T_c \) is the temperature of burnt gases obtained by introducing the approximation that the chemical reaction takes place by the one-step overall process \( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \). From Eq. 6 it follows that \( C_i = (\rho Y_{F,u} W_F) X_i \). The non-dimensional reaction rates \( w_k \) and heats of reaction \( Q_k \) are defined as

\[
\omega_k = \frac{\lambda W_F w_k}{c_p Y_{F,u} \rho_0 D_L^{2/3}}; \quad Q_k = \frac{Y_{F,u} (-\Delta H_k)}{c_p (T_c - T_u) W_F},
\]

where \( (-\Delta H_k) \) is the heat release in the global step \( k \). From the definition of \( Q_k \) it follows that \( Q_{\text{Ia}} + Q_{\text{II}} + Q_{\text{III}} = 1 \). Their values are \( Q_{\text{Ia}} = 0.3458, Q_{\text{II}} = 0.0514, \) and \( Q_{\text{III}} = 0.6028 \).

The asymptotic structure of the premixed flame is presumed to comprise a preheat zone of thickness of the order of unity, a thin reaction zone of thickness of the order of \( \epsilon \ll 1 \), and a post-flame zone. The preheat zone is located upstream of the reaction zone. It is presumed to be inert. All chemical reactions take place in the reaction zone. The post-flame zone is located downstream of the reaction zone. In this zone chemical reactions are in equilibrium and the temperature is equal to its adiabatic value \( T_b \). The equilibrium products in the post-flame zone are presumed to comprise \( \text{CO}_2, \text{H}_2\text{O}, \text{O}_2, \text{CO}, \text{H}_2, \) and \( \text{N}_2 \). The equivalence ratio, \( \phi \), for methane flames is given by \( \phi = 4 Y_{F,u} / Y_{O,u} \), where \( Y_{O,u} \) is the initial value of \( Y_O \) in the unburnt reactant mixture. For \( p = 1 \) bar, \( T_u = 300K, \) and \( 1.0 < \phi < 2.5 \); values of \( T_c, T_b, \) and
mass fractions of equilibrium products $Y_{i,b}$ are obtained. Figures 1, 2, and 3 show temperatures and normalized mass fractions of various species in the post-flame zone. Figure 1 shows $T_c$ and $T_b$. Fig. 2 shows values of $X_{i,b}$, $i = \text{CO}_2$, $\text{H}_2\text{O}$, CO, and $\text{H}_2$, and Fig. 3 shows $X_{\text{O}_2,b}$. In the analysis $X_{\text{CO}_2,b}$, $X_{\text{H}_2\text{O},b}$, $X_{\text{CO},b}$ and $X_{\text{H}_2,b}$ are presumed to be of the order of unity, and $X_{\text{O}_2,b}$ is presumed to be small.

In the preheat zone, $X_F$ and $X_{\text{O}_2}$ are of the order of unity. They are obtained by neglecting the reaction terms in the balance equations. Thus

$$X_F = 1 - \exp(Le_F x),$$  
$$X_{\text{O}_2} = X_{\text{O}_2,u} [1 - \exp(Le_{\text{O}_2} x)],$$  

where the origin of the coordinate system is so chosen that $x = 0$ at the reaction zone. $X_{\text{O}_2,u}$ is the initial value of $X_{\text{O}_2}$ in the unburnt reactant mixture.

**ASYMPTOTIC ANALYSIS OF THE REACTION ZONE**

In the asymptotic analysis of the reaction zone, the convective terms in the species balance equations and in the energy conservation equation shown in Eq. 5 are neglected because they are presumed to be small in comparison to the diffusive terms and the reactive terms. Balance equation for $X_{\text{O}_2}$, $X_F$, and $X_{\text{CO}}$ are

$$\frac{1}{Le_{\text{O}_2}} \frac{d^2 X_{\text{O}_2}}{dx^2} = \omega_{5f} + \omega_{38f} - \omega_{38b},$$  
$$\frac{1}{Le_F} \frac{d^2 X_F}{dx^2} = -\omega_{34f} + \omega_{38f} - \omega_{38b},$$  
$$\frac{1}{Le_{\text{CO}}} \frac{d^2 X_{\text{CO}}}{dx^2} = \omega_{18f} - \omega_{18b} + \omega_{34f} - \omega_{38f} + \omega_{38b},$$  

where use is made of Eq. 3. The values of $X_{\text{CO}_2}$, $X_{\text{H}_2\text{O}}$, and $X_{\text{H}_2}$ can be obtained from the following conservation equations for the elements carbon, oxygen and hydrogen.
Energy conservation gives

\[ \frac{d^2}{dx^2} \left( \frac{X_F}{L_e} + \frac{X_{CO}}{L_e} + \frac{X_{CO_2}}{L_e} \right) = 0, \]

\[ \frac{d^2}{dx^2} \left( 2 \frac{X_{O_2}}{L_eO_2} + 2 \frac{X_{CO_2}}{L_eCO_2} + \frac{X_{CO}}{L_eCO} + \frac{X_{H_2O}}{L_eH_2O} \right) = 0, \]

\[ \frac{d^2}{dx^2} \left( 2 \frac{X_F}{L_eF} + \frac{X_{H_2O}}{L_eH_2O} + \frac{X_{H_2}}{L_eH_2} \right) = 0. \] (10)

Using numerical values for \( Q_k \) the result

\[ \frac{d^2}{dx^2} \left[ \tau + Q_{III} \frac{X_{O_2}}{L_eO_2} + (1 - 2Q_{III}) \frac{X_F}{L_eF} \right. \]

\[ + \left. Q_{II} \frac{X_{CO}}{L_eCO} \right] = 0. \] (11)

is obtained.

The expansions

\[ X_{O_2} = \epsilon L e O_2 y_{O_2} + O(\epsilon^2), \]

\[ X_{F} = \epsilon L e F y_{F} + O(\epsilon^2), \]

\[ X_1 = X_{i,b} + \epsilon L e_y y_{i} + O(\epsilon^2), \]

\[ i = H_2O, CO_2, CO, H_2, \]

\[ X_H = R_{1b} L e_H y_H + O(R_H^2), \]

\[ X_{CH_3} = R_{CH_1} L e_{CH_1} y_{CH_1} + O(R_{CH_3}^2), \]

\[ \tau = \tau_b - \epsilon t + O(\epsilon^2), \]

are introduced. Here \( \tau_b = (T_b - T_u)/(T_c - T_u). \)

The dependent variables \( y_i, i = O_2, F, H_2O, \)

\( CO_2, CO, H_2, H, CH_3, \) and \( \tau \) are presumed to be of the order of unity. The expansion parameters \( \epsilon \ll 1, R_H \ll 1, \) and \( R_{CH_3} \ll 1 \) are presumed to be given by

\[ \epsilon = \frac{k_{34f,b} X_{H_2,b}}{k_{36f,b} X_{CH_1,b} L_e F}, \]

\[ R_H = \frac{k_{11b} X_{H_2,b} L e_{O_2}^2}{k_{38f,b} k_{38f,b} X_{CH_1,b} L_e F^2 L e H}. \] (14)
g_{1f} = \frac{k_{1f}}{k_{1f,b}} = \exp \left[ -8455.62 \left( \frac{1}{T} - \frac{1}{T_b} \right) \right],
\tag{20}
g_{3f} = \frac{k_{3f}C_M}{k_{3f,b}C_{M,b}} = \exp \left[ 1.80 T_{ref} \left( \frac{1}{T} - \frac{1}{T_b} \right) \right],

(21)
give changes in values of \( k_{1f} \) and \( k_{3f}C_M \) with temperature. Here the approximation \( T_{ref} = (T_{ref})^\infty \exp(\alpha_n)\exp(-\alpha_n(T_{ref}/T)) \) is applied to the rate data shown in Table 1, where \( T_{ref} \) is a reference temperature. For simplicity, values of \( Y_i \) appearing in the definition of \( C_{M,b} \) are presumed to be equal to \( Y_{i,b} \). Errors introduced from use of this approximation are presumed to be small. Asymptotic analysis that includes changes in values of \( \rho, \lambda \), and rate constants of all elementary reactions with temperature is described in the Appendix B.

Boundary conditions for Eq. 17 are obtained by matching the profiles of oxygen and fuel in the reaction zone with those in the post-flame zone. In the limit \( \zeta \to \infty \), Eq. (17) is required to satisfy the boundary conditions

\[ \frac{dy_{O_2}}{d\zeta} = 0, \quad \frac{dy_F}{d\zeta} = 0, \]

and \( y_{O_2} = 0 \) and \( y_F = y_{F,\infty} \). If backward steps of all elementary reactions are included in the analysis, the fuel will be completely consumed in the post-flame zone and the mass fractions of equilibrium products are shown in Figs. 2 and 3. For large negative values of \( \zeta \), the profiles of \( y_{O_2} \) and \( y_F \) must match with those in the preheat zone given by Eq. 8. In the limit \( \zeta \to -\infty \), the boundary conditions

\[ \frac{dy_{O_2}}{d\zeta} = -X_{O_2,u}; \quad \frac{dy_F}{d\zeta} = -1, \]

are obtained. Equation 17 is invariant to translation of the coordinate system. To fix the origin, boundary conditions are applied at some arbitrary value \( \zeta_0 \), where \( -\zeta_0 \) is large. Boundary conditions at \( \zeta_0 \) are \( y_{O_2} = -X_{O_2,u}\zeta_0 \) and \( y_F = -\zeta_0 \) in addition to those given by Eq. 22. Fuel is found to leak from the reaction zone into the post-flame zone, while leakage of oxygen is found to be negligible. The fuel leakage, \( y_{F,\infty} \), is given by the asymptotic value of \( y_F \) in the limit \( \zeta \to \infty \). The values of the eigenvalue \( L \) and \( y_{F,\infty} \) are so chosen that the boundary condition Eq. 21 is satisfied.

Equations that give the steady-state concentrations of \( \text{H} \) and \( \text{CH}_3 \) are obtained by use of Eqs. 13 and 14 in Eq. 4. The steady-state concentrations are

\[ \begin{align*}
-2g_{1f}ty_{O_2}y_H + 2g_{3f}t_ky_{O_2}y_H + \mu^2 y_H y_{CH_3}, \\
+ \psi y_H^2 y_{CH_3} - \chi y_{O_2}y_{CH_3}, \\
+ y_F y_H - y_{CH_3} = 0 \\
\mu^2 y_H y_{CH_3} + \psi y_H^2 y_{CH_3} + 2\mu^2 y_{CH_3}^2, \\
+ \chi y_{O_2}y_{CH_3} - y_F y_H + y_{CH_3} = 0
\end{align*} \]

(23)
The parameters \( \chi \) and \( \psi \) in Eq. 23 are presumed to be of the order of unity. They are given by

\[ \chi = \frac{k_{34f,b}k_{37f,b}Le_{O_2}}{k_{34f,b}k_{38f,b}Le_F}, \]

\[ \psi = \frac{k_{1f,b}k_{35f,b}X_{H_2O,b}Le_{O_2}}{k_{34,b}k_{38,b}^2K_{2,b}K_{3,b}K_{38,b}X_{H_2O,b}Le_F}. \]

(24)

To obtain the temperature in the reaction zone, the expansions given by Eq. 13 are introduced into Eq. 12 and integrated twice. The constants of integration are evaluated by imposing the constraints that at \( \zeta \to \infty \), derivatives with respect to \( \zeta \) of \( t, y_{O_2}, \) and \( y_F \) vanish, values of \( t \) and \( y_{O_2} \) vanish, and the value of \( y_F \) is \( y_{F,\infty} \). This gives

\[ t - t_\infty = 0.6028 y_{O_2} - 0.2056 (y_F - y_{F,\infty}), \]

where the approximation \( Q_H \ll 1 \) is used, and \( t_\infty \) is the value of \( t \) in the limit \( \zeta \to \infty \). The ad hoc approximation \( t_\infty = 0 \) is introduced in the analysis. The expansion for \( \tau \) in Eq. 13 gives

\[ T = T_b - \epsilon(T_c - T_u). \]

By using this expansion for \( T \), the value of \( 1/T - 1/T_b \) in Eq. 20 is evaluated from the equation

\[ \frac{1}{T} - \frac{1}{T_b} = \frac{\epsilon[0.6028 y_{O_2} - 0.2056 (y_F - y_{F,\infty})]}{T_b^2} (T_c - T_u). \]

(25)

Equation 25 is used to evaluate \( g_{1f} \) and \( g_{3f} \) in Eq. 20. Equation 17 is integrated numerically and
the burning velocity is obtained. Results are given in the following section.

RESULTS

Equations derived in the previous sections are used to obtain flame structures and burning velocities at \( p = 1 \) bar and \( T_u = 300 \) K. Values of \( L e \) are \( L e_F = L e_{CH_3} = 0.97, L e_{O_2} = 1.1, \) and \( L e_H = 0.2 \). The value of \( (\lambda_b/c_{pb}) \) in Eq. 18 is obtained from \( (\lambda_b/c_{pb}) = 2.58 \times 10^{-5} (T_b/298)^{0.7} \) kg/(m.s) \[11\]. The molecular weight of the mixture \( W \) is taken to be a constant and it is evaluated in the post-flame zone; and \( T_{ref} = 1,900 \) K.

Figure 4 shows profiles of \( y_F \) and \( y_{O_2} \) obtained from integration of Eq. 17 for \( \phi = 2.0 \). The asymptotic values of \( y_F \) and \( y_{O_2} \) for large values of \( \zeta \), give the amount fuel and oxygen leaking from the reaction zone into the post-flame zone. Figure 4 shows that fuel leaks from the reaction zone into the post-flame zone while leakage of oxygen is negligible. Figure 5 shows profiles of the steady-state species \( y_H \) and \( y_{CH_3} \) obtained from Eq. 23 for \( \phi = 2.0 \). Figure 6 shows the eigenvalue \( L \), and fuel-leakage \( y_{F,\infty} \) for various values of \( \phi \). The fuel-leakage is small. It increases with increasing \( \phi \). The burning velocity is obtained from \( L \) using Eq. 18.

Figure 7 shows that burning velocities obtained from asymptotic analysis that includes changes in values of \( k_1 \) and \( k_5 C_M \) with changes in temperature agree well with those obtained from asymptotic analysis, described in Appendix B, where changes in values of \( \rho, \lambda \) and all rate constants with temperature are included. To test the accuracy of \( s_L \) obtained from the asymptotic analysis, numerical calculations were performed by using the three-step mechanism, \( k = Ia', II', III' \), employing only the rate data shown in Table 1. The burning velocities calculated by using the asymptotic analysis agree very well with those calculated by using the three-step mechanism. To test the accuracy of \( s_L \) obtained from the asymptotic analysis, and from the three-step mechanism numerical calculations were performed using the C2 mechanism. Burning velocities were obtained. They are shown in Fig. 7 for \( 1 < \phi < 2.5 \). For \( \phi \) greater than 1.7, \( s_L \) obtained from asymptotic analysis agrees well with that obtained using the C2 mechanism. For \( \phi \) less than 1.7, the difference between the value of \( s_L \) calculated from asymptotic analysis and

Fig. 4. Profiles of \( y_F \) and \( y_{O_2} \) for \( p = 1 \) bar, \( T_u = 300 \) K and \( \phi = 2.0 \).

Fig. 5. Profiles of \( y_H \) and \( y_{CH_3} \) for \( p = 1 \) bar, \( T_u = 300 \) K and \( \phi = 2.0 \).

Fig. 6. The eigenvalue \( L \), and fuel-leakage \( y_{F,\infty} \) versus the equivalence ratio, \( \phi \), for \( p = 1 \) bar and \( T_u = 300 \).
that obtained from the C$_2$ mechanism increases as $\phi$ decreases. These differences are attributed to the various approximations introduced in the analysis including the neglect of changes in the values of CO and H$_2$ in the reaction zone. Figure 7 shows that $s_L$ obtained from previous asymptotic analysis of moderately rich flames [7] agrees well with that calculated by using the C$_2$ mechanism for $1 < \phi < 1.3$, but cannot predict the transition to rich flames.

Figures 8, 9, and 10 show $\epsilon$, $\sigma$, $\omega$, $\kappa$, $\mu$, and $\chi$ for various values of $\phi$. Figure 8 shows that the characteristic thickness of the reaction zone, represented by $\epsilon$, increases with increasing $\phi$. Figure 9 shows that $\sigma$ and $\omega$ are large for all values of $\phi$. Therefore, steady-state approximations for CH$_3$ and H are expected to be accurate. Figure 10 shows the parameters $\kappa$, $\mu$, $\chi$, and $\psi$. The value of $\psi$ is very small. This indicates that the influence of elementary reaction 35f on the structure and burning velocity of rich flames is small. This reaction, however, is found to have a significant influence on the concentration of radicals in stoichiometric flames and lean flames.

**CONCLUDING REMARKS**

The present asymptotic analysis together with previous asymptotic analyses of near stoichiometric and lean flames [2–4, 6] and moderately
rich flames [7], give a complete description of the structure of methane flames for all values of \( \phi \). For near stoichiometric and lean flames the structure of the oxidation layer was obtained by analyzing the consumption of \( \text{CO} \) and \( \text{H}_2 \) [2–4, 6]. For moderately rich flames the structure of the oxidation layer was obtained by analyzing the consumption of \( \text{O}_2 \) [7]. In these previous analyses, leakage of methane from the reaction zone into the post-flame zone was found to be negligible. For lean flames and stoichiometric flames and moderately rich flames, the values of the characteristic temperature at the inner layer, \( T_0 \), is less than the adiabatic temperature, \( T_b \). For rich flames \( \text{CH}_4 \) and \( \text{O}_2 \) are consumed in a single layer. The characteristic temperature of this layer is \( T_b \). In rich flames, the fuel leaks from the reaction zone into the post-flame zone. These are the main differences between the analysis of the asymptotic structure of rich flames and analyses of the asymptotic structures of lean flames and moderately rich flames.

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APPENDIX A

To test the accuracy of the approximations employed in the asymptotic analysis, the structure of a lean flame with \( \phi = 0.8 \), the structure of a moderately rich flame with \( \phi = 1.2 \), and the structure of a rich flame with \( \phi = 1.9 \) are calculated using the \( \text{C}_2 \)-mechanism. Figures 11, 12, and 13 show profiles of mass fractions of \( \text{CH}_4, \text{O}_2, \text{CO}_2, \text{CO}, \) and \( \text{H}_2 \) and the temperature profile for \( \phi = 0.8 \), \( \phi = 1.2 \), and \( \phi = 1.9 \), respectively. Figure 11 shows that in a lean flame, \( \text{CH}_4 \) is completely consumed in the reaction zone, the mass fractions of \( \text{CO} \) and \( \text{H}_2 \) first increase and then decrease. In this flame \( \text{O}_2 \) is consumed but its mass fraction in the reaction zone is much larger than that of \( \text{CO} \). The profiles of \( \text{CH}_4, \text{CO}, \) and \( \text{H}_2 \) in the moderately rich flame shown in Fig. 12 are similar to those in the lean flame. In the moderately rich flame \( \text{O}_2 \) is consumed and its mass fraction in the reaction zone in comparable to that of \( \text{CO} \). Figure 13 shows that in a rich flame \( \text{O}_2 \) is completely consumed in the reaction zone, while \( \text{CH}_4 \) leaks from the reaction zone into the post-flame zone. The mass fraction of \( \text{H}_2 \) increases. The decrease in the value of the mass fraction of \( \text{CO} \) in the post-flame zone, from its maximum value in the reaction zone, is very small. Thus, the structures of lean flames, moderately rich flames, and rich flames are not the same. Numerical calculations were carried out using the \( \text{C}_2 \)-mechanism including the backward steps of all elementary reactions. The profiles of all species in the lean flame and in the moder-
ately rich flame were similar to those shown in Figs. 11, and 12. The profiles of all species in the rich flame, except that of the fuel, were similar to those shown in Fig. 13. The profile of the fuel in the preheat zone and the reaction zone obtained including backward steps of all elementary reactions was similar to that shown in Fig. 13. In the post-flame zone the profile of fuel calculated including backward steps of all elementary reactions was found to decrease slowly with increasing distance from the reaction zone. Thus there is slow consumption of fuel in the post-flame zone eventually leading to equilibrium products.

Figures 14, 15, and 16 show net rates of production of \( \text{CH}_4, \text{O}_2, \text{H}_2, \) and \( \text{CO} \) in a lean flame, a moderately rich flame and a rich flame respectively. In these figures a species is produced if its net rate of production is positive and it is consumed if its net rate of production is negative. Figures 14, 15, and 16 show that \( \text{CH}_4 \) and \( \text{O}_2 \) are consumed everywhere. Figures 14 and 15 show that in the lean flame and in the moderately rich flame, \( \text{CO} \) is formed in the region where \( \text{CH}_4 \) is consumed. Consumption of \( \text{CO} \) follows consumption of \( \text{CH}_4 \). This justifies approximations employed in previous asymptotic analyses that the reaction zones of lean flames and moderately rich methane flames are made up of two layers [2–7]. Figure 16 shows that \( \text{CO} \) is produced everywhere. Consumption of \( \text{CH}_4 \) and \( \text{O}_2 \) and production of
CO and H₂ take place in the same region. Hence, in the present asymptotic analysis of rich flames all chemical reactions are presumed to take place in one layer.

Figures 17, 18, and 19 show reaction rates of the elementary steps \( \text{CH}_3 + \text{O} = \text{CH}_2\text{O} + \text{H} \), \( \text{CH}_3 + \text{H} = \text{CH}_4 \), and \( \text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6 \). They give rates of consumption of \( \text{CH}_3 \) by these reactions. Figures 17 and 18 show that in the lean flame and in the moderately rich flame the rate of consumption of \( \text{CH}_3 \) by the elementary reaction 35f is the highest. This justifies approximations introduced in previous asymptotic analyses of lean flames and moderately rich flames that, to the leading order, the rate of consumption of \( \text{CH}_3 \) is given by the rate of reaction 35f [2–7]. Figures 17 and 18 show that the rates of consumption of \( \text{CH}_3 \), by the elementary reactions 34f and 36f, in moderately rich flames are higher than those in lean flames. Hence, in previous asymptotic analyses of near stoichiometric and lean flames the contribution of reaction 34f was included as a perturbation [2–6]. In previous asymptotic analyses of moderately rich flames the contribution of reaction 34f to the rate of consumption of \( \text{CH}_3 \) was presumed to be of the same order as that of reaction 35f [7].

Figure 19 shows that in the rich flame the rate of consumption of \( \text{CH}_3 \) by the elementary reaction 36f is the highest. The rate of consumption of \( \text{CH}_3 \) by the elementary reaction 35f is very small in comparison to that by reaction 36f. Thus, in the present asymptotic analysis reaction 36f is presumed to be the principal step by which \( \text{CH}_3 \) is consumed.

**APPENDIX B**

The influence of changes in values of \( \rho \), \( \lambda \), and rate constants of all elementary reactions with temperature on the burning velocity is investigated. These changes are given by
The quantity $\alpha_T = 0.7$ accounts for changes in $\lambda/c_p$ with temperature. The quantities $g_{34f}$ and $g_{36f}$ are obtained from plots of $\ln k_{34f}$ versus $1/T$ and $\ln k_{36f}$ versus $1/T$ for $700 < T < 2000$ and $p = 1$ bar.

The differential equations for $y_{O_2}$ and $y_F$ are written as

$$\frac{d^2y_{O_2}}{d\xi^2} = LG_L \left( g_{35f}y_{O_2}y_H + g_{36f}y_Fy_H - g_{38b}y_{CH_4} \right),$$

$$\frac{d^2y_F}{d\xi^2} = LG_L \left( -g_{34f}y_Hy_{CH_4} + g_{36f}y_Fy_H - g_{38b}y_{CH_4} \right).$$

Equations that give the steady-state concentrations of $y_H$ and $y_{CH_4}$ are

$$-2g_{31f}y_Oy_H + 2g_{35f}y_{O_2}y_H + g_{34f}y_{H_2}y_{CH_4},$$

$$+ g_{35f}y_{H_2}y_{CH_4} - g_{37f}y_{O_2}y_{CH_4},$$

$$+ g_{38f}y_{F_2}y_H - g_{38b}y_{CH_4} = 0$$

$$g_{34f}y_{H_2}y_{CH_4} + g_{35f}y_{H_2}y_{CH_4} + 2g_{36f}y_{H_2}y_{CH_4}^2,$$

$$+ g_{37f}y_{O_2}y_{CH_4} - g_{38f}y_{F_2}y_H + g_{38b}y_{CH_4} = 0.$$

Boundary conditions for Eq. 27 are given by Eqs. 21 and 22. Burning velocities are shown in Fig. 7.

REFERENCES


