HIGH-TEMPERATURE RADICAL GROWTH IN THE HYDROGEN-OXYGEN COUNTERFLOW MIXING LAYER

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Introduction. The counterflow mixing layer has been widely used to investigate the interactions between flow field and chemistry in nonpremixed combustion. The steady reacting solutions in such a configuration can be characterized by the peak temperature as a function of the strain rate, giving an S-shape curve whose upper and lower turning points represent conditions for extinction and ignition, respectively [1]. A number of analytical and numerical studies have been performed on the ignition of steady hydrogen-oxygen systems in recent years, with both reduced and detailed chemistry [2]–[5]. Theoretical analyses in the high-temperature regime [3, 5] have shown that, for temperatures above the crossover value (the temperature at which the rate of the main radical-branching step, $H + O_2 \rightarrow$ OH + O, equals that of the main radical-recombination step, $H + O_2 + M \rightarrow HO_2 + M$), ignition emerges as a bifurcation from the chemically frozen branch when the Damköhler number, Δ , based on the time scales of the strain rate and the relevant branching reaction, is increased to a critical value, Δ_c , of order unity. It was also found that, for sufficiently high temperatures, the bifurcation becomes supercritical, a behavior also observed in numerical calculations [2, 4].

In contrast, relatively few studies have dealt with unsteady ignition histories in strained mixing layers [9, 10]. These analyses employ a simple Arrhenius reaction rate, and thus ignition is described by thermal runaway. However, ignition in the high-temperature hydrogen-air mixing layer for $\Delta > \Delta_c$ exhibits a more complex behavior. After a short initial period controlled by the initiation reactions, the solution undergoes a chain-branching explosion in which the radical pool increases exponentially with time. The ignition stage is completed as the radicals reach mole fractions of order unity, for which the branching reactions attain partial equilibrium. Further development of the solution involves radical recombination and significant heat release, eventually leading to the establishment of a diffusion flame.

The influence of the flow field on the spontaneous ignition history of a turbulent H_2 -O₂ mixing layer was recently investigated through a direct simulation with detailed chemistry [8]. It was found that the variation in ignition delay time is very small for a wide range of turbulence intensities, including a case where the eddy turnover time is approximately one third of the ignition delay. This largescale numerical study, however, is limited to only a few flow conditions, and thus lacks a complete parametric description of the issue. Therefore, in this paper we consider the unsteady evolution of the high-temperature hydrogen-air laminar counterflow mixing layer under a wide range of the constant strain rates, *a*. The initial conditions are chosen as those of the nonreacting mixing layer, by suppressing all the reactions. The analysis provides the ignition delay as a function of the strain rate, thereby allowing for a more concrete description of the ignition response under a wide range of flow conditions.

Reduced Kinetic Mechanism and Formulation We consider the case where the temperature is sufficiently above the crossover value. The three-body recombination reaction is then negligible, and the initiation reaction $H_2 + O_2 \xrightarrow{1} OH + OH$ and radical-branching reactions $H + O_2 \xrightarrow{2} OH + O$, $H_2 + O \xrightarrow{3} OH + H$, $H_2 + OH \xrightarrow{4} H_2O + H$ suffice to describe the branched-chain process. This scheme can be further simplified by assuming that the OH radical maintains steady state everywhere [6], reducing the four-step mechanism to the three overall reactions $3H_2 + O_2 \xrightarrow{1} 2H + 2H_2O$, $H_2 + O_2 \xrightarrow{11} O + H_2O$ and $2H_2 + O \xrightarrow{111} 2H + H_2O$ with global rates ω_1 , ω_2 , and ω_3 respectively. Updated values of the reaction-rate constants corresponding to steps 1–3 are available [7].

In the radical growth stage, reactant consumption and heat release can be neglected in the first approximation, so that chain-branching is described by integrating the radical conservation equations with the chemical terms evaluated with the frozen reactant concentration and frozen temperature profiles. We further adopt a Fickian description for the diffusion velocities and assume that the density ρ , kinematic viscosity, ν , thermal diffusivity, α , and diffusion coefficients, D_i , all have uniform values across the mixing layer. The conservation equations for the radicals then simplify to

$$\frac{\partial y_{\rm H}}{\partial \tau} - \frac{1}{\Delta} \left(\eta \frac{\partial y_{\rm H}}{\partial \eta} + \frac{1}{S_{\rm H}} \frac{\partial^2 y_{\rm H}}{\partial \eta^2} \right) = \kappa_{\rm I}(\eta) + 2\gamma \kappa_{\rm III}(\eta) y_{\rm O} \tag{1}$$

and

$$\frac{\partial y_{\rm o}}{\partial \tau} - \frac{1}{\Delta} \left(\eta \frac{\partial y_{\rm o}}{\partial \eta} + \frac{1}{S_{\rm o}} \frac{\partial^2 y_{\rm o}}{\partial \eta^2} \right) = \kappa_{\rm II}(\eta) y_{\rm H} - \gamma \kappa_{\rm III}(\eta) y_{\rm o} \tag{2}$$

with initial conditions $y_0(0,\eta) = y_H(0,\eta) = 0$ and boundary conditions $y_0(\tau,\pm\infty) = y_H(\tau,\pm\infty) = 0$, where $\eta = (a/\nu)^{1/2}y$ and $\tau = \rho k_{2\infty} Y_{O_{2\infty}} t/W_{O_2}$ are appropriate dimensionless forms of the transverse coordinate and evolution time, while $S_i = \nu/D_i$ denotes the Schmidt number of species *i*. In the formulation, W_i and y_i denote the molecular weight and mass fraction of species $i, \beta_i = E_i/(R^o T_\infty)$ is the nondimensional activation energy of reaction j evaluated at the oxidizer-side temperature. The subscripts ∞ and $-\infty$ refer to freestream properties at the oxidizer and fuel boundaries, respectively, and the subscript f denotes chemically-frozen profiles. The constant Damköhler number $\Delta = \rho k_{2\infty} Y_{Q_{2,\infty}} / (aW_{Q_{2,\infty}})$ is based on the characteristic branching time of reaction II, the functions $\kappa_{I} = \exp[\beta_{I}\theta_{f}/(1+\theta_{f})]y_{0,2f}y_{H_{2f}}$ $\kappa_{\text{II}} = \exp[\beta_2 \theta_f / (1+\theta_f)] y_{\circ_2 f}$, and $\kappa_{\text{III}} = \exp[\beta_3 \theta_f / (1+\theta_f)] y_{\text{H}_2 f}$, all quantities of order unity, represent reduced Damköler numbers evaluated across the mixing layer with the local frozen values of the reactant mass fractions and temperature. The parameter $\gamma = k_{3\infty} W_{o_2} Y_{H_2 - \infty} / k_{2\infty} W_{H_2} Y_{o_2 \infty}$ is the ratio of the characteristic branching time of reaction II to that of reaction III, a quantity that takes relatively large values for undilute fuel feed. The frozen reactant mass fractions and frozen temperature profiles are scaled according to $y_{0_{2f}} = Y_{0_{2f}}/Y_{0_{2\infty}} = 1 - 0.5 \operatorname{erfc}[(S_{0_2}/2)^{1/2}\eta], y_{H_{2f}} = Y_{H_{2f}}/Y_{H_{2-\infty}} = 0.5 \operatorname{erfc}[(S_{H_2}/2)^{1/2}\eta]$ and $\theta_f = (T_f - T_\infty)/T_\infty = 0.5 \ \theta_{-\infty} \operatorname{erfc}[(Pr/2)^{1/2}\eta]$, where $Pr = \nu/\alpha$ is the Pradtl number and $\theta_{-\infty} = (T_{-\infty} - T_{\infty})/T_{\infty}$. The radical mass fractions $y_{\rm H} = k_{2\infty}W_{\rm H_2}Y_{\rm H}/2k_{1\infty}W_{\rm H}Y_{\rm H_{2-\infty}}$ and $y_{\rm o} = k_{2\infty}W_{\rm H_2}Y_{\rm O}/2k_{1\infty}W_{\rm O}Y_{\rm H_{2-\infty}}$ are scaled with the ratio of the branching time to the initiation time $\varepsilon = k_{1\infty}/k_{2\infty}$, a very small quantity that takes, for instance, the values 1.7×10^{-7} and 4.3×10^{-5} at $T_{\infty} = 1200$ K and $T_{\infty} = 2000$ K, respectively.

The chemistry description utilized here assumes small values for the radical mass fractions, thereby neglecting the backward rates of reactions 2–4. Therefore, Eqs. 1 and 2 cease to be valid as the radical mass fractions reach values of order unity, leading through a short adjustment period not studied here to a solution with partial equilibrium of the shuffle reactions 2–4. Since this adjustment period is much shorter than the autocatalytic growth stage described here, for practical purposes one may assume that partial equilibrium is achieved as the solution to Eqs. 1 and 2 yield radical mass fractions of order unity, i.e., values of the variables $y_{\rm H}$ and $y_{\rm o}$ of order $\varepsilon^{-1} \gg 1$.

Analytical Solution. The exact solution to the linear Eqs. 1 and 2 with the previously stated initial and boundary conditions can be found in the form

$$\begin{pmatrix} y_{\rm H} \\ y_{\rm O} \end{pmatrix} = \sum_{n=1}^{\infty} \frac{\alpha_n}{\lambda_n} \begin{pmatrix} \Phi_{\rm H} \\ \Phi_{\rm O} \end{pmatrix}_n [\exp(\lambda_n \tau) - 1], \tag{3}$$

where λ_n and $(\Phi_{\rm H}, \Phi_{\rm o})_n$ denote the discrete set of eigenvalues and corresponding eigenfunctions of the associated problem

$$\begin{pmatrix} \Phi_{\rm H}^{\prime\prime}/S_{\rm H} \\ \Phi_{\rm O}^{\prime\prime}/S_{\rm O} \end{pmatrix} + \eta \begin{pmatrix} \Phi_{\rm H}^{\prime} \\ \Phi_{\rm O}^{\prime} \end{pmatrix} + \Delta \begin{bmatrix} 0 & 2\gamma\kappa_{\rm III} \\ \kappa_{\rm II} & -\gamma\kappa_{\rm III} \end{bmatrix} \begin{pmatrix} \Phi_{\rm H} \\ \Phi_{\rm O} \end{pmatrix} = \Delta\lambda_n \begin{pmatrix} \Phi_{\rm H} \\ \Phi_{\rm O} \end{pmatrix}$$
(4)

with boundary conditions $\Phi_{\rm H}(\pm\infty) = \Phi_{\rm o}(\pm\infty) = 0$. In the notation, the prime denotes differentiation with respect to the coordinate η . The constants α_n must be chosen so that

$$\begin{pmatrix} \kappa_{\rm I} \\ 0 \end{pmatrix} = \sum_{n=1}^{\infty} \alpha_n \begin{pmatrix} \Phi_{\rm H} \\ \Phi_{\rm o} \end{pmatrix}_n, \tag{5}$$

an equation that can be solved for α_n by using the orthogonality condition between the eigenfunctions of Eq. 4 and those of its corresponding adjoint problem. The eigenfunctions are normalized so that their maximum value is one.

If the Damköhler number is smaller than the critical value Δ_c mentioned above, then all resulting λ_n are negative, and the solution develops from $y_{\rm H} = y_{\rm o} = 0$ to a final state with peak values of the functions $y_{\rm H}$ and $y_{\rm o}$ of order unity corresponding to a quasi-frozen state. The value of Δ_c can be easily determined as the smallest positive value of Δ for which a nontrivial solution to Eq. 4 with $\lambda_n = 0$ exists [5]. If $\Delta > \Delta_c$, then at least one positive value of λ_n exists, and the solution undergoes a chain-branching explosion. The associated radical profiles given in Eq. 3 take for $\lambda_1 \tau \gg 1$ the simplified form

$$\begin{pmatrix} y_{\rm H} \\ y_{\rm O} \end{pmatrix} = \frac{\alpha_1}{\lambda_1} \begin{pmatrix} \Phi_{\rm H} \\ \Phi_{\rm O} \end{pmatrix}_1 \exp(\lambda_1 \tau), \tag{6}$$

where the subscript 1 refers to the largest positive eigenvalue and its corresponding eigenfunction, and the coefficient α_1 is computed from the approximate equation

$$\alpha_{1} = \frac{\int_{-\infty}^{+\infty} \left[\Phi_{\mathrm{H}} \Phi_{\mathrm{o}} \right]_{1} \left[\kappa_{\mathrm{I}}(\eta) \\ 0 \right] \mathrm{d}\eta}{\int_{-\infty}^{+\infty} \left[\Phi_{\mathrm{H}} \Phi_{\mathrm{o}} \right]_{1} \left[\Phi_{\mathrm{H}} \\ \Phi_{\mathrm{o}} \right]_{1} \mathrm{d}\eta}$$
(7)

Since ignition occurs when the scaled radical mass fractions $y_{\rm H}$ and $y_{\rm o}$ reach peak values of order ε^{-1} , Eq. 6 yields

$$\tau_{ig} = \ln(\varepsilon^{-1}) / \lambda_1 \tag{8}$$

as an approximate expression for the ignition time. The maximum value of $y_{\rm H}$ obtained from the oneterm approximation given in Eq. 6 with α_1 calculated from Eq. 7 is compared with results of numerical integrations of Eqs. 1 and 2 in figure 1, indicating that Eq. 8 provides an accurate prediction for τ_{ig} .

The Limit of Large Damköhler Numbers. When the strain time is larger than the branching time ($\Delta \gg 1$), the chemical reaction is seen to be confined to a thin layer of thickness $\Delta^{-1/4}$ where radical transport by convection is inconsequential. The resulting ignition time becomes independent of a in the first approximation. The method employed to analyse this asymptotic limit of large Damköhler numbers, as well as the main results, are summarized below.

The thin chemical-reaction layer is found to be located at $\eta = \eta^*$, with η^* determined as the location where the effective Damköhler number

$$\kappa(\eta) = \frac{-\gamma \kappa_{\text{\tiny III}}(\eta) + \sqrt{\gamma^2 \kappa_{\text{\tiny III}}(\eta)^2 + 8\gamma \kappa_{\text{\tiny III}}(\eta) \kappa_{\text{\tiny III}}(\eta)}}{2}$$

reaches its peak value $\Gamma_1 = \kappa(\eta^*)$, which turns out to be the first coefficient in the asymptotic expansion $\lambda_n = \Gamma_1 + \Delta^{-1/2}\Gamma_2 + \cdots$ for all λ_n . To determine Γ_2 one needs to investigate the leading-order form of the radical profiles $\Phi_{\rm H}(\xi)$ and $\Phi_{\rm o}(\xi) = \Gamma_1 \Phi_{\rm H}(\xi)/[2\gamma\kappa_{\rm III}(\eta^*)]$ by introducing the stretched coordinate $\xi = [-2\Delta S\kappa''(\eta^*)]^{1/4}(\eta - \eta^*)$, where $S = [2\Gamma_1 + \gamma\kappa_{\rm III}(\eta^*)]/\{[\Gamma_1 + \gamma\kappa_{\rm III}(\eta^*)]/S_{\rm H} + \Gamma_1/S_{\rm o}\}$ is an effective Schmidt number. The problem reduces to the solution of the parabolic cylinder equation [11]

$$\Phi_{\rm H}^{\prime\prime} - (\xi^2/4 + \Lambda)\Phi_{\rm H} = 0; \quad \Phi_{\rm H}(\pm\infty) = 0,$$

which possesses solutions $\Phi_{\rm H} = \exp(-\xi^2/4)$, $\xi \exp(-\xi^2/4)$, \cdots for a discrete set of eigenvalues $\Lambda = -1/2, -3/2, \cdots$, thereby determining the value of Γ_2 through the definition $\Lambda = \{-S/[2\kappa''(\eta^*)]\}^{1/2}\Gamma_2$.

In the first approximation, the asymptotic analysis gives the radical profiles

$$y_{\rm H}(\xi,\tau) = \frac{2\gamma\kappa_{\rm III}(\eta^*)}{\Gamma_1} y_{\rm O} = \frac{\sqrt{2}\kappa_{\rm I}(\eta^*)}{\Gamma_1\{1 + [2\gamma\kappa_{\rm III}(\eta^*)/\Gamma_1]^{-2}\}} \exp(-\xi^2/4) \exp[(\Gamma_1 + \Delta^{-1/2}\Gamma_2)\tau]$$
(9)

where $\Gamma_1(\gamma, \theta_{-\infty})$ and $\Gamma_2(\gamma, \theta_{-\infty})$ can be easily computed as indicated above. The analysis also yields

$$t_{ig} = \frac{W_{o_2}}{\Gamma_1 \rho k_{2\infty} Y_{o_{2\infty}}} \ln(k_{2\infty}/k_{1\infty}) \left(1 - \Delta^{-1/2} \Gamma_2/\Gamma_1\right)$$
(10)

as an approximate expression for the ignition time, which becomes increasingly accurate for increasing values of Δ as can be seen from the comparisons provided in Figures 1 and 2. Figure 2 shows comparisons of the ignition times results given by Eqs. 10 and 8 with numerical calculations of the complete conservation equations with detailed transport and chemistry description. It is seen that these results agree well for large Damköhler numbers, where the ignition delay is insensitive to the strain rate. It is also shown that the ignition delay predicted by the asymptotic solution, Eq. 10, becomes inaccurate as Δ approaches Δ_c , a limit which requires further analysis.

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Figure 1: The maximum value of $y_{\rm H}$ corresponding to undilute fuel feed ($\gamma = 200$) with $\theta_{\infty} = 0$ as obtained from the numerical integrations of Eq. 1 and 2 (solid line), from the analytical solution retaining one eigenfunction given in Eq. 6 (dashed line), and from the asymptotic solution given in Eq. 9 with one term (dotted line) and two terms (dashed-dotted line) in the eigenvalue expansion. The numerical values of the parameters in Eq. 6 are $\alpha_1 = 0.214$ and $\lambda_1 = 1.4988$ for $\Delta = 10$, and $\alpha_1 = 0.2101$ and $\lambda_1 = 1.7520$ for $\Delta = 100$, while those appearing in Eq. 9 are $\Gamma_1 = 1.8457$, $\Gamma_2 = -0.8897$, $\kappa_1(\eta^*) = 0.1434$ and $\kappa_{\rm III}(\eta^*) = 0.1462$, with $\eta^* = 2.415$.



Figure 2: Ignition delay times as obtained from numerical integrations of the complete conservation equations with detailed transport and chemistry description (solid line), from the analytical solution given in Eq. 8 (dashed line), and from the asymptotic solution given in Eq. 10 (long-dashed line).