Rate-Ratio Asymptotic Analysis of the Influence of Stoichiometric Mixture Fraction on Structure and Extinction of Laminar, Nonpremixed Methane Flames with Comparison to Experiments

Philipp Mairhofer^(a,b), Gerald Mairinger^(a,b), Kalyanasundaram Seshadri^(a), Xue-Song Bai^(c),
Reinhard Seiser^(a), Ernst Pucher^(b),

^(a) Department of Mechanical and Aerospace Engineering, University of California at San Diego, La Jolla, California 92093-0411, USA,

^(b) Institute for Powertrains and Automotive Technology, Vienna University of Technology, A-1040 Vienna, Gusshausstrasse 27-29/315, Austria,

^(c) Division of Fluid Mechanics, Department of Energy Sciences, Lund University, S 221 00 Lund, Sweden.

Corresponding author:

K. Seshadri,

Department of Mechanical and Aerospace Engineering,
University of California at San Diego,

La Jolla, California 92093-0411,

Phone: (858) 534-4876. Fax: (858) 534-5354,

email: seshadri@ucsd.edu

- Revised manuscript # PROCI-D-15-00870
- Preferred colloquium topic: Laminar Flames.
- Word-Length: 5850 words
 - Method 2 was used. The paper was formatted in the two column format recommended by Elsevier (documentclass[final,5p,times,twocolumn]{elsarticle}). The length of the paper (excluding abstract, title block and separate list of figure captions) was 6.5 pages.
 - Total number of words $6.5 \times 900 = 5850$ words
- The color reproduction charges will be paid if applicable

Thirty-Sixth International Symposium on Combustion
COEX, Seoul, Korea
July 31–August 5, 2016

Rate-Ratio Asymptotic Analysis of the Influence of Stoichiometric Mixture Fraction on Structure and Extinction of Laminar, Nonpremixed Methane Flames with Comparison to Experiments

Philipp Mairhofer^{a,b}, Gerald Mairinger^{a,b}, Kalyanasundaram Seshadri^a,
Xue-Song Bai^c, Reinhard Seiser^a, Ernst Pucher^b

^a*Department of Mechanical and Aerospace Engineering, University of California at San Diego, La Jolla, California 92093-0411, USA*

^b*Institute for Powertrains and Automotive Technology, Vienna University of Technology, A-1040 Vienna, Gusshausstrasse 27-29/315, Austria*

^c*Division of Fluid Mechanics, Department of Energy Sciences, Lund University, 22100 Lund, Sweden*

Abstract

Activation energy asymptotic analysis and rate-ratio asymptotic analysis of combustion in laminar, nonpremixed flames are often carried out using conserved scalar quantities as independent variables. One such representation of a conserved scalar quantity is the mixture fraction, ξ , based on thermal diffusivity. These analyses are carried out in the asymptotic limit of large Damköhler number, with chemical reactions presumed to take place in a thin reaction zone that is located at $\xi = \xi_{\text{st}}$. The quantity ξ_{st} is the stoichiometric mixture fraction. A characteristic diffusion time is given by the reciprocal of the scalar dissipation rate, χ . Previous computational studies have shown that the scalar dissipation rate at extinction depends on ξ_{st} and the maximum flame temperature, T_{st} . Here, a rate-ratio asymptotic analysis is carried out using reduced chemistry to elucidate the influence of ξ_{st} on critical conditions

of extinction. The scalar dissipation rate at extinction was predicted as a function of ξ_{st} with the mass fractions of reactants so chosen that the adiabatic flame temperature, T_{st} , is fixed. The predictions of the analysis show that with increasing values of ξ_{st} , the scalar dissipation rate at extinction first increases and then decreases. To test the predictions of the asymptotic analysis, critical conditions of extinction are measured on nonpremixed methane flames stabilized in the counterflow configuration. With increasing values of stoichiometric mixture fraction, the strain rate at extinction was found to increase, and the scalar dissipation rate at extinction was found to first increase and then decrease. The predictions of the asymptotic analysis agreed with experiments. A key outcome of the analysis is that with increasing ξ_{st} , the thickness of the regions where oxygen and fuel are consumed first increase and then decrease. This is responsible for the observed non-monotonic changes in the values of the scalar dissipation rate at extinction with changes in ξ_{st} .

Keywords: rate-ratio asymptotic analysis, conserved scalar, methane flames, extinction, flame structure

1. Introduction

Conserved scalar quantities are frequently employed in fundamental studies of the structure of laminar, nonpremixed flames [1–6]. Nonpremixed combustion takes place in mixing layers between a fuel stream that contains the fuel, and an oxidizer stream that contains oxygen. In analytical studies it is convenient to use these conserved scalar quantities as independent variables. There are many approaches for constructing these variables and they

differ in the manner by which the diffusion of the conserved scalar is characterized [7–9]. One such construction is to require the conserved scalar quantity represented by ξ , to satisfy the source-free conservation equation, $\rho (\vec{v} \cdot \vec{\nabla}) \xi - \vec{\nabla} \cdot [(\lambda/c_p) \vec{\nabla} \xi] = 0$, where $\vec{v}$ is the velocity vector, ρ the density, λ the thermal conductivity, and c_p the heat capacity per unit mass of the mixture. This equation for ξ is constrained to satisfy the conditions, $\xi = 0$ in the oxidizer stream far from the mixing layer and $\xi = 1$ in the fuel stream [1–6]. A characteristic diffusion is given by the reciprocal of the scalar dissipation rate, $\chi = 2[\lambda/(\rho c_p)]|\vec{\nabla} \xi|^2$, [1–6].

In asymptotic analysis of flame structure, all chemical reactions are presumed to take place in a thin reaction zone, that is located at $\xi = \xi_{st}$. To the leading order, the mass fluxes of fuel and oxygen into the reaction zone are in stoichiometric proportions. On either side of this reaction zone, the chemical reactions are presumed to be frozen [1–5] or the flow-field is inert [6, 9–12]. The scalar dissipation rate at $\xi = \xi_{st}$ is represented by χ_{st} . It has been established from activation-energy asymptotic analysis (AEA) [1–5] and rate-ratio asymptotic analysis (RRA) [6, 9–12] that the flame structure and critical conditions of extinction depend on ξ_{st} and T_{st} , where T_{st} is the adiabatic flame temperature.

Grudno and Seshadri [13] have carried out a detailed computational study of the influences of ξ_{st} and T_{st} on the strain rate at extinction, a_q , and scalar dissipation rate at extinction, $\chi_{st,q}$, where the subscript q represents conditions at extinction. This study was carried out for $\xi_{st} < 0.5$. The results

show that at fixed ξ_{st} , the value of $\chi_{st,q}$ and a_q increase with increasing values of T_{st} . At fixed T_{st} , $\chi_{st,q}$ and a_q also increase with increasing ξ_{st} . Chen and Axelbaum [14] have measured critical conditions of extinction for methane flames at fixed T_{st} , and their results show that the strain rate at extinction increases with increasing ξ_{st} . Song et al. [15] carried out an experimental and computational investigation of the effects of ξ_{st} on propagation speeds of edge flames. They found a close correlation between the influence of ξ_{st} on edge flame propagation speed and the influence of ξ_{st} on critical conditions of extinction of nonpremixed flames. In the present study, a rate-ratio asymptotic analysis is carried out to obtain an improved understanding of the influence of ξ_{st} on flame structure and critical conditions of extinction. Although, the fuel considered here is methane, the results of the analysis can be applied to other hydrocarbon fuels. Critical conditions of extinction are predicted. To test the validity of the analysis experiments are carried out on counterflow methane flame. Critical conditions of extinction are measured at fixed values of T_{st} and various values of ξ_{st} . The predictions of the RRA analysis are compared with the measurements.

2. Rate-Ratio Asymptotic Analysis

Previous rate-ratio asymptotic analyses of methane flames were applied to problems where ξ_{st} was small [9, 12]. Here, the analysis is extended to include values of $\xi_{st} > 0.5$. Consider a steady nonpremixed methane flame stabilized in the mixing layer between two laminar streams. One stream, called the fuel stream, is a mixture of methane and nitrogen, and the other stream, called the oxidizer stream, is a mixture of oxygen and nitrogen. In the fuel stream

far from the mixing layer, the mass fraction of fuel is represented by $Y_{F,1}$ and the temperature by T_1 , and in the oxidizer stream, far from the mixing layer the mass fraction of oxygen is represented by $Y_{O_2,2}$, and the temperature by T_2 . Here, subscript F refers to methane, and subscripts 1 and 2, respectively, refer to conditions in the fuel stream and oxidizer stream. If the diffusivity of methane, oxygen, and nitrogen are presumed to be equal to the thermal diffusivity, it has been shown that [9] the stoichiometric mixture fraction, ξ_{st} , is given by

$$\xi_{st} = [1 + 2Y_{F,1}W_{O_2}/(Y_{O_2,2}W_F)]^{-1} \quad (1)$$

and the adiabatic temperature by

$$T_{st} = T_u + Q_F \xi_{st} Y_{F,1} / (W_F c_{p,st}) \quad (2)$$

where W_F and W_{O_2} are the molecular weights of methane and oxygen, $T_u = T_2 + \xi_{st}(T_1 - T_2)$, Q_F is the heat release in the reaction $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, and $c_{p,st}$ is the heat capacity per unit mass of the products.

For convenience, the definitions

$$X_i \equiv Y_i W_{N_2} / W_i, \quad \tau \equiv c_p W_{N_2} (T - T_u) / Q_F, \quad (3)$$

are introduced. Here Y_i , and W_i are respectively the mass fraction and molecular weight of species i and W_{N_2} is the molecular weight of nitrogen. In the analysis, the approximation that the value of the Lewis number of species i , $Le_i = \lambda / (\rho c_p D_i)$, is unity for CH_4 , O_2 , CO_2 , H_2O , and N_2 is introduced, where D_i is the coefficient of diffusion of species i . The conserved scalar quantity, ξ , is used as the independent variable. As a consequence, the

profile of temperature and profiles of mass fractions of all species are evaluated as a function of ξ . Chemical reactions are presumed to take place in a thin reaction-zone that is located at ξ_{st} . The regions $0 \leq \xi < \xi_{\text{st}}$, and $\xi_{\text{st}} < \xi \leq 1.0$, are inert and represent the outer structure. Analysis of the outer structure provides matching conditions for the equations describing the structure of the reaction zone.

2.1. Outer Structure

The profile of temperature, T , and profiles of mass fractions of the reactants CH_4 , and O_2 , and the products CO_2 , and H_2O represent the outer structure of the flame. These profiles are linear functions of ξ , and for constant c_p , the profile of temperature T is also a linear function of ξ . At the reaction zone located at $\xi = \xi_{\text{st}}$, the mass fractions of CH_4 , and O_2 , are zero. In the region $\xi > \xi_{\text{st}}$, $Y_{\text{O}_2} = 0$, and in the region $\xi < \xi_{\text{st}}$, $Y_{\text{F}} = 0$. The gradient of τ , and those of X_i with respect to ξ , are discontinuous at $\xi = \xi_{\text{st}}$. These gradients in the region $\xi > \xi_{\text{st}}$, represented by the subscript $+$, are $(dX_{\text{F}}/d\xi)_+ = X_{\text{F},1}/(1 - \xi_{\text{st}}) = g$, $(d\tau/d\xi)_+ = -\tau_{\text{st}}/(1 - \xi_{\text{st}}) = -p$, and in the region $\xi < \xi_{\text{st}}$, represented by the subscript $-$, are $(dX_{\text{O}_2}/d\xi)_- = -X_{\text{O}_2,2}/\xi_{\text{st}} = -2g$, $(d\tau/d\xi)_- = \tau_{\text{st}}/\xi_{\text{st}} = s$. Element balance gives the relations $X_{\text{CO}_2,\text{st}} = g\xi_{\text{st}}(1 - \xi_{\text{st}})$, and $X_{\text{H}_2\text{O},\text{st}} = 2g\xi_{\text{st}}(1 - \xi_{\text{st}})$ [9]. It follows from Eqs. (2) and (3) that for constant values of the heat capacity $X_{\text{F},1}\xi_{\text{st}} = \tau_{\text{st}}$, hence $g = \tau_{\text{st}}[\xi_{\text{st}}(1 - \xi_{\text{st}})]^{-1}$. As a consequence g is proportional to the sum of the absolute values of the gradient of temperature with respect to ξ in the outer structure.

2.2. Reduced Mechanism

The reduced four-step mechanism that is employed to describe the chemical reactions taking place in the thin reaction zone at $\xi = \xi_{\text{st}}$ is (I) $\text{CH}_4 + 2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 4\text{H}_2$, (II) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, (III) $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$, and (IV) $\text{O}_2 + 3\text{H}_2 \rightleftharpoons 2\text{H} + 2\text{H}_2\text{O}$. Here, global step I represents reactions between fuel and radicals to form the intermediate product CO and H_2 . The global step II represents formation of CO_2 from CO, the global step III represents chain-breaking reactions and global step IV chain-branching reactions. Table 1 shows the elementary reactions that contribute to the

Table 1: Rate data. Units are moles, cubic centimeters, seconds, kJoules, Kelvin.

Number	Reaction	B_n	α_n	E_n
1f	$\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O}$	2.000×10^{14}	0.00	70.30
5	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	2.300×10^{18}	-0.80	0.00
6f	$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	4.400×10^6	1.50	-3.10
7f	$\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$	2.200×10^4	3.00	36.60
8	$\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$	k_0	-1.80	0.00
		k_∞	0.00	0.00
9	$\text{CH}_3 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	7.000×10^{13}	0.00	0.00

rate of these global steps of the reduced mechanism. They are the same as those employed in previous studies [9, 12]. The symbol f appearing in the first column of Table 1 refers to the forward step of a reversible elementary reaction n , and subscript b later will refer to the reverse step. Reactions 5, 8, and 9, are presumed to be irreversible. The rate constant of elementary step

n is $k_n = B_n T^{\alpha_n} \exp[-E_n/(\widehat{R}T)]$, where $\widehat{R}$ is the universal gas constant. The equilibrium constants for the reversible reactions 1, 6, and 7, respectively, are $K_1 = 12.76 \times \exp(-8032/T)$, $K_6 = 8.88 \times 10^{-3} \times \exp(11169/T)$, and $K_7 = 26.21 \times \exp(-245/T)$. The concentration of the third body is represented by C_M . The rate constant for reaction 8 is calculated using the formula given in [16], and [12]. The elementary steps (2) $\text{H}_2 + \text{O} \rightleftharpoons \text{OH} + \text{H}$, and (3) $\text{H}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{H}$ are presumed to maintain partial equilibrium. The quantities $K_2 = 2.28 \times \exp(-963/T)$, and $K_3 = 0.232 \times \exp(7536/T)$ are, respectively, the equilibrium constant of the elementary steps (2) and (3).

2.3. The Structure of the Reaction Zone

The global reactions of the reduced four-step mechanism take place in various layers within the reaction zone [9]. Since radicals participate in all elementary steps, global step IV is active in the entire reaction zone. Figure 1 is a schematic illustration of the structure of the reaction zone. The profile of temperature and profiles of CH_4 , O_2 , H_2 , CO , and H are shown. The temperature profiles shown by the dashed lines in Fig. 1 are projections from the outer structure into the reaction zone. The quantity T^0 is the peak temperature in the reaction zone. Since the chemical reactions take place with finite rates, $T^0 < T_{\text{st}}$. The reaction zone is presumed to be made up of two layers [9]. These layers are the oxidation layer of thickness of the order of ϵ , and an inner layer of thickness of the order of δ . The ordering $\delta \ll \epsilon \ll 1$, is presumed to hold [9, 12]. Figure 1 shows the relative location of these layers with respect to each other in terms of the stretched coordinate η , which is the independent variable in the analysis of the oxidation layer.

are evaluated at T^0 , and changes in the values of these rate parameters with changes in temperature are neglected [6]. The value of T^0 is also obtained in the analysis.

2.3.1. The Oxidation Layer

In the oxidation layer the concentration of fuel is negligible and H is presumed to maintain steady-state. These approximations reduce the four-step mechanism to a two-step mechanism, (II) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, and (III) $\text{O}_2 + 2 \text{H}_2 \rightleftharpoons 2 \text{H}_2\text{O}$. The expansions $\xi - \xi_{\text{st}} = \epsilon(\eta + \eta^0)$, $x_{\text{CO}} = \epsilon 2g z_{\text{CO}}$, $x_{\text{O}_2} = \epsilon g [z_{\text{O}_2} - 2(\eta + \eta^0)]$, are introduced where ϵ is small and the variables η , z_{O_2} , and z_{CO} , are presumed to be of the order of unity. From coupling relations it follows that $x_{\text{H}_2} = \epsilon 2g (z_{\text{O}_2} - z_{\text{CO}})$, and from energy conservation, $\tau = \tau_{\text{st}} - \epsilon [2gq_{\text{CO}}z_{\text{CO}} + gq_{\text{O}_2}z_{\text{O}_2} - s(\eta + \eta^0)]$ [9]. The quantity q_{O_2} represents the fractional heat release in the steps III and IV and q_{CO} the fractional heat release in II. The small expansion parameter ϵ is so chosen that it can be calculated from the equation $\epsilon = D_{\text{III}}^{-1/4}$, where D_{III} is the Damköhler number of the global step III and is given by

$$D_{\text{III}} = 2^{5/2} \rho^0 g^2 k_5^0 C_{\text{M}}^0 \left(K_1^0 K_2^0 K_3^{02} \right)^{1/2} Le_{\text{H}_2}^{3/2} Le_{\text{O}_2}^{3/2} / (\chi^0 X_{\text{H}_2\text{O},\text{st}} W_{\text{N}_2}). \quad (4)$$

It has been shown in [9] that the structure of the oxidation layer can be constructed from numerical integration of two-coupled second order differential equations, one for O_2 and another for CO . The boundary conditions for these equations are obtained from matching to the inert outer structure for large negative values of η and to the inner layer at $\eta = 0$. Figure 2 shows profiles of z_{CO} , and z_{O_2} , as functions of η . These profiles are used to obtain values of these quantities at $\eta = 0$ given by $z_{\text{O}_2}^0$ and z_{CO}^0 . They are then used

Figure 2: Profiles of z_{CO} , and z_{O_2} as functions of η obtained from numerical integration of equations describing the structure of the oxidation layer for $\xi_{\text{st}} = 0.7$ and $\chi^0 = 0.9 \text{ s}^{-1}$.

to evaluate

$$X_{\text{O}_2}^0 = \epsilon g Le_{\text{O}_2} [z_{\text{O}_2}^0 - 2\eta^0], \quad X_{\text{H}_2}^0 = \epsilon 2g Le_{\text{H}_2} (z_{\text{O}_2}^0 - z_{\text{CO}}^0), \quad (5)$$

and the temperature T^0

$$T^0 = T_{\text{st}} - \epsilon (2gq_{\text{CO}} z_{\text{CO}}^0 + gq_{\text{O}_2} z_{\text{O}_2}^0 - s\eta^0) Q_{\text{F}} / (c_{\text{p}} W_{\text{N}_2}). \quad (6)$$

These quantities are required to characterize the structure of the inner layer and calculate the scalar dissipation rate at extinction.

2.3.2. The Structure of the Inner Layer

The analysis of the inner layer is identical to those in [9, 12]. The value of δ is

$$\delta^2 = \frac{2^{3/2} g^2 k_5^0 C_M^0 k_8^0 K_2^{01/2} Le_{O_2}^{3/2} Le_{H_2}^{3/2} \epsilon^4}{k_{7f}^0 k_9^0 K_1^{01/2} Le_F X_{O_2}^0 X_{H_2}^0}. \quad (7)$$

Following the analysis in [12], two coupled second-order differential equations, one for CH_4 and the other for H , are obtained. These equations include an eigenvalue ω given by

$$\omega^2 = \frac{2^{7/2} g^4 \epsilon^4 k_5^0 C_M^0 k_8^{03} K_2^{1/2} X_{H_2O, st}^2 Le_H^2 Le_{O_2}^{3/2} Le_{H_2}^{3/2}}{k_{7f}^0 k_9^{03} K_1^{05/2} K_3^{02} X_{O_2}^0 X_{H_2}^0 Le_F}. \quad (8)$$

The coupled differential equations for CH_4 and H are required to satisfy five boundary conditions [12]. The equations are integrated numerically, with the additional boundary condition being used to obtain ω .

3. Scalar Dissipation Rate

For given values of temperature and mass fractions of the reactants at the boundaries, the outer structure can be constructed. A value of η^0 is selected. The goal is to predict the scalar dissipation rate, χ^0 , that is consistent with this selected value of η^0 . An iterative procedure is employed. It begins by selecting an appropriate value of T^0 . The equations describing the structure of the oxidation layer are integrated, and the results are used to obtain $X_{O_2}^0$ and $X_{H_2}^0$. The coupled differential equations for CH_4 , and for H describing the structure of the inner layer, are integrated, and the value of ω is obtained. This is compared with the value evaluated from Eq. (8). If they are not the same, the procedure is repeated with a different value of T^0 until the value of ω , obtained from integration of the coupled differential equations for CH_4

and H, agrees with that calculated using Eq. (8). The value of χ^0 , that is consistent with the selected value of η^0 , is calculated by recasting Eq. (4) as

$$\chi^0 = 2^{5/2} \rho^0 g^2 k_5^0 C_M^0 \left(K_1^0 K_2^0 K_3^{0^2} \right)^{1/2} Le_{H_2}^{3/2} Le_{O_2}^{3/2} \epsilon^4 / (X_{H_2O, st} W_{N_2}). \quad (9)$$

The entire procedure is repeated with another selected value of η^0 .

The classical C-shaped curve is obtained when T^0 is plotted as a function of $(\chi^0)^{-1}$. The value of $(\chi^0)^{-1}$, where its derivative with respect to T^0 in the C-shaped curve is zero, represents the critical condition at extinction. At this critical condition, the value of χ^0 is denoted by χ_q^0 . To facilitate comparison of predictions of asymptotic analysis of critical conditions of extinction, with experimental results, the scalar dissipation rate at ξ_{st} , denoted χ_{st} , is calculated using the expression [2, 10, 11]

$$\chi_{st} = \chi^0 \exp \left[-2\epsilon \eta^0 / \xi_{st} \right]. \quad (10)$$

The value of χ_{st} at extinction is represented by $\chi_{st,q}$.

4. Experimental Measurements

To test the predictions of the RRA analysis, critical conditions of extinction are measured. Steady, axisymmetric, laminar flow of two counterflowing streams toward a stagnation plane is considered. The counterflow burner used in the experimental study has two ducts. From one duct, called the fuel-duct, a fuel stream made up of methane and nitrogen is injected with a speed of V_1 toward the mixing layer. From the other duct, called the oxidizer duct, an oxidizer stream made up of a mixture of oxygen and nitrogen is injected

at a speed of V_2 . The notation introduced in the RRA analysis is employed to represent the mass fractions of the reactants and their temperatures at the injection planes. The experiments are conducted with $T_1 = T_2 = 298$ K. Hence $T_u = 298$ K, and $Q_F = 803000$ J per mole of methane consumed [17]. Experimental data on critical conditions of extinction are obtained with the values of $Y_{F,1}$ and $Y_{O_2,2}$ so chosen that $T_{st} = 2000$ K. At these conditions, $c_{p,st} = 1300$ J/(kg·K)[17]. It follows from Eq. (2) that $Y_{F,1}\xi_{st} = 0.044$ and from Eq. (1) that $Y_{O_2,2}(1 - \xi_{st}) = 0.177$. These relations are used to evaluate $Y_{F,1}$ and $Y_{O_2,2}$ from selected values of ξ_{st} . The experiments are conducted for values of $0.044 \leq \xi_{st} < 0.823$. For, $\xi_{st} = 0.044$, $Y_{F,1} = 1$, and for $\xi_{st} = 0.823$, $Y_{O_2,2} = 1$.

In experimental studies, a convenient parameter to characterize the residence time is the reciprocal of the strain rate. For the counterflow configuration considered here, the value of the strain rate, defined as the normal gradient of the normal component of the flow velocity, changes from the exit of the fuel duct to the exit of the oxidizer duct [18]. It is discontinuous across the stagnation plane. The local strain rate on the oxidizer side of the stagnation plane, is $a_2 = (2|V_2|/L) [1 + |V_1|\sqrt{\rho_1}/(|V_2|\sqrt{\rho_2})]$ [18]. Here, ρ_1 and ρ_2 are the densities of the reactant streams at the injection plane of the fuel duct and at the injection plane of the oxidizer duct, respectively. The separation distance between the ducts is L . The quantity a_2 is a good measure of the characteristic residence time for $0 < \xi_{st} \leq 0.5$. On the fuel side of the stagnation plane, the local strain rate $a_1 = a_2\sqrt{\rho_2/\rho_1}$, and it represents a better measure of the characteristic residence time for $0.5 \leq \xi_{st} < 1.0$. At

$\xi_{st} = 0.5$, the strain rates of these two measures are discontinuous but do not differ much. The expressions for the strain rates are an exact solution of the inviscid, but rotational, equation of motion obtained in the asymptotic limit of large Reynolds numbers of the reactant streams at the injection planes [18] and are, therefore, fundamentally appropriate representations of the residence time [19].

At a selected ξ_{st} , the values $Y_{F,1}$ and $Y_{O_2,2}$ are calculated and a flame is established at some value of the strain rate less than the extinction strain rate. The strain rate is then increased by increasing V_1 and V_2 simultaneously until extinction is observed. The strain rate at extinction, $a_{2,q}$ and $a_{1,q}$, are recorded as a function of ξ_{st} . The quantities $a_{2,q}$ and $a_{1,q}$ are the values of a_2 and a_1 at extinction. To facilitate comparison of experimental measurements with predictions of RRA analysis, the scalar dissipation rate at extinction, $\chi_{st,q}$ is calculated from a_q using a relation derived by Kim and Williams [20]. This relation is

$$\chi_{st,q} = \frac{a_{2,q}}{2\pi} \frac{3 \left[(T_{st}/T_u)^{1/2} + 1 \right]^2}{2 (T_{st}/T_u)^{1/2} + 1} \times \exp \left\{ -2 \left[\text{erfc}^{-1} (2\xi_{st}) \right]^2 \right\}. \quad (11)$$

Here erfc^{-1} is the inverse of the complimentary error function. Equation (11) is used for evaluating $\chi_{st,q}$ from experimental data for $\xi_{st} < 0.5$. For $\xi_{st} > 0.5$, $\chi_{st,q}$ is calculated with $a_{2,q}$ and ξ_{st} in Eq. (11), respectively, replaced by $a_{1,q}$ and $(1 - \xi_{st})$.

Figure 3 shows the measured strain rates at extinction, and the scalar dissipation rate at extinction $\chi_{st,q}$ as functions of ξ_{st} calculated there from

Figure 3: The measured local strain rates at extinction, $a_{2,q}$ and $a_{1,q}$, and the scalar dissipation rate at extinction $\chi_{st,q}$ calculated using Eq. (11) as functions of ξ_{st} at fixed values of $T_{st} = 2000$ K.

by Eq. (11). In general, at a given ξ_{st} , the values of $a_{2,q}$ and $a_{1,q}$ are nearly the same. The experimental data shows that the strain rates at extinction increase with increasing ξ_{st} . These results are in agreement with previous findings [14]. It is noteworthy that, as ξ_{st} increases from small values, the scalar dissipation rate at extinction, $\chi_{st,q}$, first increases and then decreases. Computations were performed using the San Diego Mechanism [21], and the flame structure and critical conditions of extinction were predicted. The predictions were quite similar to those obtained using the USC II mechanism [22]. The predictions showed that the strain rate at extinction increased with increasing ξ_{st} , while the scalar dissipation rate at extinction first increased and then decreased, in agreement with the trend obtained in the measurements. The computational predictions of the strain rate at extinction were

close to the measurements for small values of ξ_{st} , while for larger values of ξ_{st} , the predictions were higher than the measurements by a factor not greater than 1.5.

To obtain an improved understanding for the reasons for the increase in values of $a_{2,q}$ and $a_{1,q}$ with increase in ξ_{st} , the temperature profile and profiles of mass fraction of various species were calculated using detailed chemistry at a fixed value of the strain rate and various values of ξ_{st} . For all values of ξ_{st} there was nearly complete consumption of CH_4 , but there was leakage of O_2 from the reaction zone (measured as the value of the mass fraction of O_2 at ξ_{st}). Net rates of consumption of CH_4 and O_2 were calculated. With increasing ξ_{st} , the thickness of the regions where these reactants are consumed are found to increase, and leakage of oxygen at conditions close to extinction was found to increase.

5. Results and Discussion

To evaluate critical conditions of extinction, for simplicity, the concentration of the third body, C_M^0 , the density, ρ^0 , and the heat capacity, c_p , are evaluated using the relations $C_M^0 = 20270/T^0 \text{ mol/m}^3$, $\rho^0 = 351/T^0 \text{ kg/m}^3$, and $c_p = 1045 + 0.24T - 0.2T^{-2} \text{ J/(kg}\cdot\text{K)}$ [9, 12, 23]. The molecular weights are $W_F = 0.016 \text{ kg/mol}$, $W_{\text{N}_2} = 0.028 \text{ kg/mol}$, $W_{\text{O}_2} = 0.032 \text{ kg/mol}$, and $W_{\text{H}_2} = 0.002 \text{ kg/mol}$, and the Lewis numbers of various species are $Le_F = 0.97$, $Le_{\text{H}_2} = 0.3$, $Le_{\text{CO}} = 1.11$, and $Le_{\text{H}} = 0.2$ [23], and the fractional heat release $q_{\text{O}_2} = 0.602$, and $q_{\text{CO}} = 0.052$.

Figure 4: The flame temperature, T^0 , as a function of $(\chi^0)^{-1}$ [s], for various values of ξ_{st} and at fixed $T_{st} = 2000$.

Figure 4 shows T^0 and Fig. 5 shows $X_{O_2}^0$ both as functions of $(\chi^0)^{-1}$ for various values of ξ_{st} . All show the classical C-shaped behavior. The upper branches of the C-shaped curves for T^0 vs. $(\chi^0)^{-1}$ and the lower branches for $X_{O_2}^0$ vs. $(\chi^0)^{-1}$ are stable. With decreasing values of $(\chi^0)^{-1}$, the flame temperature decreases and the oxidizer leakage represented by $X_{O_2}^0$ increases. All curves show that there are no solutions for values of $(\chi^0)^{-1}$ below a critical value. This critical value of χ^0 is the scalar dissipation rate at extinction represented by χ_q^0 . It is noteworthy, that at extinction the values of T^0 are nearly the same, while the value of $X_{O_2}^0$ increases with increasing ξ_{st} . The value of the scalar dissipation rate at extinction evaluated at ξ_{st} , $\chi_{st,q}^0$, is obtained from χ_q^0 using Eq. (10).

Figure 5: The normalized mass fraction of O₂, $X_{\text{O}_2}^0$, as a function of $(\chi^0)^{-1}$ [s], for various values of ξ_{st} and at fixed $T_{\text{st}} = 2000$.

Fig. 6 shows the ratio $\chi_{\text{st,q}}/\chi_{\text{st,q,ref}}$ as a function of ξ_{st} . The symbols are experimental data and the solid lines are predictions of the asymptotic analysis. The quantity $\chi_{\text{st,q,ref}}$ is the maximum value of $\chi_{\text{st,q}}$. In the asymptotic analysis, this peak value of 127 s^{-1} is attained at $\xi_{\text{st}} = 0.7$. The symbols in Fig. 6 represent values of $\chi_{\text{st,q}}$ calculated using Eq. (11) and the experimental data for $a_{2,\text{q}}$ for $0 < \xi_{\text{st}} \leq 0.5$ and $a_{1,\text{q}}$ for $0.5 < \xi_{\text{st}} < 1$. The predictions agree well with experimental data. The predictions show that $\chi_{\text{st,q}}$ first increases with increasing ξ_{st} , reaches a peak value and then decreases. Fig. 7 shows values of $z_{\text{O}_2}^0$, z_{CO}^0 , and η^0 as functions of ξ_{st} . The changes in values of these quantities with changes in ξ_{st} are small.

Figure 6: The ratio $\chi_{st,q}/\chi_{st,q,ref}$ at extinction for various values of ξ_{st} and at fixed $T_{st} = 2000$. The symbols represent experimental data and the solid lines are predictions of the asymptotic analysis.

6. The Influence of ξ_{st} On Extinction

The results of the asymptotic analysis are used to obtain an improved understanding of the influence of ξ_{st} on critical conditions of extinction. Figure 8 shows values of ϵ and δ as a function of ξ_{st} . For all ξ_{st} , the value of δ is less than that of ϵ , and both are less than 0.1. This confirms the ordering $\delta \ll \epsilon \ll 1$ employed in the analysis. A key finding is that the value of ϵ and δ increases with ξ_{st} and is consistent with computational predictions of changes in thickness of the regions of oxygen consumption and fuel consumption.

Equation (9) shows that χ^0 depends on T^0 , ϵ , g and $X_{H_2O,st}$, and Eq.

Figure 7: Values of $z_{\text{O}_2}^0$, z_{CO}^0 , and η^0 as function of ξ_{st} .

(6) shows that ϵ depends on g , $z_{\text{O}_2}^0$, z_{CO}^0 , and η^0 . At fixed $T_{\text{st}} = 2000$ K considered here, $\tau_{\text{st}} = 0.0772$, $g = 0.0772 / [\xi_{\text{st}} (1 - \xi_{\text{st}})]$, $X_{\text{H}_2\text{O},\text{st}} = 0.1552$, and $s/g \approx (1 - \xi_{\text{st}})$. Results of the asymptotic analysis described here shows that at conditions close to extinction, changes in the values of T^0 , $z_{\text{O}_2}^0$, z_{CO}^0 , and η^0 with changes in ξ_{st} are small, and their values are, respectively, 1400 K, 0.9, 0.4, -1.2 . After substitution of these values in Eqs. (6) and (5) it follows that

$$\epsilon \approx 0.33 [\xi_{\text{st}} (1 - \xi_{\text{st}})] / (2.0 - 1.3\xi_{\text{st}}), \quad X_{\text{O}_2}^0 = 0.09 / (2.0 - 1.3\xi_{\text{st}}). \quad (12)$$

The peak value of ϵ is around $\xi_{\text{st}} = 0.63$. The value of ϵ obtained from Eq. (12) is plotted in Fig. 8, and it is close to the values obtained from the asymptotic analysis. Equation (12) shows that the leakage of oxygen from the reaction zone increases with increasing ξ_{st} . This is in agreement with the

Figure 8: Predicted value of ϵ and δ as a function of ξ_{st} . The figure also shows the approximate value of ϵ calculated using Eq. (12)

results shown in Fig. 5 and with predictions using detailed chemistry. Equation (7) shows that δ is proportional to ϵ . Thus, changes in the thickness of the inner layer are similar to that of the oxidation layer.

It follows from Eq. (12) that at fixed $T_{st} = 2000$ K and close to critical conditions of extinction, $\epsilon g \approx 0.025 / (2.0 - 1.3\xi_{st})$. Hence the scalar dissipation rate at extinction, χ_q^0 , deduced from Eq. (9) is

$$\chi_q^0 \propto \epsilon^2 / (2.0 - 1.3\xi_{st})^2, \quad (13)$$

Equation (13) shows that χ_q^0 is proportional to ϵ^2 . For fixed $(T_{st} - T_u)$, the quantity $\xi_{st}(1 - \xi_{st})$ is inversely proportional to the sum of the absolute values of the temperature gradients in the outer structure. Therefore it follows from Eqs. (12) and (13) that χ_q^0 is inversely proportional to the square of the sum of the absolute values of the temperature gradients in the outer

structure.

7. Concluding Remarks

The asymptotic analysis gives a clear description of the influence of ξ_{st} on critical conditions of extinction of nonpremixed methane flames. At fixed T_{st} starting from small ξ_{st} , with increasing ξ_{st} , predictions of the asymptotic analysis show that the scalar dissipation rate at extinction, $\chi_{st,q}$, first increases, attains a peak value, and then decreases. Experimental data confirm the accuracy of this prediction. A noteworthy observation is that with increasing ξ_{st} , the thicknesses of the reaction zones first increase and then decrease. The sum of the absolute values of the temperature gradients in the outer structure is inversely proportional to the thickness of the reaction zone. Thus changes in the values of $\chi_{st,q}$ with changes in ξ_{st} follow the changes in values of the thickness of the oxidation layer and as a consequence the sum of the absolute value of the temperature gradient in the outer structure. Another important prediction is that with an increase in values of ξ_{st} , the leakage of oxygen through the reaction zone increases. This occurs because of the shallower concentration gradient on the oxygen side, which affects its evolution through the oxygen-consumption (ϵ) layer.

Computational investigation also was carried out to characterize the influence of ξ_{st} on critical conditions of extinction of methane flames with the chemistry represented by a one-step irreversible reaction $\text{Fuel} + \text{Oxygen} \rightarrow \text{Products}$. It was found that (1) for small ξ_{st} there was leakage of fuel, while for small $(1 - \xi_{st})$ there was leakage of oxygen, and (2) there were very little

changes in the values of the strain rate at extinction with changes in the values of ξ_{st} . Thus, there are fundamental differences in predictions obtained employing detailed chemistry and one-step chemistry.

Acknowledgments

The authors acknowledge the valuable assistance of Dr. Ulrich Niemann with the experimental part of this work. The authors thank Professor P. D. Ronney and Professor F. A. Williams for their comments and helpful discussions. The research at UCSD is supported by the National Science Foundation, award # CBET-1404026.

References

- [1] N. Peters, *Combustion Science and Technology* 30 (1983) 1–17.
- [2] N. Peters, *Progress in Energy and Combustion Science* 10 (1984) 319–339.
- [3] A. Liñán, *Acta Astronautica* 1 (1974) 1007–1039.
- [4] F. A. Williams, *Combustion Theory*, Addison-Wesley Publishing Company, Redwood City, CA, 2 edition, 1985.
- [5] A. Liñán, F. A. Williams, volume 34 of *Oxford Engineering Science Series*, Oxford University Press, New York, 1993.
- [6] K. Seshadri, *Proceedings of the Combustion Institute* 26 (1996) 831–846.
- [7] K. Seshadri, C. Trevino, *Combustion Science and Technology* 64 (1989) 243–261.

- [8] U. Niemann, K. Seshadri, F. A. Williams, *Combustion Theory and Modelling* 17 (2013) 563–576.
- [9] K. Seshadri, X. S. Bai, *Combustion Science and Technology* 187 (2015) 3–26.
- [10] K. Seshadri, N. Peters, *Combustion and Flame* 73 (1988) 23–44.
- [11] B. Yang, K. Seshadri, *Combustion Science and Technology* 88 (1992) 115–132.
- [12] X. S. Bai, K. Seshadri, *Combustion Theory and Modelling* 3 (1999) 51–75.
- [13] A. Grudno, K. Seshadri, *Combustion Science and Technology*, 112 (1996) 199–210.
- [14] R. Chen, R. L. Axelbaum, *Combustion and Flame* 142 (2005) 62–71.
- [15] H. Song, P. Wang, R. S. Boles, D. Matinyan, H. Praphanphap, J. Piotrowicz, P. D. Ronney, in: Paper # 1B05 presented at the 2016 Spring Technical Meeting of the Western States Section Combustion Institute, University of Washington, Seattle, WA.
- [16] N. Peters, in: N. Peters, B. Rogg (Eds.), *Reduced Kinetic Mechanisms for Applications in Combustion Systems*, volume m15 of *Lecture Notes in Physics*, Springer-Verlag, Heidelberg, 1993, pp. 1–13.
- [17] NIST-JANAF Thermochemical Tables, <http://kinetics.nist.gov/janaf/>, 2013.

- [18] K. Seshadri, F. A. Williams, International Journal of Heat and Mass Transfer 21 (1978) 251–253.
- [19] H. Schlichting, Boundary-Layer Theory, Mc Graw Hill, Inc, 1968.
- [20] J. S. Kim, F. A. Williams, SIAM Journal on Applied Mathematics 53 (1993) 1551–1566.
- [21] P. Saxena, Numerical and Experimental Studies of Ethanol Flames and Autoignition Theory for Higher Alkanes, Ph.d thesis, University of California at San Diego, Department of Mechanical and Aerospace Engineering, 2007.
- [22] H. Wang, X. You, A. V. Joshi, S. G. Davis, A. Laskin, F. Egolfopoulos, C. K. Law, Usc mech version II. High-Temperature Combustion Reaction Model of H₂/CO/C₁-C₄ Compounds. http://ignis.usc.edu/usc_mech_ii.htm, 2007.
- [23] M. D. Smooke, V. Giovangigli, in: M. D. Smooke (Ed.), Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames, volume 384 of *Lecture Notes in Physics*, Springer Verlag Berlin Heidelberg, 1991, pp. 1–28.

List of Tables

1	Rate data. Units are moles, cubic centimeters, seconds, kJoules, Kelvin.	7
---	--	---

List of Figures

1	Schematic illustration of the structure of the reaction zone at ξ_{st} . The figure shows the inner layer and the oxidation layer. .	9
2	Profiles of z_{CO} , and z_{O_2} as functions of η obtained from numerical integration of equations describing the structure of the oxidation layer for $\xi_{st} = 0.7$ and $\chi^0 = 0.9 \text{ s}^{-1}$	11
3	The measured local strain rates at extinction, $a_{2,q}$ and $a_{1,q}$, and the scalar dissipation rate at extinction $\chi_{st,q}$ calculated using Eq. (11) as functions of ξ_{st} at fixed values of $T_{st} = 2000 \text{ K}$.	16
4	The flame temperature, T^0 , as a function of $(\chi^0)^{-1} [\text{s}]$, for various values of ξ_{st} and at fixed $T_{st} = 2000$	18
5	The normalized mass fraction of O_2 , $X_{O_2}^0$, as a function of $(\chi^0)^{-1} [\text{s}]$, for various values of ξ_{st} and at fixed $T_{st} = 2000$	19
6	The ratio $\chi_{st,q}/\chi_{st,q,ref}$ at extinction for various values of ξ_{st} and at fixed $T_{st} = 2000$. The symbols represent experimental data and the solid lines are predictions of the asymptotic analysis.	20
7	Values of $z_{O_2}^0$, z_{CO}^0 , and η^0 as function of ξ_{st}	21
8	Predicted value of ϵ and δ as a function of ξ_{st} . The figure also shows the approximate value of ϵ calculated using Eq. (12) . .	22