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Measurement and correlation of laminar flame speeds of CO and C₂ hydrocarbons with hydrogen addition at atmospheric and elevated pressures

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ABSTRACT

The laminar flame speeds of mixtures of ethane, ethylene, acetylene, and carbon monoxide with small amount of hydrogen addition at atmospheric and elevated pressures were experimentally and computationally determined. It was found that the approximate linear correlation identified previously between the laminar flame speeds and an appropriate definition of the amount of hydrogen addition for methane, propane and *n*-butane at atmospheric pressure also largely applies to ethane, ethylene, and acetylene at atmospheric as well as elevated pressures. The linear correlation, however, does not hold for carbon monoxide, at all pressures, due to the strong catalytic effect of hydrogen on the oxidation of carbon monoxide. A mechanistic analysis shows that both the Arrhenius and diffusive contributions to the laminar flame speed are nearly linear functions of the hydrogen addition, which explains this overall approximate linear correlation.

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1. Introduction

The strong reactivity of hydrogen renders it an attractive additive to enhance flame propagation and extend the flammability limits of fuel/air mixtures, and as such offers rich potential to promote combustion efficiency and reduce pollutant and greenhouse gas emissions. The fundamental combustion parameter that compactly characterizes and quantifies the effects of hydrogen addition is the laminar flame speed, which embodies information about the exothermicity, reactivity and diffusivity of the mixture.

In 1959, Scholte and Vaags [1,2] measured the flame speeds of hydrogen/methane and hydrogen/carbon monoxide mixtures with a tube burner. More recently [3–31], experimental work on the effects of hydrogen addition has been conducted using the expanding spherical flame method

[3,4,9–11,14–24,26,28,31], the counterflow, stagnation flame method [5,6,8,27,29], the flat-burner flame method [7,12,13,25] and the Bunsen flame method [29,30]. These studies cover hydrogen mixtures with methane [3–6,8–10,12–16,20–22,25], ethylene [9], acetylene [4], propane [3,4,6,9,17,18], *n*-butane [7,24], iso-octane [16,23], carbon monoxide [2,26–31] and natural gas [11,19]. Most of these studies [1–5,8–23,25–31] employed the hydrogen mole fraction in the fuel mixture to characterize the amount of hydrogen addition. The results for hydrocarbon/air mixtures showed a weak dependence on hydrogen addition up to about 50% hydrogen mole fraction, and a rapid increase thereafter. For carbon monoxide, the flame speed increases rapidly in a catalytic manner with even a small amount of hydrogen addition.

Yu et al. [6] used the symmetric counterflow flame to measure the laminar flame speeds of methane/air and

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propane/air mixtures with hydrogen addition, and characterized the amount of addition with a parameter R_H , which will be defined later. The results showed that regardless of whether the mixture was lean or rich, the increase in the flame speed can be approximately linearly correlated with R_H . This simple correlation has generated considerable interest with substantial follow-on investigations. In particular, Sher and Ozdor [7] and Tang et al. [24] used the flat-burner flame method and the expanding spherical flame method, respectively, to measure the laminar flame speeds of n-butane/air mixtures with hydrogen addition, and found that the linear correlation again holds approximately. Additionally, Tang et al. [24] noted that hydrogen addition influences the flame speed through increased flame temperature (thermal effect), enhanced reactivity (kinetic effect) and facilitated diffusion (diffusion effect). Furthermore, their sensitivity analysis showed that the kinetic effect is the most prominent, followed by the thermal effect, with the diffusion effect being minimal.

The primary motivation for the present investigation is the recognition that while the approximate linear correlation has been demonstrated for three fuels, namely methane [6], propane [6] and n-butane [7,24], they are all n-alkanes and as such have similar kinetic and thermal characteristics. Because of the strong kinetic and thermal effects associated with hydrogen addition, as demonstrated in Ref. [24], it behooves us to extend the investigation to fuels with distinctively different kinetic and thermal characteristics. We have therefore conducted our assessment along the following three considerations.

First, we have studied the C_2 -group of the paraffins, namely ethane, ethylene and acetylene, because they have distinctively different kinetic and thermal properties among themselves. Furthermore, since they have similar diffusivities, potential differences in the diffusion effect are suppressed. Second, we have also used carbon monoxide as a target fuel because hydrogen is known to have a strong catalytic effect on the oxidation of carbon monoxide, and as such its use would provide a critical assessment on the potential deviation from linearity due to strong kinetic coupling. Third, we have further manipulated the kinetic effect by performing experiments under elevated pressures, recognizing the strong kinetic influence on the progress of reactions through pressure variations, which facilitate three-body termination reactions relative to the two-body carrying and branching reactions.

Results from these three series of assessments are presented in the following, after specifications of the experimental and computational aspects of the investigation.

2. Experimental and computational specifications

2.1. Experimental setup

The laminar flame speed was determined by using expanding spherical flames, employing the dual-chamber design of Tse et al. [34]. This apparatus has been used to generate extensive data on the laminar flame speeds of a variety of fuels in recent years. Details of the design and operational procedure are given in Ref. [34]. Briefly, the apparatus consists of a small

inner chamber surrounded by a substantially larger outer chamber. The inner chamber is filled with the test mixture while the outer chamber is filled with a mixture of inert gases whose density and pressure match those of the test mixture. The test mixture in the inner chamber is subsequently spark-ignited, resulting in an expanding spherical flame. Just prior to the moment of spark ignition a series of holes are aligned to connect the environments of the inner and outer chambers such that flame propagation is naturally quenched as the flame reaches the interface of the chambers. This dual-chamber design also ensures that flame propagation takes place at constant pressure and upstream temperature due to the large volume of the inert gases in the outer chamber. The maximum pressure rise has been measured to be less than 3% for the entire chamber [34]. The time-resolved schlieren flame images are recorded using a high-speed digital camera and the flame radius can be determined as a function of time by tracking the flame front image.

Standard air was used as the oxidizer for experimentation at atmospheric pressure. At elevated pressures oxygen/helium mixtures were used because helium has a higher thermal conductivity than nitrogen and thus can increase the mixture's Lewis number and suppress the onset of cellular instabilities. All hydrocarbon fuels had a minimum purity of 99.5% while hydrogen had a purity of 99.99%. Carbon monoxide had a purity of 99.99%, with the total moisture, hydrogen and hydrocarbon concentrations less than 10 ppm. The air or oxygen/inert mixtures used were synthetic mixtures of pure oxygen and pure inert (nitrogen or helium), both of which had a minimum purity of 99.99%; however, the oxygen/inert ratio in these mixtures had a relative uncertainty of approximately $\pm 2\%$. The experimental uncertainty in the equivalence ratio was approximately $\pm 2\%$ and the hydrogen addition parameter, R_H , had an absolute uncertainty of approximately ± 0.005 .

2.2. Data analysis

The experimental data on the propagation speed of expanding spherical flames was used to extrapolate the laminar flame speed using a nonlinear equation recently derived by Kelley et al. [35],

$$S_b^0 = \frac{dr_f}{dt} \left(1 + \frac{2L_b}{r_f} + \frac{4L_b^2}{r_f^2} + \frac{16L_b^3}{3r_f^3} \right) \quad (1)$$

where S_b^0 is the adiabatic, unstretched gas speed of the burned mixture relative to the flame, r_f the flame radius, L_b the Markstein length and t the time. This equation was derived from an asymptotic analysis based on large activation energy for premixed flames allowing general Lewis numbers. It contains up to third order accuracy in terms of inverse powers of radius of the nonlinear relationship between stretch and flame speed.

Integrating Eq. (1) yields

$$S_b^0 t + C = r_f + 2L_b \ln r_f - \frac{4L_b^2}{r_f} - \frac{8L_b^3}{3r_f^2} \quad (2)$$

based on which S_b^0 and L_b can be determined through least-square fitting of the experimental data of r_f versus t . The

laminar flame speed, S_u^0 , can then be calculated from the continuity relation,

$$\rho_u^0 S_u^0 = \rho_b^0 S_b^0 \quad (3)$$

where ρ_u^0 and ρ_b^0 are respectively the densities of the unburned and burned mixtures, which can be calculated by using the STANJAN equilibrium program [40].

For flame speed measurements using expanding spherical flames, the data chosen for extrapolation need to be in a certain radius range in that the small and large radius data are contaminated by the influences of ignition and the hydrodynamic aspects of chamber confinement, respectively. In the present study, we used the data in the radius range between 0.7 cm and 1.5 cm. Based on repeated measurements and the sensitivity of selection of the data range for extrapolation, all reported laminar flame speeds in this paper have an absolute uncertainty of ± 1.5 cm/s and relative uncertainty of $\pm 4\%$ approximately.

2.3. Composition parameters

The conventional parameters used in most previous studies to designate the amount of hydrogen addition is the mole fraction of hydrogen in the total fuel mixture defined as

$$\frac{C_H}{C_H + C_F} \quad (4)$$

where C_F and C_H are the mole concentrations of the fuel (other than hydrogen) and hydrogen, respectively. This definition imposes a disproportionately larger measure of the hydrogen concentration on the flame response because, on a molar basis, the consumption of hydrogen requires much less oxygen, releases much less heat, and heats up much less of the nitrogen associated with the corresponding amount of oxygen in the air, as compared to a typical hydrocarbon which consists of not only carbon atom(s) but also substantially more hydrogen atoms.

Recognizing the skewed nature of Eq. (4), Yu et al. [6] proposed the following composition parameters for a more balance indication of the hydrogen addition:

$$R_H = \frac{C_H + C_H/(C_H/C_A)_{st}}{C_F + [C_A - C_H/(C_H/C_A)_{st}]} \quad (5)$$

$$\phi_F = \frac{C_F/[C_A - C_H/(C_H/C_A)_{st}]}{(C_F/C_A)_{st}} \quad (6)$$

where the subscript st designates the stoichiometric state. For instance, $(C_H/C_A)_{st}$ is 0.42 for hydrogen in air and $(C_F/C_A)_{st}$ is 0.07 for ethylene in air.

The parameter R_H of Eq. (5) is the ratio of the amount of hydrogen plus the stoichiometric amount of air needed for its oxidation, to the amount of fuel plus the remaining air left for its oxidation. Thus the numerator properly accounts for all the gases that participate in the oxidation of hydrogen. Consequently ϕ_F of Eq. (6) represents an effective equivalence ratio of the fuel. Implicit in the adoption of these parameters is the anticipation that hydrogen is preferentially oxidized as compared to the fuel as its consumption is stoichiometric and hence complete, leaving the remaining oxygen to react with

the fuel. While such an assumption is reasonable considering the highly reactive and diffusive nature of hydrogen, as compared to the fuel, and the relatively small amount of hydrogen addition, its ultimate justification lies in how well R_H can provide a more balanced indication of the fact that hydrogen addition is small and hence its effect can be linearly described.

2.4. Computational specification

Laminar flame speeds were calculated using the PREMIX code [36] in conjunction with the CHEMKIN [37] and TRANSPORT [38] packages. The solution was obtained allowing multi-component formulation of the transport properties and thermal diffusion. The kinetic mechanism employed is USC Mech II [39], which is a high-temperature reaction model consisting of 111 species and 784 reactions, developed for the prediction of $H_2/CO/C_1-C_4$ hydrocarbon combustion.

Effects of hydrogen addition on the laminar flame speed were interpreted through its expression obtained with a one-step overall reaction and constant transport properties,

$$S_u^0 \sim (\alpha Le)^{1/2} \exp(-T_a/2T_{ad}) \quad (7)$$

where α is the thermal diffusivity, Le the Lewis number, T_a the overall activation temperature, and T_{ad} the adiabatic temperature. Eq. (7) shows the dominant functional dependence of the laminar flame speed on the transport and thermo-kinetic parameters, and provides a viable expression to guide the interpretation of the flame response to the complex diffusive and chemical processes constituting the flame.

The T_{ad} in Eq. (7) is evaluated using the STANJAN equilibrium program [40]. We followed the numerical approach employed in Refs. [24,32] to evaluate the global activation temperature T_a . For sufficiently off-stoichiometric mixtures, T_a can be readily extracted through the relation [33,41],

$$T_a = -2 \frac{d \ln(f)}{d(1/T_{ad})} \quad (8)$$

where $f = \rho_u S_u^0$ is the laminar burning flux. The differentiation can be evaluated by slightly varying the flame temperature by substituting a small quantity of nitrogen by argon. Since Eq. (8) is only valid for sufficiently off-stoichiometric mixtures for which the reaction rate is controlled by the deficient reactant, for near-stoichiometric mixtures, T_a is interpolated from the results of off-stoichiometric mixtures.

The thermal diffusivity α and other transport coefficients are evaluated using the TRANSPORT package [38]. For simplicity the transport coefficients are evaluated at the unburned gas temperature. The effective Lewis number for the entire mixture, Le_{eff} , is given by [42,43],

$$Le_{HF} = 1 + \frac{q_H(Le_H - 1) + q_F(Le_F - 1)}{q_H + q_F} \quad (9)$$

$$Le_{eff} = \begin{cases} 1 + \frac{(Le_{HF} - 1) + [1 + Ze(\phi_F - 1)](Le_O - 1)}{2 + Ze(\phi_F - 1)}, & \text{for } \phi_F > 1 \\ 1 + \frac{[1 + Ze(\phi_F^{-1} - 1)](Le_{HF} - 1) + (Le_O - 1)}{2 + Ze(\phi_F^{-1} - 1)}, & \text{for } \phi_F < 1 \end{cases} \quad (10)$$

where Le_H , Le_F and Le_O are the Lewis numbers of hydrogen, fuel and oxygen; q_H and q_F are the nondimensional heat releases

of the hydrogen and fuel in the mixture; and Ze is the Zel'dovich number.

Having determined the above parameters, the influence of hydrogen addition due to different effects can be evaluated. It is also noted that since the kinetic and thermal effects are lumped through the exponential factor $\exp(-T_a/2T_{ad})$, their effects can be treated as a combined Arrhenius effect. Similarly, $(\alpha Le)^{1/2}$ represents the diffusion effect.

3. Results and discussion

3.1. Results on ethane, ethylene and acetylene

The measured and calculated laminar flame speeds of ethane/air, ethylene/air and acetylene/air mixtures with hydrogen addition at atmospheric pressure are shown in Figs. 1–3. Three values of ϕ_F : 0.7, 1.0 and 1.6, were chosen for each fuel. All curves are plotted as a function of R_H . In addition, the laminar flame speeds are correlated with R_H by the linear relation [6],

$$S_u^0(\phi_F, R_H) = S_u^0(\phi_F, 0) + k(\phi_F)R_H \quad (11)$$

where $k(\phi_F)$ is a coefficient that represents the sensitivity of the laminar flame speed to hydrogen addition. The values of $k(\phi_F)$ for both calculated and measured curves are given in the figures.

The results show that the measured and calculated flame speeds agree reasonably well for ethylene. However, for ethane the calculation mostly over-predicts the flame

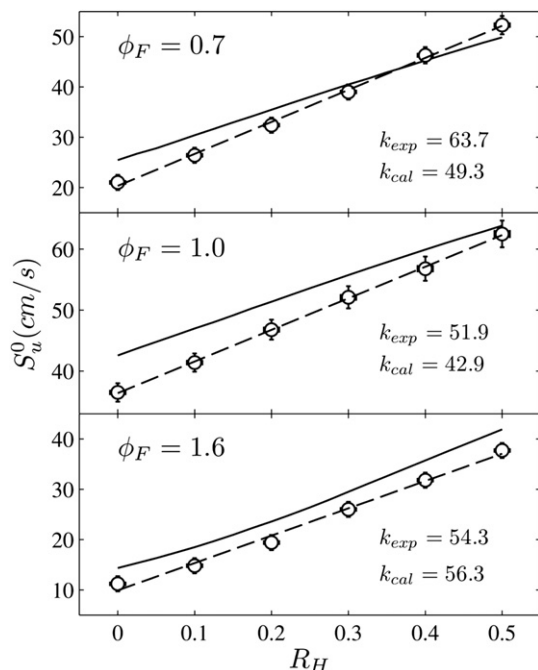


Fig. 1 – Laminar flame speeds of ethane–air mixtures with hydrogen addition at atmospheric pressure (initial temperature: 293 ± 2 K; circles: measured results; solid lines: calculated results using USC Mech II; dashed lines: linear fit of measured results).

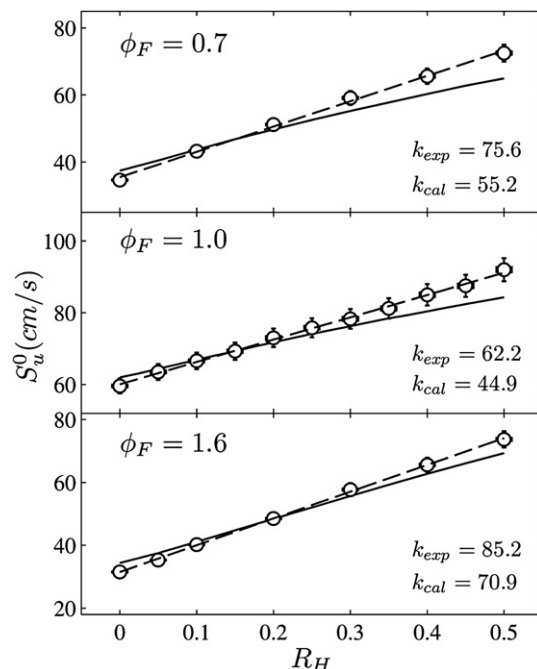


Fig. 2 – Laminar flame speeds of ethylene–air mixtures with hydrogen addition at atmospheric pressure (initial temperature: 293 ± 2 K; circles: measured results; solid lines: calculated results using USC Mech II; dashed lines: linear fit of measured results).

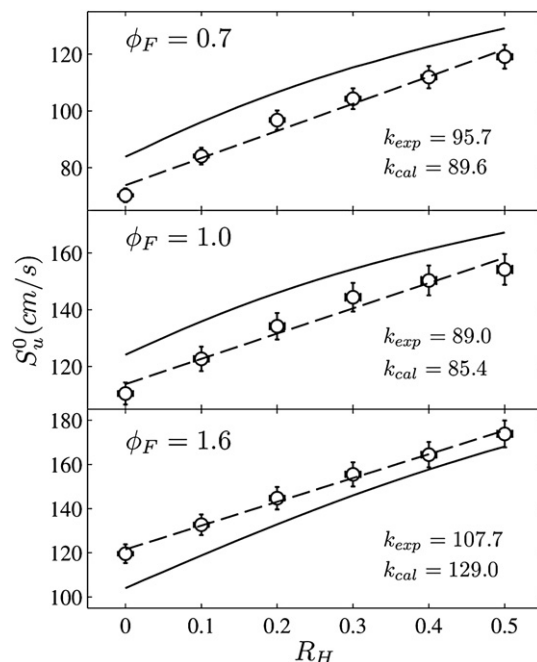


Fig. 3 – Laminar flame speeds of acetylene–air mixtures with hydrogen addition at atmospheric pressure (initial temperature: 293 ± 2 K; circles: measured results; solid lines: calculated results using USC Mech II; dashed lines: linear fit of measured results).

speeds, while for acetylene it over-predicts the lean and stoichiometric flame speeds and under-predicts the rich flame speeds. In addition, the calculated values of $k(\phi_F)$ are also mostly lower than the measured ones for all curves except the rich acetylene mixture. These results should not be interpreted as indications that the mechanism is “good” for ethylene and less accurate for ethane and acetylene for different conditions. Rather, the different extents of agreement versus disagreement simply imply that the reaction mechanism is not sufficiently comprehensive in its description of the three fuels as well as the diverse range of the experiments conducted herein.

Figs. 1–3 further show that the correlations between the laminar flame speeds and R_H for all three fuels are approximately linear. This therefore corroborates the approximate linear correlation previously observed for methane, propane and n-butane mixtures [6,7,24], even for the present fuels of distinctively different kinetic and thermal properties.

To assess the relative influences of the Arrhenius and diffusion factors, we plot in Figs. 4–6 their normalized values relative to the case of no hydrogen addition, superscripted by “o”, as well as the combined effect. It is seen that the normalized Arrhenius factor dominates over the normalized diffusion factor for all cases except that of the lean acetylene/air flame, for which the diffusion factor is larger. This is reasonable because acetylene is characterized by strong reactivity and high exothermicity, and as such hydrogen

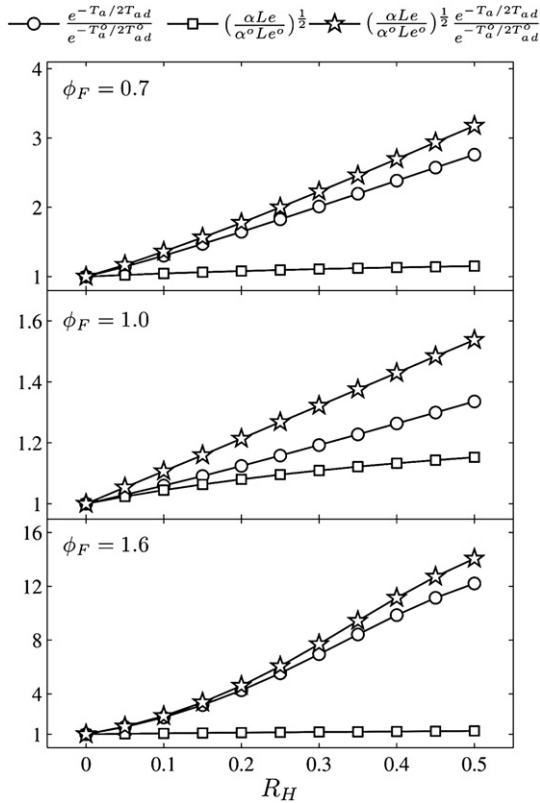


Fig. 4 – Normalized values of Arrhenius and diffusion factors by their values at zero hydrogen addition for ethane–air mixtures at atmospheric pressure (initial temperature: 293 K).

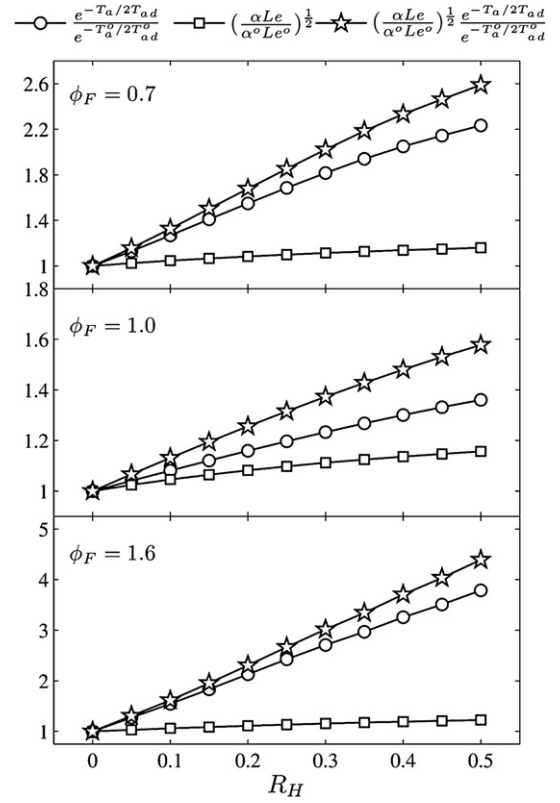


Fig. 5 – Normalized values of Arrhenius and diffusion factors by their values at no hydrogen addition for ethylene–air mixtures at atmospheric pressure (initial temperature: 293 K).

addition does not necessarily enhance its oxidation kinetics. Figs. 4–6 further show that both the Arrhenius and diffusion factors are nearly linear functions of R_H for all three fuels, implying that the approximate linear dependence of laminar flame speeds is due to the approximate linear variation of both factors instead of through some compensatory effects.

To further understand the dependence of the Arrhenius effect on hydrogen addition, we re-arrange the normalized Arrhenius factor as,

$$\frac{\exp(-T_a/2T_{ad})}{\exp(-T_a^0/2T_{ad}^0)} = \exp\left[\frac{Ar^0}{2}\left(1 - \frac{Ar}{Ar^0}\right)\right] \quad (12)$$

where $Ar = T_a/T_{ad}$ is the Arrhenius number. The factor $(1 - Ar/Ar^0)$ measures the relative modification of Ar by hydrogen addition from its original value Ar^0 , i.e., the percentage change in the mixture's kinetics. Its value is plotted in Fig. 7 along with the changes in activation energy and flame temperature as functions of R_H for the ethylene/air mixture at $\phi_F = 1.6$ as an example. Here we first note that it is the variation of T_a/T_{ad}^0 that mainly contributes to the changes in $(1 - Ar/Ar^0)$, hence indicating that hydrogen addition enhances flame speeds mainly through the modification of the activation temperature rather than the flame temperature, i.e., the kinetic effect is stronger than the thermal effect. Furthermore, the approximate linear dependence of the Arrhenius factor on hydrogen addition is caused by the logarithm-like variation of $(1 - Ar/Ar^0)$ with R_H ,

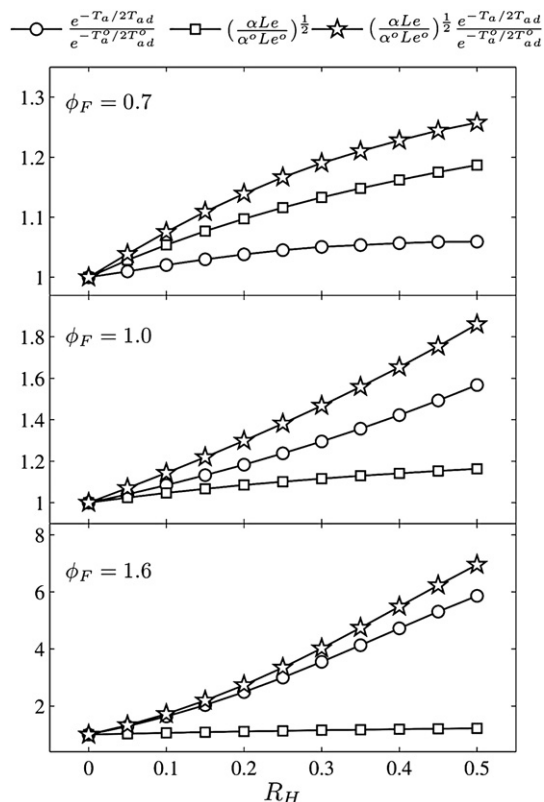


Fig. 6 – Normalized values of Arrhenius and diffusion factors by their values at no hydrogen addition for acetylene–air mixtures at atmospheric pressure (initial temperature: 293 K).

leading to a linear variation after exponentiation. This variation of the slope is reasonable by recognizing that the effect of hydrogen addition on kinetics should become weaker as more hydrogen is added to the mixture.

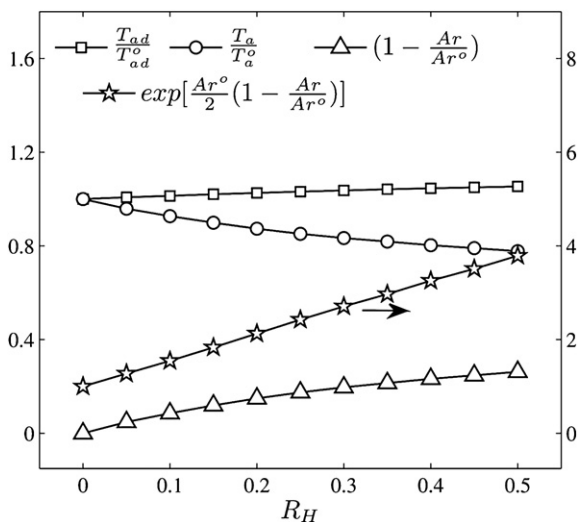


Fig. 7 – Normalized values of various factors that contribute to the Arrhenius factor for a rich ethylene–air mixture with hydrogen addition at atmospheric pressure (initial temperature: 293 K; $\phi_F = 1.6$).

3.2. Results on carbon monoxide

The measured and calculated flame speeds of carbon monoxide/air mixtures with hydrogen addition at atmospheric pressure are shown in Fig. 8. First, good agreement between calculation and experiment is seen for all three curves, both in the values of laminar flame speeds and their dependence on hydrogen addition, hence demonstrating the satisfactory state of the oxidative mechanism of carbon monoxide. In addition, the laminar flame speeds of carbon monoxide/air mixture with hydrogen addition exhibit a highly nonlinear dependence on R_H : (1) The laminar flame speed of pure carbon monoxide/air mixture is very close to zero. In fact, in experiments it was not possible to ignite a pure carbon monoxide mixture. (2) The laminar flame speed increases rapidly as R_H increases from 0 to 0.1. (3) Further increasing R_H beyond 0.1 results in a nearly linear relationship.

To assess the relative influence of the kinetic versus diffusion factors, Fig. 9 plots the normalized Arrhenius, diffusion and the combined factors for $\phi_F = 1.0$ as an example. The normalized activation temperature and flame temperature as well as the values of $(1 - Ar/Ar^0)$ are plotted in Fig. 10. As expected, the Arrhenius factor is seen to dominate over the diffusion factor, and the increase in the Arrhenius factor is not due to modification of the flame temperature but rather the activation temperature. Compared to the hydrocarbons, the kinetic effect of hydrogen addition on carbon monoxide oxidation is much stronger, especially for small values of R_H . This strong catalytic effect substantially reduces the activation temperature and consequently increases the Arrhenius factor, leading to a nonlinear dependence of the laminar flame speed

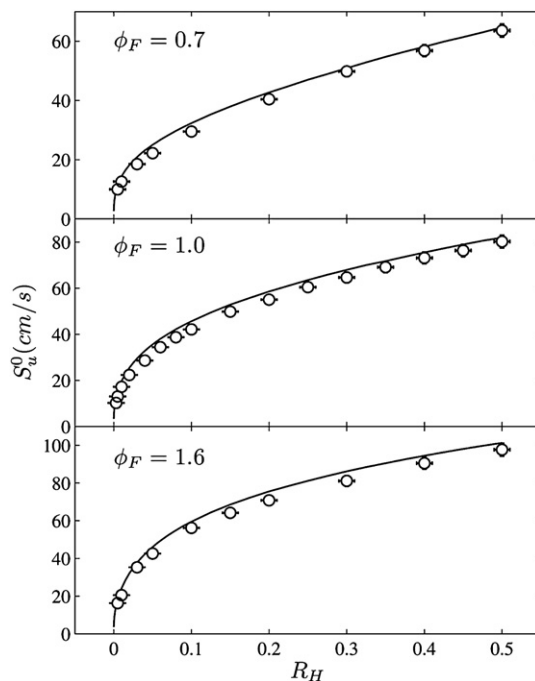


Fig. 8 – Laminar flame speeds of carbon monoxide–air mixtures with hydrogen addition at atmospheric pressure (initial temperature: 293 ± 2 K; circles: measured results; solid lines: calculated results using USC Mech II).

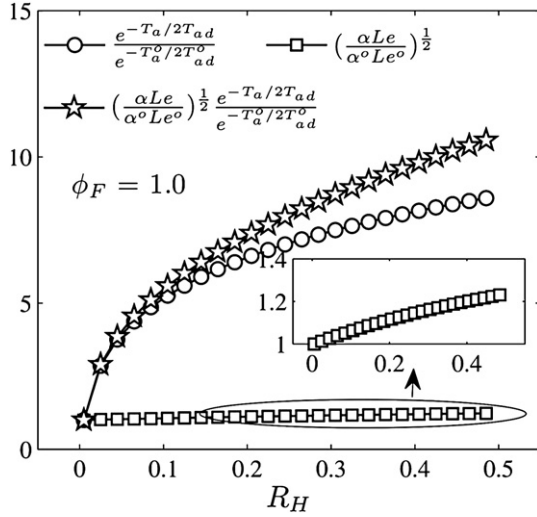


Fig. 9 – Normalized values of Arrhenius and diffusion factors by their values at no hydrogen addition for a stoichiometric carbon monoxide–air mixture with hydrogen addition at atmospheric pressure (initial temperature: 293 K).

on hydrogen addition. However, the modification of the activation temperature by hydrogen becomes much smaller for R_H larger than 0.2, and the sensitivity of the Arrhenius effect becomes moderate and is comparable with that of diffusion effect. This can be demonstrated by the sensitivity of Eq. (7) on R_H ,

$$\frac{1}{S_u^0} \frac{\partial S_u^0}{\partial R_H} = -\frac{\partial}{\partial R_H} \left(\frac{T_a}{2T_{ad}} \right) + \frac{1}{2\alpha Le} \frac{\partial(\alpha Le)}{\partial R_H} \quad (13)$$

where the first and second terms on the RHS indicate the sensitivity of the Arrhenius effect and the diffusion effect, respectively. Eq. (13), plotted in Fig. 11, shows that while the sensitivity of the Arrhenius effect dominates for R_H less than

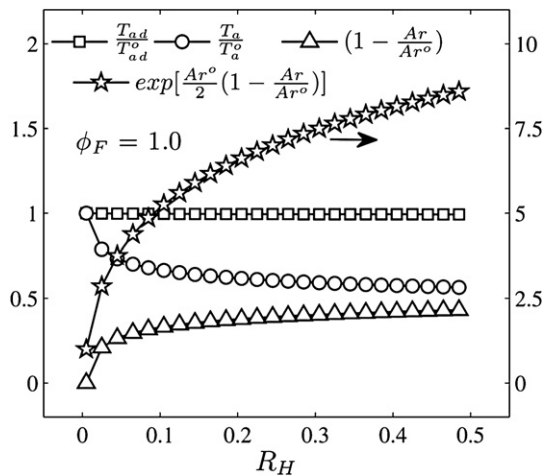


Fig. 10 – Normalized values of various factors that contribute to the Arrhenius factor for a stoichiometric carbon monoxide–air mixture with hydrogen addition at atmospheric pressure (initial temperature: 293 K).

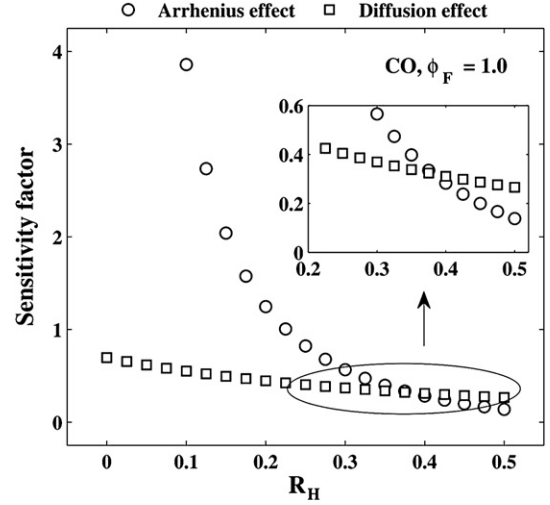


Fig. 11 – Sensitivity factors defined in Eq. (13) measuring the sensitivity of the Arrhenius effect and the diffusion effect for carbon monoxide–air mixture at $\phi_F = 1.0$.

0.2, it becomes comparable to that of diffusion effect for larger R_H , and even lower for R_H greater than 0.35. From Figs. 8–10 we see that this moderate sensitivity leads to an approximate linear dependence of the Arrhenius factor and thus the laminar flame speed for R_H less than 0.2. The result indicates that the catalytic effect becomes saturated as more hydrogen is added to the mixture.

3.3. Results at elevated pressures

Experiments at elevated pressures were conducted for three cases: (1) an ethylene/air mixture at $\phi_F = 0.7$ and pressure of 5 atm; (2) a propane/oxygen/helium mixture at $\phi_F = 0.6$ and pressure of 20 atm with reduced oxygen concentration; (3) a carbon monoxide/oxygen/helium mixture at $\phi_F = 1.0$ and pressure of 20 atm.

Fig. 12 shows the measured and calculated flame speeds of lean ethylene/air mixtures at 5 atm. It is seen that there are considerable differences between experiment and calculation particularly in the values of the sensitivity coefficient k . Nevertheless both curves show approximate linear correlation between laminar flame speeds and R_H . Only results at R_H from 0 to 0.2 are shown because the flame speed measurement is only possible for small values of R_H , as further increasing R_H causes cellular instabilities to develop because the increased flame speed reduces the flame thickness which, together with the increased pressure, promotes the onset of flame front hydrodynamic instability [32,33]. This phenomenon does not appear at atmospheric pressure because the flame is thicker and as such is hydrodynamically stabilized.

Fig. 13 shows the measured and calculated flame speeds of the lean propane/air mixture at 20 atm. As pressure increases the flame again becomes harder to stabilize because of the decrease in the flame thickness. Therefore to suppress cellular instabilities at 20 atm, we used helium to replace the nitrogen in air to further stabilize the flame. It is seen from Fig. 13 that the calculation largely under-predicts the flame speeds and

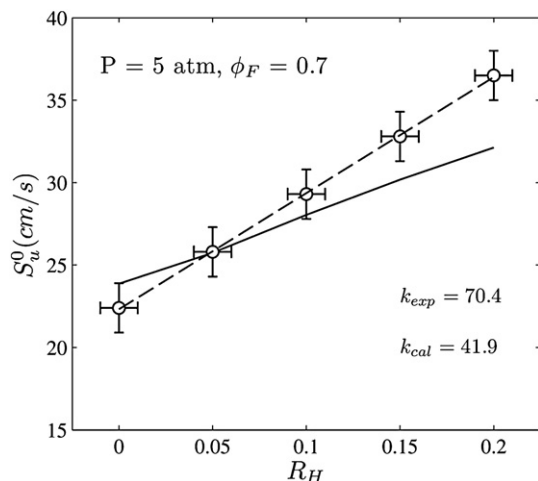


Fig. 12 – Laminar flame speeds of ethylene–air mixtures with hydrogen addition at $\phi_F = 0.7$ at pressure = 5 atm (initial temperature: 293 ± 2 K; circles: measured results; solid line: calculated results with USC Mech II; dashed line: linear fit of measured results).

the sensitivity coefficient k for this case. However, the approximate linear correlation between the laminar flame speeds and R_H still holds for both measured and calculated results even at 20 atm pressure. The linear correlation of hydrogen addition on laminar flame speeds for hydrocarbon/air mixtures is therefore extended to normal and elevated pressures.

Fig. 14 shows the measured and calculated laminar flame speeds of the carbon monoxide/oxygen/helium mixture at $\phi_F = 1.0$ at 20 atm pressure. It is seen that while the calculation and experiment have good agreement for small hydrogen additions, it under-predicts the flame speeds at higher

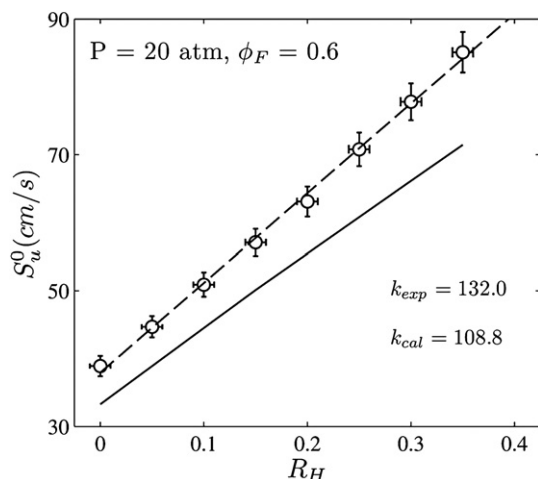


Fig. 13 – Laminar flame speeds of propane–oxygen–helium mixtures with hydrogen addition at $\phi_F = 0.6$ at pressure = 20 atm (O_2 Vol.%, He Vol.%, 21:79; initial temperature: 293 ± 2 K; circles: measured results; solid line: calculated results using USC Mech II; dashed line: linear fit of measured results).

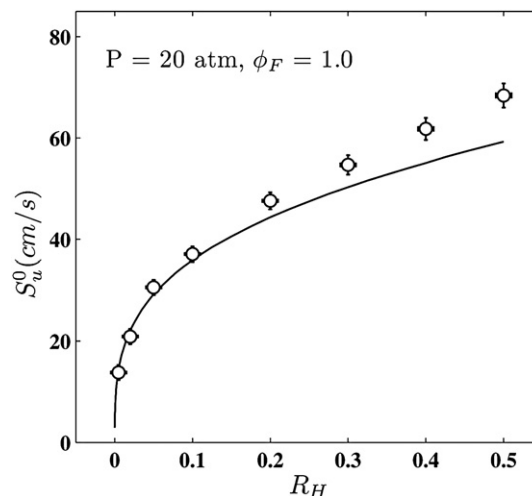


Fig. 14 – Laminar flame speeds of carbon monoxide–oxygen–helium mixture with hydrogen addition at $\phi_F = 1.0$ at pressure = 20 atm (O_2 Vol.%, He Vol.%, 12.5:87.5; initial temperature: 293 ± 2 K; circles: measured results; solid line: calculated results using USC Mech II).

hydrogen addition. The overall agreement between calculation and experiment is not as good as those at atmospheric pressure. In addition, the flame speeds in Fig. 14 show a nonlinear dependence on R_H , which is similar in trend as the results at atmospheric pressure. This indicates that the influence of hydrogen addition on carbon monoxide oxidation is still characterized by the catalytic effect.

4. Conclusion

The following conclusions can be made from the present study:

- 1) The approximate linear correlation between laminar flame speed and hydrogen addition was experimentally and computationally demonstrated at atmospheric pressure for ethane, ethylene and acetylene.
- 2) Computation agrees moderately well with data; deviations between computation and experiment suggest that aspects of the mechanism (USC Mech II) require further revision.
- 3) Evaluation of the governing flame parameters shows that both the Arrhenius and diffusive contributions to laminar flame speeds are nearly linear functions of hydrogen addition, which explains the approximate linear correlation identified.
- 4) Linear correlation between laminar flame speeds and hydrogen addition was also experimentally and computationally demonstrated to approximately apply for ethylene and propane at elevated pressures.
- 5) Different from hydrocarbon fuels, the increase in the laminar flame speed of carbon monoxide exhibits a highly nonlinear dependence with hydrogen addition due to the strong catalytic effect of hydrogen on the oxidation of CO.

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REFERENCES

- [1] Scholte TG, Vaags PB. Burning velocities of mixtures of hydrogen, carbon monoxide and methane with air. *Combustion and Flame* 1959;3:511–24.
- [2] Scholte TG, Vaags PB. The influence of small quantities of hydrogen and hydrogen compounds on the burning velocity of carbon monoxide–air flames. *Combustion and Flame* 1959;3:503–10.
- [3] Refael S, Sher E. Reaction kinetics of hydrogen-enriched methane–air and propane–air flames. *Combustion and Flame* 1989;78:326–38.
- [4] Milton BE, Keck JC. Laminar burning velocities in stoichiometric hydrogen and hydrogen–hydrocarbon gas mixtures. *Combustion and Flame* 1984;58:13–22.
- [5] Liu Y, Lenze B, Leuckel W. Investigation on the laminar and turbulent burning velocities of premixed lean and rich flames of methane–hydrogen–air mixtures. *Progress in Astronautics and Aeronautics* 1991;131:259–74.
- [6] Yu G, Law CK, Wu CK. Laminar flame speeds of hydrocarbon–air mixtures with hydrogen addition. *Combustion and Flame* 1986;63:339–47.
- [7] Sher E, Ozdor N. Laminar burning velocities of *n*-butane–air mixtures enriched with hydrogen. *Combustion and Flame* 1992;89:214–20.
- [8] Ren JY, Qin W, Egolfopoulos FN, Tsotsis TT. Strain-rate effects on hydrogen-enhanced lean premixed combustion. *Combustion and Flame* 2001;124:717–20.
- [9] Law CK, Kwon OC. Effects of hydrocarbon substitution on atmospheric hydrogen–air flame propagation. *International Journal of Hydrogen Energy* 2004;29:867–79.
- [10] Halter F, Chauveau C, Gokalp I. Characterization of the effects of hydrogen addition in premixed methane/air flames. *International Journal of Hydrogen Energy* 2007;32:2585–92.
- [11] Huang Z, Zhang Y, Zeng K, Liu B, Wang Q, Jiang D. Measurements of laminar burning velocities for natural gas–hydrogen–air mixtures. *Combustion and Flame* 2006;146:302–11.
- [12] Coppens FHV, De Ruyck J, Konnov AA. Effects of hydrogen enrichment on adiabatic burning velocity and no formation in methane + air flames. *Experimental Thermal and Fluid Science* 2007;31:437–44.
- [13] Coppens FHV, De Ruyck J, Konnov AA. The effects of composition on burning velocity and nitric oxide formation in laminar premixed flames of $\text{CH}_4 + \text{H}_2 + \text{O}_2 + \text{N}_2$. *Combustion and Flame* 2007;149:409–17.
- [14] Ilbas M, Crayford A, Yilmaz I, Bowen P, Syred N. Laminar-burning velocities of hydrogen–air and hydrogen–methane–air mixtures: an experimental study. *International Journal of Hydrogen Energy* 2006;31:1768–79.
- [15] Halter F, Chauveau C, Djebaili-Chaumeix N, Gokalp I. Characterization of the effects of pressure and hydrogen concentration on laminar burning velocities of methane–hydrogen–air mixtures. *Proceedings of the Combustion Institute* 2005;30:201–8.
- [16] Mandilas C, Ormsby MP, Sheppard CGW, Woolley R. Effects of hydrogen addition on laminar and turbulent premixed methane and iso-octane–air flames. *Proceedings of the Combustion Institute* 2007;31:1443–50.
- [17] Tang C, Huang Z, Jin C, He J, Wang J, Wang X, et al. Laminar burning velocities and combustion characteristics of propane–hydrogen–air premixed flames. *International Journal of Hydrogen Energy* 2008;33:4906–14.
- [18] Tang C, He J, Huang Z, Jin C, Wang J, Wang X, et al. Measurements of laminar burning velocities and markstein lengths of propane–hydrogen–air mixtures at elevated pressures and temperatures. *International Journal of Hydrogen Energy* 2008;33:7274–85.
- [19] Miao H, Jiao Q, Huang Z, Jiang D. Measurement of laminar burning velocities and markstein lengths of diluted hydrogen-enriched natural gas. *International Journal of Hydrogen Energy* 2009;34:507–18.
- [20] Hu E, Huang Z, He J, Miao H. Experimental and numerical study on lean premixed methane–hydrogen–air flames at elevated pressures and temperatures. *International Journal of Hydrogen Energy* 2009;34:6951–60.
- [21] Hu E, Huang Z, He J, Jin C, Zheng J. Experimental and numerical study on laminar burning characteristics of premixed methane–hydrogen–air flames. *International Journal of Hydrogen Energy* 2009;34:4876–88.
- [22] Tahtouh T, Halter F, Samson E, Mounaïm-Rousselle C. Effects of hydrogen addition and nitrogen dilution on the laminar flame characteristics of premixed methane–air flames. *International Journal of Hydrogen Energy* 2009;34:8329–38.
- [23] Tahtouh T, Halter F, Mounaïm-Rousselle C. Laminar premixed flame characteristics of hydrogen blended iso-octane–air–nitrogen mixtures. *International Journal of Hydrogen Energy* 2011;36:985–91.
- [24] Tang C, Huang Z, Law CK. Determination, correlation, and mechanistic interpretation of effects of hydrogen addition on laminar flame speeds of hydrocarbon–air mixtures. *Proceedings of the Combustion Institute* 2011;33:921–8.
- [25] Hermanns RTE, Konnov AA, Bastiaans RJM, de Goey LPH, Lucka K, Köhne H. Effects of temperature and composition on the laminar burning velocity of $\text{CH}_4 + \text{H}_2 + \text{O}_2 + \text{N}_2$ flames. *Fuel* 2010;89:114–21.
- [26] Mclean IC, Smith DB, Taylor SC. The use of carbon monoxide–hydrogen burning velocities to examine the rate of the $\text{CO} + \text{OH}$ reaction. In: *Twenty-fifth international symposium on combustion*; 1994. p. 749–57.
- [27] Vagelopoulos CM, Egolfopoulos FN. Laminar flame speeds and extinction strain rates of mixtures of carbon monoxide with hydrogen, methane and air. In: *Twenty-fifth international symposium on combustion*; 1994. p. 1317–23.
- [28] Sun H, Yang SI, Jomaas G, Law CK. High-pressure laminar flame speeds and kinetic modeling of carbon monoxide/hydrogen combustion. *Proceedings of the Combustion Institute* 2007;31:439–46.
- [29] Natarajan J, Lieuwen T, Seitzman J. Laminar flame speeds of H_2 – CO mixtures: effect of CO_2 dilution, preheat temperature, and pressure. *Combustion and Flame* 2007;151:104–19.
- [30] Dong C, Zhou Q, Zhao Q, Zhang Y, Xu T, Hui S. Experimental study on the laminar flame speed of hydrogen–carbon monoxide–air mixtures. *Fuel* 2009;88:1858–63.
- [31] Hassan MI, Aung KT, Faeth GM. Properties of laminar premixed CO – H_2 –air flames at various pressures. *Journal of Propulsion and Power* 1997;13(2):239–45.
- [32] Jomaas G, Law CK, Bechtold JK. On transition to cellularity in expanding spherical flames. *Journal of Fluid Mechanics* 2007;583:1–26.
- [33] Law CK. *Combustion physics*. Cambridge University Press; 2006.

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- [34] Tse SD, Zhu D, Law CK. Optically accessible high-pressure combustion apparatus. *Review of Scientific Instruments* 2004;75(1):233–9.
- [35] Kelley AP, Bechtold JK, Law CK. Confined propagation of premixed flames. In: 7th U.S. National technical meeting of the combustion institute; 2011.
- [36] Kee RJ, Grcar JF, Smooke MD, Miller JA, Meeks E. Sandia report 85-8240. Sandia National Laboratories; 1998.
- [37] Kee RJ, Rupley FM, Miller JA. Sandia report 89-8009b. Sandia National Laboratories; 1989.
- [38] Kee RJ, Warnatz J, Miller JA. Sandia report 83-8209. Sandia National Laboratories; 1983.
- [39] Wang H, You XQ, Joshi AV, Davis SG, Laskin A, Egolfopoulos FN. USC Mech Version II. High-temperature combustion reaction model of $H_2/CO/C_1-C_4$ compounds, http://ignis.usc.edu/USC_Mech_II.htm; May 2007.
- [40] Lutz AE, Rupley FM, Kee RJ, Reynolds WC. Equil: a CHEMKIN implementation of STANJAN for computing chemical equilibria; 1998.
- [41] Law CK, Sung CJ. Structure, aerodynamics, and geometry of premixed flamelets. *Progress in Energy and Combustion Science* 2000;26:459–505.
- [42] Law CK, Jomaas G, Bechtold JK. Cellular instabilities of expanding hydrogen–propane spherical flames at elevated pressures: theory and experiment. *Proceedings of the Combustion Institute* 2005;30:159–67.
- [43] Bechtold JK, Matalon M. The dependence of the markstein length on stoichiometry. *Combustion and Flame* 2001;127:1906–13.