JOURNAL OF PROPULSION AND POWER
Vol. 13, No. 2, March–April 1997

Properties of Laminar Premixed CO/H$_2$/Air Flames at Various Pressures

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Effects of positive flame stretch on the laminar burning velocities of CO/H$_2$/air mixtures were studied both experimentally and computationally for outwardly propagating spherical laminar premixed flames having concentrations of hydrogen in the fuel mixture of 3–50% by volume, fuel-equivalence ratios of 0.6–5.0, and pressures of 0.5–4.0 atm. Both measured and predicted ratios of unstretched to stretched laminar burning velocities varied linearly with Karlovitz numbers, yielding constant Markstein numbers for each reactant mixture and pressure. Effects of stretch on laminar burning velocities were modest at low hydrogen concentrations, but approached earlier results for hydrogen/air flames as hydrogen concentrations increased. Predicted and measured flame properties were in reasonably good agreement using several contemporary chemical reaction mechanisms.

Nomenclature

D = mass diffusivity
K = flame stretch, or the normalized rate of increase of flame surface area, Eq. (4)
Ka = Karlovitz number, KD_u/S_L^2
L = Markstein length, Eq. (1)
Ma = Markstein number, L/δ_D
P = pressure
r_f = flame radius
S_L = laminar burning velocity based on unburned gas properties
S_L' = value of S_L at largest radius observed
t = time
δ_D = characteristic flame thickness, D_u/S_L
ρ = density
ϕ = fuel-equivalence ratio

Subscripts

b = burned gas
max = maximum observed value
u = unburned gas
∞ = unstretched flame condition

Introduction

RECENT experimental and computational studies of the effects of flame stretch on laminar premixed flames of hydrogen/oxygen/nitrogen and hydrocarbon/air mixtures in this laboratory[1–5] were extended to consider CO/H$_2$/air flames at normal temperature (298 ± 2 K) and pressures of 0.5–4.0 atm. This work was undertaken to systematically address results pertinent to C/H/O chemistry fundamental to practical hydrocarbon/air combustion processes and to consider effects of pressure variations that also are relevant to practical flames. Outwardly propagating spherical laminar premixed flames were observed to find the sensitivities of laminar burning velocities to flame stretch, represented by Markstein numbers, and the fundamental laminar burning velocities of unstretched flames. In addition, the measurements were used to evaluate C/H/O chemical reaction rate mechanisms used by the authors of Refs. 6–9, based on corresponding numerical simulations of outwardly propagating spherical laminar premixed flames that were analyzed in the same manner as the measurements. The following description of the study is brief, see Refs. 1–5 for more details about experimental and computational methods.

Present experiments and computational results were analyzed to find preferential-diffusion/stretch interactions in the same way as earlier studies of outwardly propagating spherical laminar premixed flames in this laboratory.[1–5] Problems of flame thickness variations, curvature, and unsteadiness caused by laminar burning velocity variations with flame radius were minimized when flame properties were interpreted by only considering conditions where $\delta_D/r_f << 1$.[2,4] Effects of stretch on laminar burning velocities were correlated according to an early proposal of Markstein,[10] after later extension at the limit of small stretch by Clavin,[11] as follows[2,4]:

$$S_L = S_{L\infty} - LK \tag{1}$$

To account for relatively large values of stretch during the present study, Eq. (1) was extended so that the flame response to stretch was represented by the characteristic length and time scales of stretched flames, δ_D and δ_D/S_L, rather than corresponding scales for unstretched flames that can be very different. The diffusivity D_u used to find δ_D is arbitrary[4]; therefore, D_u was taken to be the binary diffusivity of hydrogen with respect to nitrogen, for several reasons:

1) It provides a conservative (or large) estimate of δ_D when conditions having $\delta_D/r_f << 1$ were identified.

2) It allows direct comparison of the present results with earlier findings for H/O/N flames.

3) The large values of hydrogen mass diffusivity compared to other diffusivities suggests that preferential diffusion of this species may be mainly responsible for the premixed-flame/stretch interactions of the present flames. Naturally, present results can be interpreted in terms of any other diffusivity by simple ratios of diffusivities, if desired. Introducing δ_D and δ_D/S_L into Eq. (1) yields[1–5]

$$S_{L\infty}/S_L = 1 + MaKa \tag{2}$$

It should not be inferred that Eqs. (1) and (2) are linear in K or Ka, implying constant values of L or Ma, outside the small

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Received Aug. 9, 1996; revision received Dec. 6, 1996; accepted for publication Dec. 30, 1996.

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stretch limit; nevertheless, past observations generally show that Ma is independent of Ka when $\delta_D/r_f << 1$, which provides a concise summary of flame/stretch interactions.[2,4] The small stretch limit of Eq. (2) is also of interest because of its relevance to classical asymptotic theories[11]; this expression can be found from Eq. (2), as follows[4]:

$$S_L/S_{L\infty} = 1 - Ma_\infty Ka_\infty, \qquad Ka_\infty << 1 \tag{3}$$

Notably, Eq. (3) is identical to the findings of classical theories,[11] except for the trivial differences concerning the selection of D_u for normalization as discussed earlier.

The present characterization of premixed-flame/stretch interactions is not unique but has several advantages pending the development of generally accepted methods to treat these interactions outside the small stretch limit. Data reduction does not involve flame structure models that are difficult to fully define and are likely to be revised, the characterization is concise, which facilitates use of the results by others, the positive and negative ranges of Ma provide a direct characterization of stable and unstable flame surface conditions with respect to preferential diffusion, and the results can be readily transformed to provide direct comparisons with other characterizations of premixed-flame/stretch interactions. Nevertheless, the present approach has only been applied to outwardly propagating spherical laminar-premixed flames when $\delta_D/r_f << 1$ and effects of ignition disturbances and radiation are small. The limitations of this approach for more general conditions are not known so that direct use of the present Ma to characterize effects of stretch in other circumstances should be approached with caution.

The properties of the laminar burning velocities of CO/H_2/air flames at normal temperature and pressure (NTP) have been considered during several previous experimental investigations.[12–20] The earliest studies[12–17] did not consider effects of flame stretch on laminar burning velocities and are of questionable accuracy. Subsequently, Vagelopoulos and Egolfopoulos[18] measured the laminar burning velocities using the counterflow twin-flame technique while extrapolating measurements at finite stretch rates to estimate fundamental unstretched laminar burning velocities; however, these results were limited to lean flames and flame response to stretch was not quantified. McLean et al.[19] and Brown et al.[20] studied outwardly propagating spherical flames similar to the present investigation while using a different extrapolation procedure to estimate effects of stretch on the laminar burning velocities for H_2 concentrations of 5 and 50% by volume in the fuel mixture; however, effects of flame response to stretch were limited to small values of stretch while effects of pressure were not quantified.

Because of the importance of C/H/O chemistry for practical combustion processes, numerical simulations of wet-carbon-dioxide/air flames and other reaction processes involving mixtures containing carbon monoxide and hydrogen have received considerable attention. Past studies include McLean et al.,[19] Brown et al.,[20] Cherian et al.,[21] Dixon-Lewis,[22] and Olsson and Olsson,[23] for laminar premixed CO/H_2/air flames, as well as simulations of flow reactor processes from Yetter et al.[6] and Kim et al.[7] Similar to past experimental work concerning laminar premixed CO/H_2/air flames; however, most of these studies did not address flame response to stretch while the considerations of McLean et al.[19] and Brown et al.[20] were limited to small values of stretch at atmospheric pressure.

In view of the current status of understanding about preferential-diffusion/stretch interactions of laminar premixed CO/H_2/air flames, the objectives of the present study were as follows:

1) To measure the properties of outwardly propagating spherical laminar premixed flames of CO/H_2/air mixtures for various H_2 concentrations, fuel-equivalence ratios and pressures, considering finite levels of stretch.

2) To complete corresponding numerical simulations of the test flames.

3) To reduce both the measurements and the numerical simulations to find laminar premixed flame properties ($S_{L\infty}$ and Ma).

4) To compare measurements and predictions with each other and with earlier results in the literature.

The present discussion begins with descriptions of experimental and computational methods. Results are then considered, treating flame response to stretch and unstretched laminar burning velocities, in turn.

Experimental Methods

The experiments were carried out in the spherical-windowed chamber used for recent H/O/N flame studies.[4,5] The reactant mixture was prepared in a separate chamber by adding gases at appropriate partial pressures and allowed to stand overnight and then checked using gas chromatography before use. The combustible mixture was spark-ignited at the center of the chamber, adjusting spark energies by trial so that they were close to the minimum ignition energy to control spark disturbances. Motion picture shadowgraphy was used to observe the motion of the flame surface and the possible development of wrinkled surfaces caused by the effects of instabilities. Measurements were limited to flames having diameters less than 60 mm, which implies pressure increases less than 0.4% of the initial pressure during the period of propagation. Finally, earlier measurements have shown that effects of burned gas motion and wall disturbances are small for the present test arrangement.[1]

Measurements were limited to $\delta_D/r_f \leq 2\%$ so that effects of curvature and transient phenomena associated with flame thicknesses were small.[2] In addition, rates of radiative heat loss were less than 6% of the rate of chemical energy release within the flames, based on computations assuming adiabatic flame conditions throughout the burned gas and carried out as discussed by Siegal and Howell.[24] These radiative heat losses imply corresponding corrections of laminar burning velocities for effects of radiation less than 6% as well.[25] Minimum flame radii were generally greater than 5 mm to avoid ignition disturbances and satisfy the minimum δ_D/r_f criterion mentioned earlier. For these conditions, the laminar burning velocity and flame stretch are given by[26]

$$S_L = \frac{\rho_b}{\rho_u}\frac{dr_f}{dt}, \qquad K = \frac{2}{r_f}\frac{dr_f}{dt} \tag{4}$$

Similar to past work,[1–5] the density ratio needed in Eq. (4) was computed assuming adiabatic combustion at constant pressure with the reactant temperature equal to the initial temperature and with the same fuel-equivalence ratio (i.e., the same elemental composition) in the unburned and burned gases. These computations were carried out using the adiabatic flame algorithms of Refs. 27 and 28, both yielding the same results. It should be noted, however, that use of the unstretched flame density ratio in this manner is a convention that ignores preferential diffusion effects that modify the local mixture fraction and thermal energy transport for stretched flames, and thus the density ratio of stretched flames. This convention is convenient, however, because a single density ratio is used to relate flame speeds and laminar burning velocities for all values of flame stretch, which avoids current uncertainties about the effects of stretch on flame jump conditions and corresponds to methods used during past studies of preferential-diffusion/stretch interactions[1–5,18–20] which simplifies comparisons of various determinations of flame properties. Fortunately, variations of flame properties because of variations of density ratios with stretch for present conditions do not exceed 10%, based on the results of the present numerical simulations, which is comparable to present experimental uncertainties. In addition, use of the present density ratio convention does not affect comparisons between measurements and predictions because both are treated the same way. Nevertheless, given successful evaluation of methods of predicting the structure of stretched CO/H_2/air flames, density ratios should be computed for various degrees of stretch so that present measurements can be used to more accurately estimate the mass burning rates of these flames.

Final results were obtained by averaging the measurements of 4–6 tests at each condition. Methods of estimating experimental uncertainties are discussed elsewhere[4]; the present uncertainties (95% confidence) are as follows: S_L is less than 9%, Ka is less than 21%, $S_{L\infty}$ is less than 12%, and Ma is less than 25% for $|Ma| > 1$, with uncertainties of $|Ma|$ increasing inversely proportional to $|Ma|$ for values less than unity.

Present test parameters and major results (D_u, ρ_u/ρ_b, $S_{L\infty}$, $Ka_{\max}$ and Ma) are summarized in Tables 1 and 2 for findings at atmospheric pressure for various concentrations of H_2 in the fuel mixture, and for an H_2 concentration in the fuel mixture of 5% by volume at various pressures, respectively. The total test range includes concentrations of H_2 in the fuel mixture of 3–50% by volume, pressures of 0.5–4.0 atm and fuel-equivalence ratios of 0.6–5.0. It should be noted that some entries of Tables 1 and 2 are provided for information purposes only, because they involve either values of δ_D/r_f outside the allowable range or excessive effects of buoyancy or both. Similar to earlier observations for hydrogen/air flames,[1,4] wrinkled flame surfaces because of preferential diffusion and hydrodynamic instabilities were observed in some instances (see Ref. 1 for sample photographs for flame surfaces before and after wrinkling appears). Nevertheless, all present measurements were limited to conditions where flame surfaces were smooth, i.e., data reduction was ended as soon as cellular disturbances appeared on the film records.

Computational Methods

The numerical simulations of outwardly propagating spherical laminar flames were similar to past work,[4,5] based on the unsteady, one-dimensional governing equations incorporated in the computer code RUN-1DL.[29] Corresponding calculations for unstretched (plane) flames were carried out using the steady, one-dimensional laminar premixed flame computer code PREMIX.[30–34] In both cases, thermochemical and trans-

Table 1 Summary of test conditions[a]

ϕ	0.6	0.8	1.0	1.2	1.6	2.0	2.4	2.8	3.0	3.5	4.0	4.5	5.0
97% CO + 3% H_2													
ρ_u/ρ_b	5.94	6.67	6.98	7.06	6.83	6.45	6.10	——	5.65	5.33	5.06	——	4.60
$S_{L\infty}$, mm/s	130[b]	220	260	330	430	470	470	——	460	440	320	——	200[c]
$Ka_{\max}$	0.99	0.97	0.65	0.47	0.68	0.51	0.47	——	0.4	0.51	0.76	——	0.98
Ma	0.3	0.3	0.0	−0.3	−0.3	−0.2	−0.1	——	−0.1	0.0	0.0	——	0.5
95% CO + 5% H_2													
ρ_u/ρ_b	5.82	6.66	6.98	7.06	6.82	6.43	6.08	5.78	5.63	5.32	5.04	4.80	4.59
$S_{L\infty}$, mm/s	200[b]	280	340	430	520	590	630	630	590	580	480	400	280[c]
$Ka_{\max}$	0.61	0.51	0.47	0.51	0.36	0.32	0.32	0.32	0.36	0.29	0.29	0.29	0.51
Ma	−0.3	−0.1	−0.3	0.0	0.0	0.0	0.3	0.2	0.0	0.0	0.3	0.0	0.5
90% CO + 10% H_2													
ρ_u/ρ_b	5.79	6.65	6.97	7.04	6.79	6.40	6.05	5.74	5.60	5.29	5.02	4.78	4.57
$S_{L\infty}$, mm/s	240	360	550	540	710	790	830	790	790	730	540	410	290[c]
$Ka_{\max}$	0.61	0.65	0.43	0.40	0.36	0.25	0.22	0.25	0.22	0.29	0.32	0.29	0.43
Ma	−0.3	−0.1	−0.1	0.1	0.2	0.3	0.3	0.6	0.7	0.4	0.7	0.6	0.6
75% CO + 25% H_2													
ρ_u/ρ_b	5.86	6.61	6.95	7.01	6.71	6.31	5.97	5.66	5.53	5.22	4.95	4.71	4.51
$S_{L\infty}$, mm/s	320	520	710	830	1070	1160	1160	1110	1030	840	640	410	290[c]
$Ka_{\max}$	0.32	0.32	0.29	0.29	0.25	0.22	0.22	0.14	0.18	0.22	0.22	0.65	0.98
Ma	−0.9	−0.6	−0.4	−0.2	0.3	0.2	0.0	0.1	0.7	1.0	1.0	1.2	2.0
50% CO + 50% H_2													
ρ_u/ρ_b	5.76	6.65	7.01	6.96	6.60	6.21	5.87	5.58	5.44	5.14	4.87	4.65	——
$S_{L\infty}$, mm/s	500	880	1100	1290	1650	1730	1700	1520	1370	1070	880	560	——
$Ka_{\max}$	0.25	0.25	0.22	0.18	0.14	0.14	0.14	0.11	0.18	0.22	0.65	0.51	——
Ma	−1.4	−0.9	−0.7	−0.2	0.0	0.4	0.2	0.8	0.8	1.2	1.2	2.1	——

[a] CO/H_2/air flames at NTP condition (D_u = 72.9 mm^2/s).
[b] Provisional results because $\delta_D/r_f > 0.02$ for a portion of the database.
[c] Provisional results because the flame was somewhat distorted by buoyancy for a portion of the database.

Table 2 Summary of test conditions[a]

ϕ	0.6	0.8	1.0	1.2	1.6	2.0	2.4	2.8	3.0	3.5	4.0	4.5	5.0
P = 0.5 atm													
ρ_u/ρ_b	——	6.62	6.91	6.99	6.80	6.43	6.10	5.77	5.63	5.32	5.04	4.80	——
$S_{L\infty}$, mm/s	——	280	340	430	540	620	650	640	630	590	560	450	——
$Ka_{\max}$	——	0.65	0.61	0.54	0.43	0.36	0.32	0.32	0.25	0.32	0.29	0.36	——
Ma	——	−0.1	0.1	0.2	0.5	0.6	0.7	0.4	0.5	0.4	0.5	0.6	——
P = 2.0													
ρ_u/ρ_b	5.93	6.70	7.04	7.12	6.82	6.43	6.09	5.92	5.63	5.32	5.04	——	4.59
$S_{L\infty}$, mm/s	150[b]	240	320	390	480	550	610	590	00	570	440	——	260[c]
$Ka_{\max}$	0.38	0.28	0.30	0.23	0.20	0.20	0.17	0.16	0.14	0.14	0.16	——	0.18
Ma	−0.3	−0.2	−0.1	−0.1	−0.1	−0.1	−0.1	0.0	0.0	0.0	0.0	——	0.0
P = 4.0													
ρ_u/ρ_b	5.71	6.74	7.11	7.17	6.83	6.43	6.09	——	5.63	5.31	5.04	——	4.59
$S_{L\infty}$, mm/s	130[b]	220	310	360	480	520	540	——	500	430	300	——	140[c]
$Ka_{\max}$	0.30	0.20	0.15	0.12	0.10	0.09	0.08	——	0.10	0.09	0.15	——	0.18
Ma	−0.7	−0.7	−0.6	−1.4	−1.7	−2.0	−1.6	——	−1.3	−1.3	−0.5	——	−0.5

[a] 95% CO + 5% H_2/air flames at 298 K (D_u = 72.9/P mm^2/s).
[b] Provisional results because $\delta_D/r_f > 0.02$ for a portion of the database.
[c] Provisional results because the flame was somewhat distorted by buoyancy for a portion of the database.

port properties were found from Kee et al.,[30–32] except for the thermochemical properties of those species given by Kim et al.[7] and Frenklach et al.[8] All properties were checked against original sources. Similar to the measurements, effects of radiation were ignored and computed results were reduced only when r_f was large enough so that effects of initial conditions were small (typically $r_f > 5$ mm) and $\delta_D/r_f \leq 2\%$. Various transport approximations were considered, including mixture-averaged multicomponent mass diffusion with and without thermal diffusion, and complete multicomponent mass diffusion with and without thermal diffusion and the Dufour effect. The findings were similar to earlier evaluations of transport approximations for hydrogen/air flames[4]: effects of the Dufour effect were small, effects of thermal diffusion were important, and predictions using mixture-averaged and complete multicomponent mass diffusion differed by less than 10%, which corresponds to present levels of experimental uncertainties. Thus, present calculations were carried out using the mixture-averaged multicomponent transport approximation plus thermal diffusion while ignoring the Dufour effect.

Three detailed reaction rate mechanisms involving C/H/O kinetics were considered: Kim et al.[7] (since results for Yetter et al.[6] were similar), GRI-Mech 2.1 from Frenklach et al.,[8] and Wang and Rogg.[9] The potential importance of N/O chemistry was evaluated based on the mechanism of Miller and Bowman.[35] Similar to hydrogen/air flames,[4] however, the N/O reactions were not important for the flame properties of interest here and were ignored to minimize the complexity of the chemical reaction mechanisms. The final reduced chemical reaction mechanism involved 12 species and the following numbers of reversible reactions (not counting the range of third-body collision efficiencies): 30 reversible reactions for Kim et al.,[7] 39 reversible reactions for Frenklach et al.,[8] and 31 reactions for Wang and Rogg.[9] The backward rates were found from chemical equilibrium considerations using the CHEMKIN package,[32] unless the mechanism provided an alternative formulation.

Results and Discussion

Flame Response to Stretch

Values of $S_{L\infty}$ were found from Eq. (2) by plotting $S'_{L\infty}/S_L$ as a function of *Ka* similar to earlier work.[1–5] This yielded linear plots so that extrapolation to $Ka = 0$ gave $S'_{L\infty}/S_{L\infty}$ and thus $S_{L\infty}$ as summarized in Tables 1 and 2. Then given $S_{L\infty}$, plots of $S_{L\infty}/S_L$ as a function of *Ka* can be constructed for a given reactant mixture and pressure as suggested by Eq. (2). Typical measured and predicted plots of this type are illustrated in Figs. 1 and 2 for reactant mixtures involving 5 and 50% hydrogen by volume in the fuel mixture. Results at conditions that are stable (unstable) with respect to preferential-diffusion effects, corresponding to $Ma > 0$ ($Ma < 0$), are indicated by opened (darkened) symbols on these plots. The computed laminar burning velocities on these plots are based on the kinetics of Kim et al.[7] Results for the other mechanisms are similar and will be quantified when values of *Ma* are considered.

Results of both measurements and predictions illustrated in Figs. 1 and 2 show the linear relationship between $S_{L\infty}/S_L$ and *Ka* that was exploited to find $S_{L\infty}$; similar behavior was observed previously.[1–5] Thus, the slope of each plot, which is equal to the Markstein number, is independent of *Ka* over the range of the present measurements. This range involves $Ka < 0.5$, which is not close to extinction conditions (where *Ka* would be on the order of unity, see Law[36]) where the response of the flames to variations of *Ka* is likely to change. In contrast to earlier findings for hydrocarbon/air and hydrogen/air flames,[1–5] however, the response of CO/H_2/air flames to stretch at low hydrogen concentrations is rather weak, for example, values of $S_{L\infty}/S_L$ only vary in the range 0.85–1.25 for H_2 concentrations in the fuel mixture $\leq 5\%$ by volume and $Ka < 0.5$. In contrast, the flames are much more sensitive to stretch at large hydrogen concentrations, for example, values of $S_{L\infty}/S_L$ vary in the range 0.5–2.0 for H_2 concentrations in the fuel of 50% by volume and $Ka < 0.5$. Thus, CO/H_2/air flames having small H_2 concentrations could serve as useful reactant mixtures for studies of passive flame distortion by turbulence, i.e., conditions where effects of preferential diffusion neither counteract nor enhance flame surface distortion by turbulence to a significant degree. Finally, results of the simulations are seen to be qualitatively similar to the measurements; however, evaluation of predicted preferential-diffusion/stretch properties is best seen from Markstein numbers, which are considered next.

Present experimentally determined Markstein numbers are summarized in Tables 1 and 2. Markstein numbers for various concentrations of H_2 in the fuel mixture at atmospheric pressure are plotted in Fig. 3, including present measurements and predictions as well as the measurements of Brown et al.[20] for

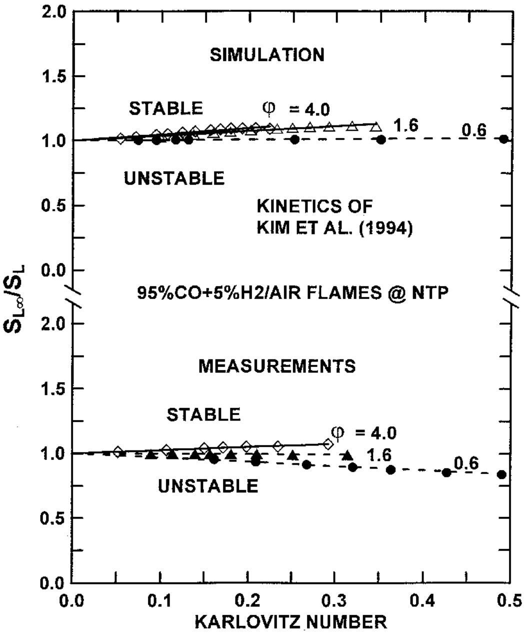

Fig. 1 Measured and predicted laminar burning velocities as a function of *Ka* and fuel-equivalence ratio for an H_2 concentration in the fuel of 5% by volume at NTP.

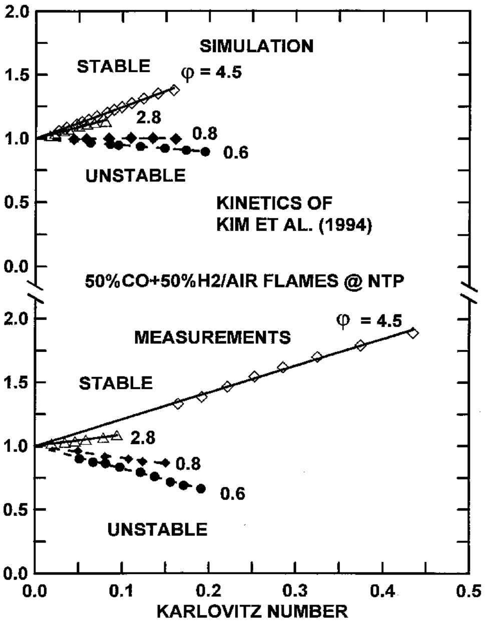

Fig. 2 Measured and predicted laminar burning velocities as a function of *Ka* and fuel-equivalence ratio for an H_2 concentration in the fuel of 50% by volume at NTP.

concentrations of H_2 in the fuel mixture of 5 and 50% at the limit of small stretch that have been normalized in the same manner as the present measurements. Present measurements and predictions of Markstein numbers at various pressures for concentrations of H_2 in the fuel mixture of 5% by volume are plotted in Fig. 4. Predictions are illustrated for all three mechanisms: Kim et al.,[7] GRI-Mech 2.1 from Frenklach et al.[8] and Wang and Rogg.[9]

Results discussed earlier show that Markstein numbers are independent of *Ka* for a given reactant mixture and pressure over the present test range. Thus, present measurements of Markstein numbers can be compared with those of Brown et al.,[20] found at the limit of small stretch, in Fig. 3; the two sets of measurements are seen to agree well within experimental uncertainties. Measurements at atmospheric pressure, Fig. 3, show that values of $Ma \approx 0$ within experimental uncertainties for concentrations of H_2 in the fuel mixture $\leq 5\%$ by volume (recalling that results at the extreme values of fuel-equivalence ratios involve conditions outside planned tolerances for present experiments and are somewhat suspect as a result). These observations of weak effects of stretch superficially agree with qualitative ideas about preferential-diffusion effects because the mass diffusivities of the major reactants (CO and O_2) and the diluent (N_2), and the thermal diffusivities of the mixture, are similar. In addition, present results also agree with earlier findings for ethylene and ethane/air flames at atmospheric pressure where *Ma* values are small when the mass diffusivities of the major reactants (C_2H_4, C_2H_6, and O_2) and the diluent (N_2), and the thermal diffusivities of the mixture, are comparable.[3] On the other hand, hydrogen and other light radicals are crucial to oxidation processes in all of these flames and their preferential-diffusion behavior might be expected to cause greater sensitivity to stretch.

As concentrations of H_2 in the fuel mixture increase beyond 5% by volume, the results illustrated in Fig. 3 show that absolute values of *Ma* increase. In fact, the properties of *Ma* at lean conditions for concentrations of H_2 in the fuel mixture of 50% by volume are comparable to those observed for pure H_2/air flames[4]: values of $|Ma|$ are comparable, and neutral conditions ($Ma = 0$) are observed near $\phi = 0.7$ and 1.0 for the pure H_2 and CO/H_2/air flames, respectively. More effects of reduced flame response to stretch because of the presence of carbon monoxide can be seen for rich flames, however, where values of $|Ma|$ for 50% H_2 by volume in the fuel mixture are only about one-third as large as those observed for pure H_2/air flames.[4]

The measured properties of *Ma* for pressures in the range 0.5–2.0 atm, Fig. 4, are qualitatively similar to results at atmospheric pressure. Thus, values of $Ma \approx 0$ within experimental uncertainties for H_2 concentrations in the fuel mixture of 5% by volume. A striking change occurs at 4.0 atm, however, where $|Ma|$ approaches values of 2 for intermediate fuel-equivalence ratios (in the range $\phi = 1-3$) and the flames are unstable to preferential-diffusion effects over most of the present range of fuel-equivalence ratios. This increased sensitivity to preferential-diffusion effects at increased pressures could be caused by reduced concentrations of small, fast-diffusing, radicals in the reaction zone, because of increased rates of three-body recombination reactions at increased pressures. Nevertheless, a satisfactory explanation of this behavior will require more study and provides strong motivation for measurements of the response of CO/H_2/air flames at high pressures.

Measured and predicted *Ma* are in reasonably good agreement in Figs. 3 and 4, with the predictions correctly indicating the relatively small values of $|Ma|$ at small H_2 concentrations in the fuel mixture, the relatively slow variation of *Ma* with ϕ at small H_2 concentrations in the fuel mixture, the tendency for unstable (stable) preferential-diffusion behavior at fuel-lean (fuel-rich) conditions, and the tendency for $|Ma|$ to increase as the H_2 concentrations in the fuel increases. The greatest difference between measurements and predictions is observed for $P = 4$ atm in Fig. 4 for H_2 concentrations in the fuel mixture of 5% by volume, but even here the theories qualitatively support the tendency for *Ma* to dip toward negative values at intermediate values of ϕ, a trend not seen n other measurements or predictions considered thus far.[1–5] Thus, in view of the novelty of Markstein numbers as a property of laminar premixed flames, and the fact that the development of chemical reaction mechanisms has not involved consideration of Mark-

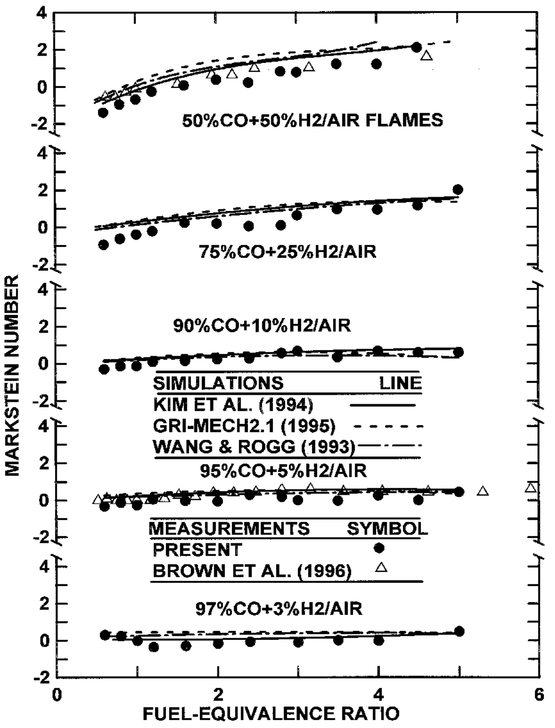

Fig. 3 Measured and predicted *Ma* as a function of the H_2 concentration in the fuel and fuel-equivalence ratio at NTP.

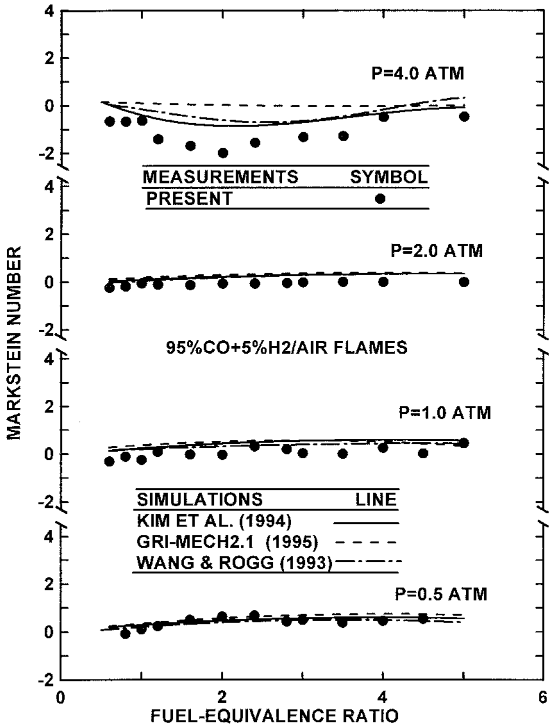

Fig. 4 Measured and predicted *Ma* as a function of fuel-equivalence ratio and pressure for an H_2 concentration in the fuel of 5% by volume.

stein numbers, the agreement between measurements and predictions seen in Figs. 3 and 4 is quite satisfying.

Unstretched Laminar Burning Velocities

Measured unstretched laminar burning velocities are summarized in Tables 1 and 2. Both measured and predicted unstretched laminar burning velocities for various concentrations of H_2 in the fuel mixture are plotted in Fig. 5; corresponding results for concentrations of H_2 in the fuel mixture of 5% by volume at various pressures are plotted in Fig. 6. Results illustrated in these figures include the measurements of Scholte and Vaags,[14] Vagelopoulos and Egolfopoulos,[18] McLean et al.,[19] and the present investigation, along with predictions based on the chemical reaction mechanisms of Kim et al,[7] GRI-Mech 2.1 from Frenklach et al.,[8] and Wang and Rogg.[9] Except for the measurements of Scholte and Vaags,[14] all of these results have been corrected to provide estimates of measured unstretched laminar burning velocities. The results of Scholte and Vaags[14] are in remarkably good agreement with the stretch-corrected results; nevertheless, this agreement is largely fortuitous, as discussed by McLean et al.[19] The various stretch-corrected results agree with each other within the present experimental uncertainties as well. This includes reaching maximum laminar burning velocities for relatively high values of fuel-equivalence ratios in the range 2–3 (tending to decrease with increasing H_2 concentrations in the fuel mixture), even though maximum flame temperatures are reached near stoichiometric conditions. This behavior is somewhat analogous to the behavior of hydrogen/air flames[4]; in particular, predictions show that maximum laminar burning velocities correlate reasonably well with maximum radial concentrations in the reaction zone for both H_2/air and CO/H_2/air flames.

The comparisons between predictions and measurements of unstretched laminar burning velocities in Figs. 5 and 6 are quite good, including the estimation of fuel-equivalence ratios for maximum laminar burning velocities and the effects of added hydrogen concentrations in the fuel mixture. This is particularly true for low concentrations of H_2 in the fuel mixture. As a result, comments about the comparison between predictions and measurements are similar to those for H/O/N flames.[4,5] In particular, the predictions are quite good at fuel-lean conditions, with somewhat larger discrepancies between measurements and predictions at fuel-rich conditions.

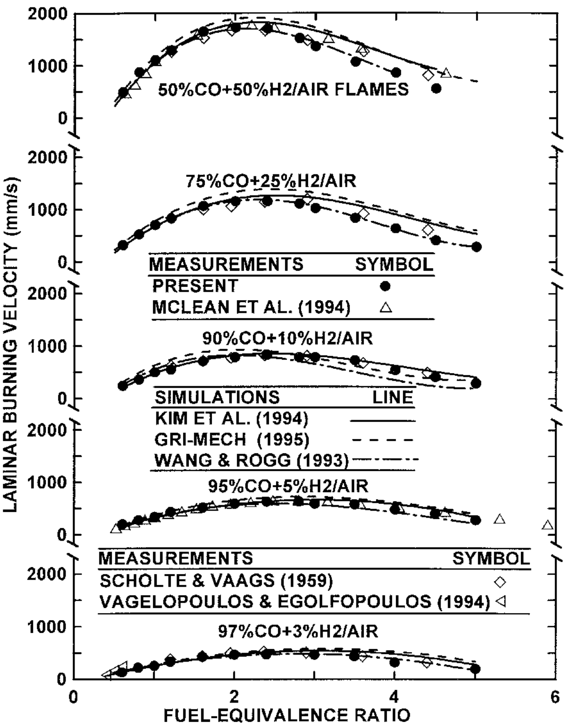

Fig. 5 Measured and predicted unstretched laminar burning velocities as a function of fuel-equivalence ratio and H_2 concentration in the fuel at NTP.

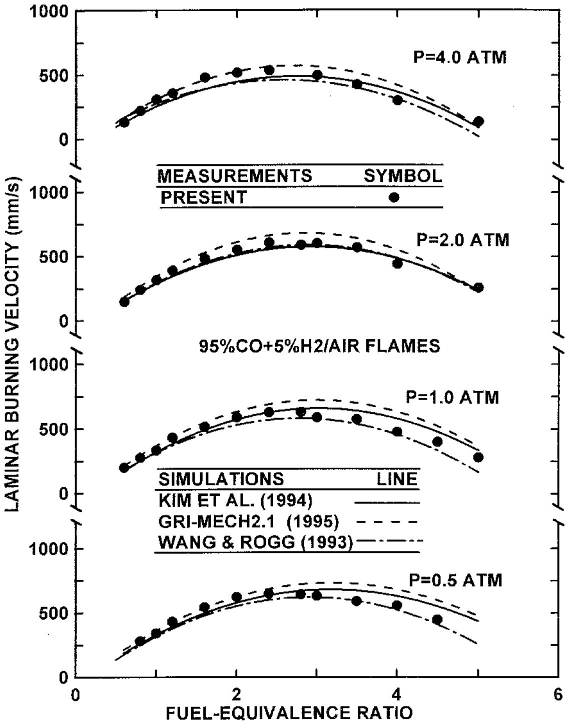

Fig. 6 Measured and predicted unstretched laminar burning velocities as a function of fuel-equivalence ratio and pressure for an H_2 concentration in the fuel of 5% by volume.

Insight about the most important chemical reaction needed to predict the laminar burning velocities of CO/H_2/air flames was sought by carrying out sensitivity calculations using the methods described by Kee et al.[33] and Grcar et al.[34] These evaluations were carried out for concentrations of hydrogen in the fuel mixture of 3 and 50% by volume, which bound present measurements. Results at the larger hydrogen concentrations are similar to earlier findings for H_2/air flames,[4] and will not be discussed here. Not surprisingly, the most sensitive reaction over the entire fuel-equivalence range for small H_2 concentrations was the carbon monoxide oxidation step, $CO + OH = CO_2 + H$, where recent studies have raised questions about past estimates of this reaction rate constant that merit consideration (see the discussion of McLean et al.[19]). Other important reactions involve H and O that have already been discussed in Ref. 4 in connection with the H_2/air flames.

Conclusions

Effects of positive stretch on the laminar burning velocities observed in outwardly propagating spherical laminar premixed flames involving CO/H_2/air mixtures were studied experimentally and computationally. Experiments were carried out at normal temperature (298 ± 2 K) with concentrations of hydrogen in the fuel mixture of 3–50% by volume, fuel-equivalence ratios of 0.6–5.0 and pressures of 0.5–4.0 atm. The major conclusions of the study are as follows:

1) Preferential-diffusion/stretch interactions for both measurements and predictions could be correlated according to $S_{L\infty}/S_L = 1 + MaKa$, where $S_{L\infty}/S_L$ varied linearly with Ka, yielding Markstein numbers that were only functions of reactant composition and pressure, similar to past work in this laboratory.[1–5]

2) Effects of flame stretch on laminar burning velocities were modest at low H_2 concentrations, yielding Markstein numbers based on hydrogen diffusivities less than unity for

low H_2 concentrations $\leq 10\%$ by volume in the reactant mixture, suggesting that such mixtures might be useful for studies of passive distortion of thin laminar flamelets by turbulence; effects of flame stretch on laminar burning velocities were more significant for larger H_2 concentrations, approaching the behavior of H_2/air flames at the largest H_2 concentrations considered here.

3) Predicted and measured flame properties were in reasonably good agreement using the chemical reaction mechanisms of Kim et al.,[7] GRI-Mech (2.1 version) from Frenklach et al.,[8] and Wang and Rogg[9]; not surprisingly, predictions were most sensitive to the $CO + OH = CO_2 + H$ reaction at low H_2 concentrations, particularly at lean conditions. In addition, present measurements of Markstein numbers and unstretched laminar burning velocities agreed with earlier results in the literature,[16–20] within experimental uncertainties, in the region where these measurements overlap.

Acknowledgments

This research was supported by NSF Grants CTS-9019813 and 9321959 under the technical management of M. J. Linevsky and F. Fisher. Support from the Peace Fellowship Program of Egypt for M. I. Hassan is also gratefully acknowledged.

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