



# Laminar flame speeds of H<sub>2</sub>/CO with CO<sub>2</sub> dilution at normal and elevated pressures and temperatures



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## HIGHLIGHTS

- Laminar flame speeds of syngas with CO<sub>2</sub> dilution are measured.
- Predictive capabilities of three mechanisms are discussed.
- Radiation re-sorption effect of CO<sub>2</sub> dilution is considered.
- Markstein lengths at elevated pressures and temperatures are measured.
- Chemical effects of CO<sub>2</sub> dilution on flame speeds and temperatures are analyzed.

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## ABSTRACT

Laminar flame speeds and Markstein lengths of H<sub>2</sub>/CO with CO<sub>2</sub> dilution were measured at normal and elevated pressures (0.1 MPa, 0.5 MPa, 1.0 MPa) and temperatures (298 K, 375 K, 450 K) using outwardly propagating spherical flame method. Simulation considering detailed chemistry and transport was conducted to examine the effects of radiation re-absorption of CO<sub>2</sub> dilution on flame propagation. The laminar flame speeds measured in experiments were compared with prediction by detailed chemistry and the performance of three different chemical mechanisms recently developed for syngas oxidation was discussed. It is found that the laminar flame speed decreases linearly with CO<sub>2</sub> dilution ratio. The Markstein length remains positive and decreases with pressure. At atmospheric pressure, increasing CO<sub>2</sub> dilution ratio and preheat temperature can reduce the Markstein length, and thereby promote the diffusive-thermal instability. The chemical effects of CO<sub>2</sub> dilution, including the direct reaction effect and the three-body effect, were quantitatively analyzed using the pseudo CO<sub>2</sub> strategy. The direct reaction effect of CO<sub>2</sub> dilution mainly reduces the CO oxidation rate through reaction CO + OH = CO<sub>2</sub> + H and competes H atoms with the main chain-branching reaction H + O<sub>2</sub> = O + OH, resulting in reduced laminar flame speed and flame temperature. And the three-body effect of CO<sub>2</sub> dilution prompts three-body reactions with negative influence on flame speeds. Numerical results demonstrate that both chemical effects on flame speeds are enhanced by elevating CO<sub>2</sub> dilution ratio and pressure but reduced by elevating temperature.

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## 1. Introduction

Synthesis gas (syngas) is one of the promising alternative fuels that can be used in the Integrated Gasification Combined Cycle (IGCC). The main components of syngas are H<sub>2</sub>, CO, N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O. However, the different gasification sources and procedures make the syngas composition change significantly. The H<sub>2</sub> content

in syngas varies from 10% to 60%, the CO content varies from 1% to 55%, and the amount of diluents (N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O) varies from 5% to 70% [1]. This brings challenges for combustor designers since typical combustor design tools require data on various fundamental gas combustion properties in order to design an efficient fuel flexible combustor. Therefore, it is essential to study the fundamental burning properties of syngas over a wide range of composition under representative operating conditions of advanced gas turbines. With the development of carbon capture and storage (CCS) technique [2], burning syngas with large amount of CO<sub>2</sub> dilution

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becomes an effective way to reduce NO<sub>x</sub> emission (e.g. in oxy–fuel combustion). Therefore, it is necessary to obtain the laminar flame speed of syngas with CO<sub>2</sub> dilution at normal and more actual operating conditions (elevated pressures and temperatures).

In the literature there are many studies on the laminar flame speeds of syngas (e.g. [3–17]) at ambient pressure and temperature. The syngas studies at elevated pressure and/or temperature attracted more interest in recent years. The laminar flame speeds of H<sub>2</sub>/CO/O<sub>2</sub>/dilute mixtures were measured at different elevated pressures [6,7,9,10,13,14] and elevated temperatures [6,7,13,14,17] using Bunsen flames, stagnation flames or propagating spherical flames. Additionally, Kéromnès et al. [13] updated coefficients for some element reactions and developed a new chemical mechanism for high initial pressure syngas oxidation. However, syngas studies at elevated pressures and temperatures are still inadequate. As reported in [9,13], there were also large differences between the results in the literature, such as the disagreement of measured results of the Kéromnès et al. [13] with the data of Sun et al. [10], which implied further study is needed.

As for CO<sub>2</sub> dilution, several studies have analyzed the thermal effect, chemical effect, and radiation effect of CO<sub>2</sub> dilution on methane flames or hydrogen flames (e.g. [18–23]). However, only a few studies [1,8,12,15,16] examined the effects of CO<sub>2</sub> dilution on syngas flames. Natarajan [1] measured laminar flame speeds of different H<sub>2</sub>/CO ratios with varying CO<sub>2</sub> dilution ratio at normal and elevated pressures and temperatures (up to 1.5 MPa, 600 K) using Bunsen and stagnation flame methods. Burke et al. [8] measured laminar flame speeds of 25% H<sub>2</sub>–75% CO mixture with CO<sub>2</sub> dilution ratio varying from 0% to 25% at 1.0 MPa using spherical flame method. Prathap et al. [12] and Burbano et al. [15] examined the effect of CO<sub>2</sub> dilution on laminar flame speeds and flame stability. Wang et al. [16] measured the laminar flame speeds of syngas/O<sub>2</sub>/CO<sub>2</sub> and discussed different effects caused by CO<sub>2</sub> dilution. Zhou et al. [24] numerically investigated the flame behavior of H<sub>2</sub>/CO/air mixtures near CO<sub>2</sub> dilution limit at high initial temperatures and pressures.

The effects of CO<sub>2</sub> dilution on the laminar flame speed of syngas at elevated pressures and temperatures are still not well known and there is limited amount of experimental data available for chemical mechanism validation and optimization. There is a lack of discussion in the literature about the effect of CO<sub>2</sub> dilution on Markstein lengths as well as flame stability of syngas flames at elevated pressures and temperatures. The coupled chemical effects of CO<sub>2</sub> dilution on syngas flames at elevated pressures and temperature are not separately analyzed. The radiation re-absorption effect of large CO<sub>2</sub> dilution ratio also needs further analysis. Therefore, in the present work the laminar flame speeds and Markstein lengths of CO<sub>2</sub>-diluted syngas flames were measured at normal and elevated pressures and temperatures by using the outwardly propagating spherical flame method. Numerical simulation considering detailed chemistry and transport was performed to investigate the effects of radiation re-absorption of CO<sub>2</sub> dilution on the laminar flame propagation characteristics. Three chemical mechanisms for syngas [13,25,26] were used in the numerical simulations. The experimental laminar flame speeds are compared with the predictions and the predictive capacities of the adopted kinetic mechanism were discussed. Furthermore, two kinds of chemical effects (the direct reaction effect and the three-body effect) of CO<sub>2</sub> dilution are assessed.

## 2. Experimental and numerical methods

Experiments were conducted in a dual-chambered, pressure-release type cylindrical chamber [27], which was designed to withstand pressure up to 4 MPa. The inner diameters of two concentric

cylindrical vessels are 100 mm and 300 mm, respectively. In experiments, the pressure of the outer chamber is slightly higher than that of the inner chamber. Two optical quartz windows are mounted on each end of inner chamber and can withstand high pressure wave and high temperature. The tungsten electrodes are vertically mounted with diameters of 0.4 mm and gap of 1 mm. The ignition was triggered by a high voltage spark generator. The preheating device consists of four thermal resistance heaters mounted in the outer chamber and an adjustable transformer is adopted to provide the appropriate voltage for the heaters to maintain the thermal equilibrium between the device and surroundings. The gas mixture in the inner chamber was heated by heat conduction from the outer chamber. The temperature of inner and outer chambers was measured by two K-type thermocouples: the inner temperature is the required experimental temperature and the outer temperature, smaller than the inner, is used to adjust the transformer. High-speed schlieren photography was utilized to measure the propagating spherical flames. The shutter speed of the high-speed digital camera is 1/117,000 s and the frame rate is 8000 fps. The mixtures were prepared using the partial pressure method. High purity gases (purity level: 99.999% for H<sub>2</sub>, 99.99% for CO, 99.5% for CO<sub>2</sub>, 99.999% for O<sub>2</sub>, 99.999% for N<sub>2</sub>, and 99.999% for He) are used. In this study, the CO<sub>2</sub> dilution is the mole fraction of CO<sub>2</sub> in fuels (H<sub>2</sub>, CO and CO<sub>2</sub>). The details of experimental facility and procedure can be found in our previous work [27]. All the experimental results are the average of at least three repeated experiments and up-down error bars are plotted to indicate the standard deviation.

Only smooth spherical flames are used in data processing so that the effect of flame instability on flame speed determination is eliminated. The flame radius ( $R_f$ ) range of  $0.8 < R_f < 2.0$  cm is used in the linear extrapolation from the stretched flame speed so that the effects of ignition [28] and compression [29] can be minimized. The uncertainty in the determination of radius and that in the linear extrapolation of the stretched propagation velocity to zeros stretch make up the main uncertainty of the unstretched laminar flame speed. As discussed in our previous work [27], the overall uncertainty of unstretched laminar flame speed was within 5%.

When the compression and radiation effects are negligible, the burned gas can be assumed to be quiescent [29]. As a result, the propagation speed of the experimentally visualized flame front is equal to the flame speed with respect to the burned mixture, i.e.  $S_b = dR_f/dt$ . At moderate stretch rate, the flame speed can change linearly with the stretch rate [30]:

$$S_b = S_b^0 - L_b K \quad (1)$$

where  $S_b^0$  and  $L_b$  are, respectively, the unstretched laminar flame speed and the Markstein length with respect to the burned mixture.  $K = (2/R_f)dR_f/dt$  is the stretch rate for a propagating spherical flame. Therefore, according to the theoretical model given by Eq. (1),  $S_b^0$  and  $L_b$  can be obtained from the linear extrapolation based on the plot of  $S_b$  versus  $K$ . Knowing  $S_b^0$ , the unstretched laminar flame speed relative to the unburned mixture,  $S_u^0$ , can be deduced through mass conservation:  $S_u^0 = \sigma S_b^0$ , where  $\sigma = \rho_b/\rho_u$  is the density ratio of burned to unburned mixture. For the mixture considered in this study, the laminar flame speed is above 26 cm/s. According to the recent study of Yu et al. [31], the radiation-induced uncertainty (due to thermal and flow effects caused by radiation) in laminar flame speed measured from propagating spherical flames is within 2%, indicating that linear extrapolation based on Eq. (1) can be conducted. Moreover, the absolute value of Markstein length is less than 1 mm for all the mixtures considered here. Therefore, the nonlinear stretch behavior is not observed and linear extrapolation based on Eq. (1) can be conducted [32].

Numerical simulation of laminar flame speeds is conducted by 1-D, planar, freely-propagating, CHEMKIN-PREMIX code [33]. The transport properties are evaluated by multi-component formulation and thermal diffusion of all species is considered. To ensure the results are grid-independent, the grid number is always above 200. Two well cited mechanisms developed by Davis et al. [25] and Li et al. [26] for syngas oxidation as well as a newly updated mechanism developed by K eromn es et al. [13] for high pressure syngas oxidation are adopted. The predicted flame speeds are compared with these obtained in experiments. A space-adaptive numerical solver for Adaptive Simulation of Unsteady Reactive Flow (A-SURF) is used to calculate the Markstein lengths and also the simulation results are compared with experimental Markstein lengths. A-SURF has been adopted and validated in our previous studies [28,29,31,34,35] and the details on the governing equations, numerical schemes, and code validation can be found in Refs. [28,29].

It is known that CO<sub>2</sub> is not only a radiation emitter, but also a strong radiation absorber [19,29]. The radiation emission reduces the flame temperatures while the radiation re-absorption in the preheat zone increases the temperature of reactants and thus increases the laminar flame speed. It is found that the relative difference between results with and without considering the radiation re-absorption effect is about 8.5% for 40% CO<sub>2</sub> dilution at normal condition and equivalence ratio of  $\Phi = 0.8$ . Therefore, the radiation re-absorption effect cannot be neglected. The statistical narrow band correlated-k method (SNBCK) [36] model is used in the present work to consider both radiation emission and re-absorption.

### 3. Results and discussion

#### 3.1. Effect of CO<sub>2</sub> dilution on laminar flame speeds

To validate the present experiment system, the laminar flame speeds of H<sub>2</sub>/CO/air flames with different H<sub>2</sub>/CO ratios of 1:1, 3:1 and 1:3 are shown in Fig. 1 as a function of equivalence ratios without CO<sub>2</sub> dilution at ambient condition (298 K, 0.1 MPa). The present measurements, together with those of McLean et al. [37], Sun et al. [10], Singh et al. [17] and Natarajan et al. [6], are plotted in symbols, while the predictions from the mechanisms of Davis et al. [25], K eromn es et al. [13], and Li et al. [26] are plotted in lines. Good agreement between measurements and prediction is observed for H<sub>2</sub>/CO ratios of 1:1 and 1:3. For H<sub>2</sub>/CO ratio of 3:1,

only the results of Singh et al. [17] is available in the literature. It is seen that the results of Singh et al. [17] are slightly higher than the present ones. Moreover, the present experimental syngas flame data are in good agreement with the predictions from the three mechanisms. In particular, the predictions from the mechanism of Davis et al. [25] agree very well with present measurements for all the cases. These results confirm the reliability of the present experimental system.

Fig. 2 shows the measured laminar flame speeds at ambient condition and  $\Phi = 0.8$ . The laminar flame speeds measured by Prathap et al. [12] are also presented for comparison and good agreement with present data is observed. Fig. 2 shows that for a given CO<sub>2</sub> dilution ratio the values predicted by the three mechanisms increase in the order Davis < Li < K eromn es and the discrepancies of the values increase with elevating H<sub>2</sub>/CO ratio. The peak temperature changes slightly with H<sub>2</sub>/CO ratio at a given CO<sub>2</sub> dilution level, for example for CO<sub>2</sub> = 20%, peak temperatures are 2058.6 K, 2042.6 K and 2017 K with increasing H<sub>2</sub> level (H<sub>2</sub>/CO = 1/3, 1/1 and 3/1). The slightly higher peak temperature of high CO level is owing to the higher molar heating value of CO. Also the increase of H<sub>2</sub>/CO ratio worsens the predictive capabilities of those mechanisms. Generally, the predicted values by Davis et al. [25] mechanism agree better with the experimental results especially for H<sub>2</sub>/CO ratios of 1:3.

Fig. 3 shows the measured laminar flame speeds at elevated pressures (0.5 MPa and 1.0 MPa, 298 K) for H<sub>2</sub>/CO = 1:3 and O<sub>2</sub>/He = 1:6 and CO<sub>2</sub> dilution ratio variation from 0% to 30%. The 1:6 M ratio of O<sub>2</sub>/He mixture was selected to eliminate diffusional-thermal and hydrodynamic instability while maintain nearly the same flame temperature [27]. It is observed that the predicted results by three mechanisms are very close and this trend is true especially for high CO<sub>2</sub> dilution ratio. The recently updated mechanism by K eromn es et al. [13] is better for this case prediction, especially for high pressure of 1.0 MPa as shown in Fig. 3, confirming the suitability of this mechanism for syngas oxidation at elevated pressures.

Fig. 4 shows the measured laminar flame speeds at elevated temperatures (298 K, 375 K and 450 K, 0.1 MPa) and  $\Phi = 1$  for H<sub>2</sub>/CO = 1:1 and CO<sub>2</sub> dilution ratio from 0% to 40%. The good agreement between the present data with data of Prathap et al. [12] is also obtained in Fig. 4. For a given CO<sub>2</sub> dilution ratio, like ambient cases, the values predicted by the three mechanisms increase in the order Davis < Li < K eromn es and the discrepancies of the values increase with elevating temperature. It is seen from Fig. 4 that the experimental results are predicted by Davis et al. [25] mechanism

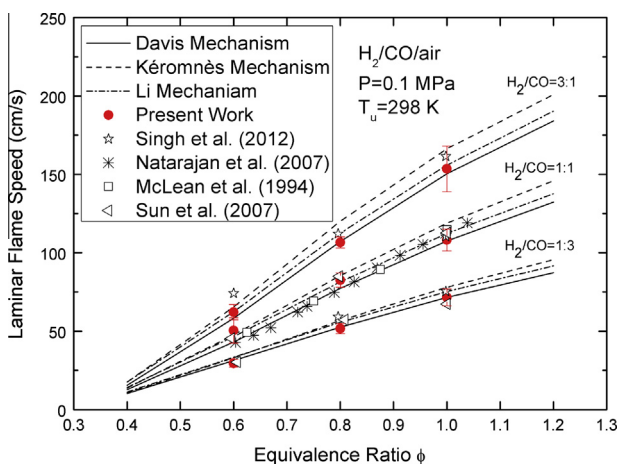


Fig. 1. Laminar flame speeds as a function of equivalence ratio for H<sub>2</sub>/CO/air mixtures with different H<sub>2</sub>/CO ratios at ambient condition.

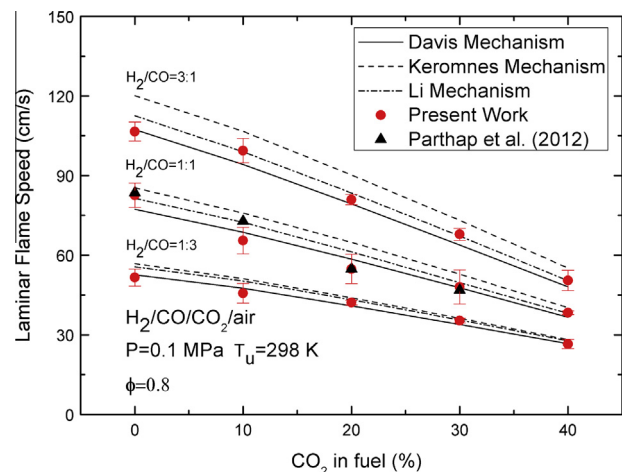


Fig. 2. Laminar flame speeds of H<sub>2</sub>/CO/CO<sub>2</sub>/air mixtures as a function of CO<sub>2</sub> dilution ratio in H<sub>2</sub>/CO/CO<sub>2</sub>.

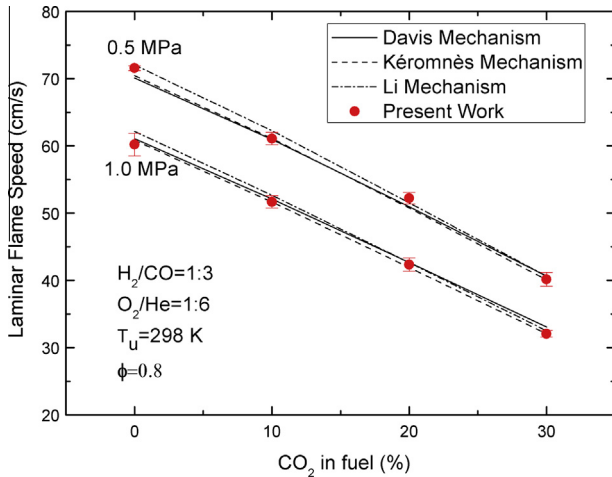


Fig. 3. Laminar flame speeds of H<sub>2</sub>/CO/CO<sub>2</sub>/O<sub>2</sub>/He mixtures as a function of CO<sub>2</sub> dilution ratio in H<sub>2</sub>/CO/CO<sub>2</sub> and pressure.

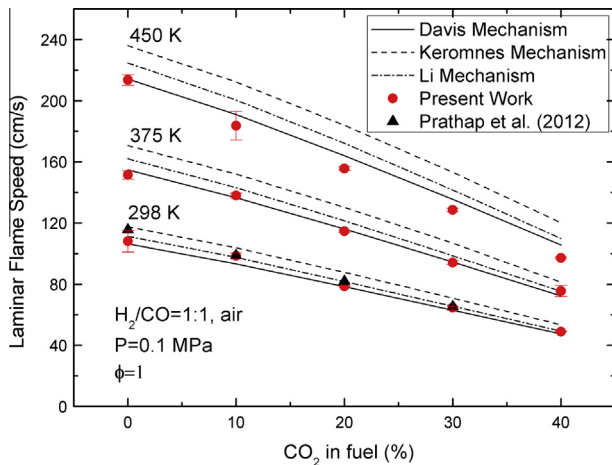


Fig. 4. Laminar flame speeds of H<sub>2</sub>/CO/CO<sub>2</sub>/air mixtures as a function of CO<sub>2</sub> dilution ratio in H<sub>2</sub>/CO/CO<sub>2</sub> and preheating temperatures.

better at 298 K and 375 K, while a slightly over-prediction at 450 K. The possible reason is that the coefficients, provided in above mechanisms for calculating the forward reaction rate constants (based on Arrhenius Law) in PREMIX, may be inaccurate of certain elementary reactions at elevated temperature cases. Consequently, the reaction rates of above elementary reactions will deviate from real reaction rates, resulting in the discrepancy between the experimental laminar flame speeds and predictions at elevated temperatures.

Figs. 2–4 indicates that CO<sub>2</sub> dilution significantly reduces the laminar flame speed and the laminar flame speed decreases almost linearly with CO<sub>2</sub> dilution ratio in all cases (similar trend was also reported by Burke et al. [8] for P = 1.0 MPa). The Davis et al. [25] mechanism predicts experimental results better at normal and elevated temperatures, while the Kéromnès et al. [13] mechanism shows a better agreement with experimental results at elevated pressures. Moreover, the predictive performance of those mechanisms is shown to be not significantly affected by CO<sub>2</sub> dilution ratio, which indicates that the effect of CO<sub>2</sub> dilution on laminar flame speeds in present experiments is well considered in these chemical mechanisms.

### 3.2. Markstein length

Fig. 5 shows the measured and computed Markstein length,  $L_b$ , determined by  $S_b = S_b^0 - L_b K$ , as a function of CO<sub>2</sub> dilution percentage in the H<sub>2</sub>/CO/CO<sub>2</sub> fuel. Markstein length is governed by the effective Lewis number ( $Le_{eff}$ ) [12,38] of the mixture and is a measure of the flame response to flame stretch. The positive (negative) Markstein length implies that the propagating flame is stable (unstable). The effective Lewis number,  $Le_{eff}$ , which decreases with CO<sub>2</sub> dilution ratio [23], was calculated as summarized in Ai et al. [27] and Bouvet et al. [38] and is shown in Table 1. It is seen from Fig. 5a, the sign of  $L_b$  remains positive and its value are almost constant at different pressures with increasing CO<sub>2</sub> dilution ratio, indicating that the H<sub>2</sub>/CO/CO<sub>2</sub>-O<sub>2</sub>/He flames are stable and insensitive to flame stretch. There is a good agreement between experimental and simulation results. For H<sub>2</sub>/CO/CO<sub>2</sub>-O<sub>2</sub>/He flames, helium becomes dominant and governs the property ( $Le$ ) of the mixture, thus the effective Lewis number, shown in Table 1, is greater than unity, and the flame is subjected to thermal diffusive stability. However the Markstein length,  $L_b$ , decreases with the increase of the pressure due to the decrease of the flame thickness and the stability of propagating flame is reduced. At sufficiently high pressure, although the Lewis number is still greater than unity, the Markstein length,  $L_b$ , will change sign from positive to negative. The hydrodynamic instability will become dominant, thus the flame instability will occur.

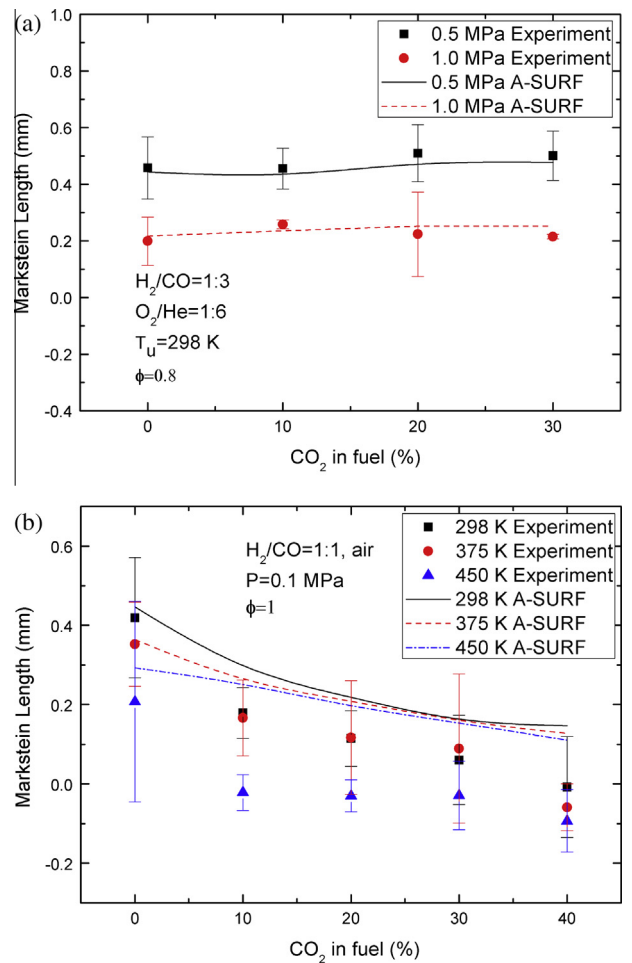


Fig. 5. Markstein lengths of H<sub>2</sub>/CO/CO<sub>2</sub>/air (O<sub>2</sub>/He) mixtures as a function of CO<sub>2</sub> dilution ratio in H<sub>2</sub>/CO/CO<sub>2</sub> under the conditions of (a) elevated pressures; (b) elevated preheating temperature.

**Table 1**  
Effective Lewis number for elevated pressures and temperatures.

Pressure (MPa)	Temperature (K)	CO <sub>2</sub> ratio in fuels (%)	Le <sub>eff</sub> <sup>a</sup>
0.5 (1.0) <sup>b</sup>	298	0	1.603
0.5 (1.0)	298	10	1.560
0.5 (1.0)	298	20	1.515
0.5 (1.0)	298	30	1.469
0.1	298	0	1.040
0.1	298	10	1.021
0.1	298	20	0.999
0.1	298	30	0.975
0.1	298	40	0.946
0.1	375	0	1.025
0.1	375	10	1.006
0.1	375	20	0.984
0.1	375	30	0.956
0.1	375	40	0.931
0.1	450	0	1.020
0.1	450	10	1.000
0.1	450	20	0.978
0.1	450	30	0.952
0.1	450	40	0.923

<sup>a</sup> The diffusion-based effective Lewis number formulations for bi-component fuels.

<sup>b</sup> The calculated effective Lewis number of 0.5 MPa is the same as that of 1.0 MPa.

Fig. 5b shows the Markstein lengths of H<sub>2</sub>/CO/air flames as a function of CO<sub>2</sub> dilution percentage in the H<sub>2</sub>/CO/CO<sub>2</sub> fuel and the preheating temperature. For this case, even though the agreement between the measurements and simulations is not good, the overall trend of the experimental and numerical results is consistent: increasing CO<sub>2</sub> dilution ratio and preheat temperature can reduce the effective Lewis number (see in Table 1) thus generally decreases the Markstein lengths and prompts the instability. The measurements also show that, for 298 K and 375 K cases, the Markstein lengths change sign from positive to negative for 40% CO<sub>2</sub>, indicating the occurrence of instability. With further increase of the preheat temperature to 450 K, the Markstein lengths still decrease and change sign from positive to negative for most of cases, corresponding with the trend in Ai et al. [27], and the flame is subjected to diffusive-thermal instability.

### 3.3. Chemical effect of CO<sub>2</sub> dilution

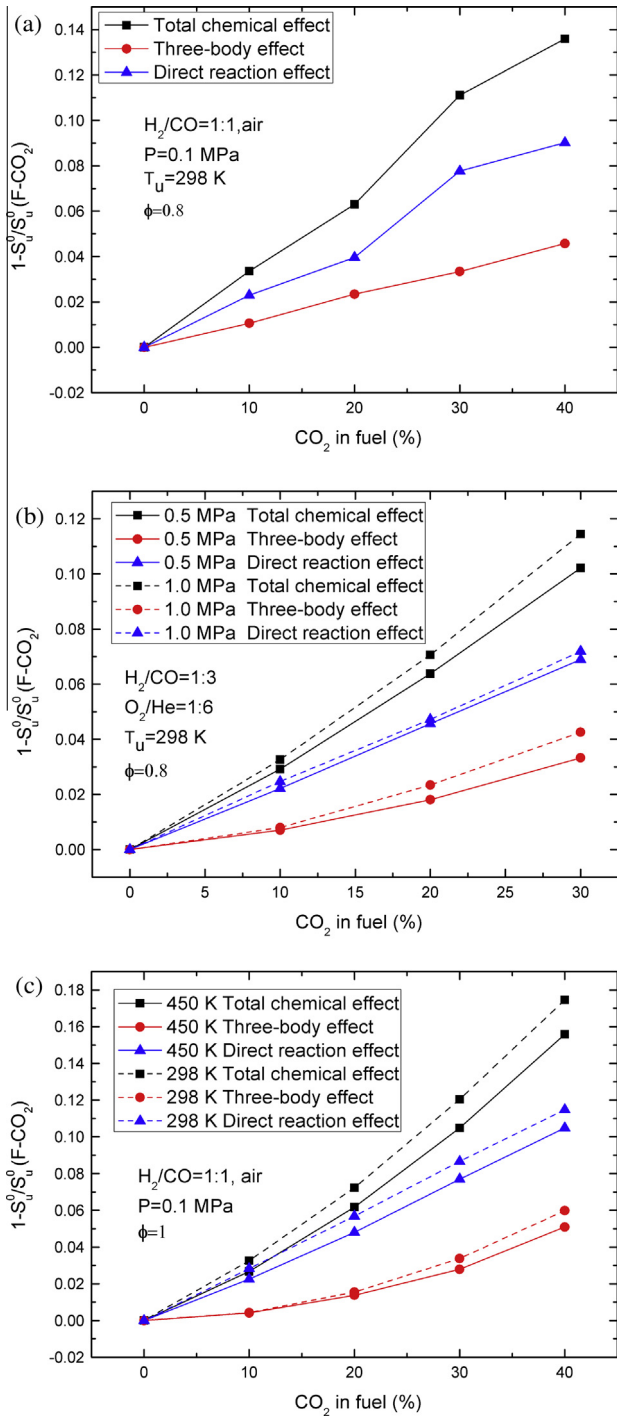
As discussed by Liu et al. [18,39], the introduction of CO<sub>2</sub> on fuel side in general affects flame through the following three paths: (1) dilution effect because of reduction in the concentrations of the reactive species leading to the variation of the transport and thermal properties of the mixture; (2) thermal effect because of the change in flame temperature due to the increase in the specific heat capacity of fuel mixtures and the enhanced radiation transfer by CO<sub>2</sub>; and (3) the direct chemical effect because of the participation of the additive in chemical reactions. CO<sub>2</sub> mainly impedes the CO oxidation reaction CO + OH = CO<sub>2</sub> + H, thus reduces the concentration of H, O and OH [39] and decreases the laminar flame speeds. In reality, these three effects occur simultaneously and are intimately coupled. In the present work, in order to investigate the chemical effects of the addition of CO<sub>2</sub> on the syngas fuel side, the numerical strategy developed by Liu et al. [39] and Zhang et al.

[23] were used to identify the chemical effects. In this strategy three numerical solutions need to be obtained (shown in Table 2). One is for addition of normal CO<sub>2</sub> (in the sense that the added CO<sub>2</sub> is allowed to participate in chemical reactions). The second is for addition of fictitious CO<sub>2</sub>, referred to as F-CO<sub>2</sub> hereafter. The fictitious CO<sub>2</sub> is defined as such that it has exactly the same thermochemical and transport properties as the normal CO<sub>2</sub> but is not allowed to participate in any chemical reactions, that is, chemically inert. Since the three-body recombination reactions are very important for highly diluted mixtures [23], The third is to consider the artificial inert CO<sub>2</sub> (referred to as T-CO<sub>2</sub> hereafter) in the simulation still acting as a three-body (the three-body coefficient of T-CO<sub>2</sub> is the same as CO<sub>2</sub>). Besides, the radiation property of three dilutions (CO<sub>2</sub>, F-CO<sub>2</sub> and T-CO<sub>2</sub>) is the same, thus the radiation effects caused by three dilutions at a given dilution ratio are the same (slight discrepancy caused by the decomposition of CO<sub>2</sub> is negligible). For the purpose of isolating the chemical effects and simplifying simulations, the radiation effect is neglected in numerical calculations in this chapter. Differences between the solutions for CO<sub>2</sub> and F-CO<sub>2</sub> dilutions, if there are any, are therefore entirely attributed to the chemical effects of CO<sub>2</sub>, referred to as total chemical effect hereafter. For the laminar flame speeds, the dimensionless relative variation for the total chemical effect is expressed as  $\frac{S_{li}^0(F-CO_2) - S_{li}^0(CO_2)}{S_{li}^0(F-CO_2)}$ . Differences between the solutions for F-CO<sub>2</sub> and T-CO<sub>2</sub> dilutions, if there are any, are therefore attributed to the three-body CO<sub>2</sub> effects, referred to as three-body effect hereafter. The dimensionless relative variation for the three-body effect is expressed as  $\frac{S_{li}^0(F-CO_2) - S_{li}^0(T-CO_2)}{S_{li}^0(F-CO_2)}$ . Differences between the total chemical effect and the three-body effect are defined as the direct reaction effect.

Fig. 6 shows the dimensionless relative variation of laminar flame speeds of H<sub>2</sub>/CO/CO<sub>2</sub>/air (O<sub>2</sub>/He) flames as a function of CO<sub>2</sub> dilution percentage in the H<sub>2</sub>/CO/CO<sub>2</sub> fuel under the conditions of (a) ambient; (b) elevated pressures; (c) elevated preheating temperature. It is seen from Fig. 6a that two kinds of chemical effect are amplified and both seem to have a negative influence on laminar flame speeds with increasing CO<sub>2</sub> dilution ratio. Namely, the three-body reactions CO<sub>2</sub> involved also show the inhibiting effect on laminar flame speeds. Comparing the two chemical effects, the direct reaction effect is larger and more significant than the three-body effect in syngas flames. For elevated pressure cases, it can be seen from Fig. 6b that the direct reaction effect does not significantly increase, whereas the difference between three-body effects is enlarged with increasing pressure. Numerical results demonstrate that the pressure increase does not significantly affect the effect of the CO oxidation reaction CO + OH = CO<sub>2</sub> + H on laminar flame speeds, but the increase of CO<sub>2</sub> concentration obviously accelerates the three-body effect, which results in the increase of total chemical effect on laminar flame speeds. Different from high pressure results, the chemical effect, including the direct reaction effect and the three-body effect, shows a negative correlation with temperatures, shown in Fig. 6c. Elevating preheat temperature can enhance the decomposition of CO<sub>2</sub> reinforcing the reverse reaction of the reaction CO + OH = CO<sub>2</sub> + H and prompt the three-body reactions. However, considering that the chemical effects are represented by relative variations of laminar flame speeds, the

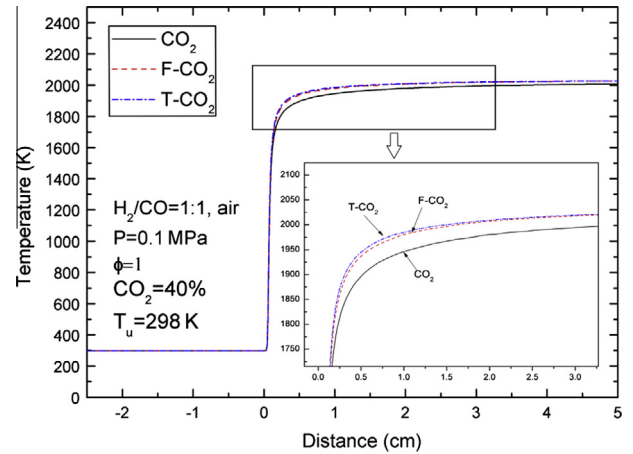
**Table 2**  
Three numerical methods for analyzing chemical effects of CO<sub>2</sub> dilution.

Case	Dilution	Direct reaction effect considered	Three-body effect considered	Calculated laminar flame speed
1	Normal CO <sub>2</sub>	Yes	Yes	S <sub>li</sub> <sup>0</sup> (CO <sub>2</sub> )
2	F-CO <sub>2</sub>	No	No	S <sub>li</sub> <sup>0</sup> (FCO <sub>2</sub> )
3	T-CO <sub>2</sub>	No	Yes	S <sub>li</sub> <sup>0</sup> (TCO <sub>2</sub> )



**Fig. 6.** Dimensionless relative variation of laminar flame speeds of  $\text{H}_2/\text{CO}/\text{CO}_2/\text{air}$  flames as a function of  $\text{CO}_2$  dilution ratio in  $\text{H}_2/\text{CO}/\text{CO}_2$  under the conditions of (a) ambient; (b) elevated pressures; (c) elevated preheating temperature.

present results indicates that the impact of increased chemical inhibition effect of  $\text{CO}_2$  dilution is weaker than the impact of increased total reaction rate caused by high preheat temperature, thus leading to the decrease of chemical effects of  $\text{CO}_2$  dilution on laminar flame speeds. Furthermore, as Qiao et al. [40] pointed out that the chemical effect of  $\text{CO}_2$  dilution is more significant in methane flames and Zhang et al. [23] pointed out that the three-body effect of  $\text{CO}_2$  dilution will be more important in Hydrogen flames at extinction limits, it will be interesting to investigate the chemical effect of  $\text{CO}_2$  dilution on syngas flames at extinction limits at elevated pressures and/or temperatures in the future studies.



**Fig. 7.** Comparison of temperature distributions in  $\text{CO}_2$ ,  $\text{F-CO}_2$  and  $\text{T-CO}_2$  diluted flames.

Except for the chemical effect of  $\text{CO}_2$  dilution on laminar flame speeds, its effect on flame temperatures is also considered. Specially, temperature distributions with  $\text{CO}_2$ ,  $\text{F-CO}_2$  and  $\text{T-CO}_2$  dilution (ambient condition, 40% dilution ratio) are compared in Fig. 7. It is seen that the flame temperatures for  $\text{F-CO}_2$  and  $\text{T-CO}_2$  dilution are very close, and calculated peak temperatures for  $\text{F-CO}_2$  and  $\text{T-CO}_2$  dilution are 2077.2 K and 2026.8 K, respectively. However, the flame temperatures for  $\text{CO}_2$  dilution are lower than others, and calculated peak temperature for  $\text{CO}_2$  dilution is 2006.4 K. Numerical results demonstrate that, without thermal effect interference, the decrease of flame temperature is mainly due to the direct reaction effect of  $\text{CO}_2$  and the three-body effect is negligible.

#### 4. Conclusion

Laminar flame speeds and Markstein lengths of syngas with  $\text{CO}_2$  dilution were measured at normal and elevated pressures and temperatures using outwardly propagating spherical flame method. The experimental laminar flame speeds were compared with predictions using three chemical mechanisms for syngas oxidation. The main conclusions are:

1. The measured laminar flame speeds decrease linearly with  $\text{CO}_2$  dilution ratio at all conditions. The mechanism of Davis et al. [25] predicts experimental results well at ambient condition and 298 K and 375 K, but slight over-prediction is observed at 450 K. At elevated pressures, the mechanism of Kéromnès et al. [13] shows a better agreement with experimental results. The effect of  $\text{CO}_2$  dilution in the present experiments is well considered in these mechanisms.
2. The Markstein lengths remain positive and decrease with elevating pressure and are almost constant at each elevated pressure with increasing  $\text{CO}_2$  dilution ratio. Increasing  $\text{CO}_2$  dilution ratio and preheat temperature can generally decrease the Markstein lengths of syngas flames at different preheat temperatures. The sign of the Markstein lengths change from positive to negative for high dilution ratio (40%) and high preheat temperature (450 K), where the flames become slightly diffusive-thermal instable.
3.  $\text{CO}_2$  dilution can affect the elementary reaction rates. The chemical effects, including the direct reaction effect and the three-body effect, increase with increasing  $\text{CO}_2$  dilution ratio and pressure but decreases with elevating preheat temperature. The decrease of flame temperatures is mainly caused by the direct chemical effect of  $\text{CO}_2$  dilution.

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## References

- Natarajan J. Experimental and Numerical Investigation of Laminar flame speeds of H<sub>2</sub>/CO/CO<sub>2</sub>/N<sub>2</sub> Mixtures. Georgia Institute of Technology; 2008.
- Richards GA, Casleton KH, Chorpene BT. CO<sub>2</sub> and H<sub>2</sub>O diluted oxy-fuel combustion for zero-emission power. Proc IME J Power Energy 2005;219:121–6.
- Brown MJ, McLean IC, Smith DB, Taylor SC. Markstein lengths of CO/H<sub>2</sub>/air flames, using expanding spherical flames. Proc Combust Inst 1996;26:875–81.
- Hassan M, Aung K, Faeth G. Markstein numbers and unstretched laminar burning velocities of wet carbon monoxide flames. AIAA Paper 1996:96–0912.
- Hassan M, Aung K, Faeth G. Properties of laminar premixed CO/H<sub>2</sub>/air flames at various pressures. J Propul Power 1997;13:239–45.
- Natarajan J, Lieuwen T, Seitzman J. Laminar flame speeds of H<sub>2</sub>/CO mixtures: effect of CO<sub>2</sub> dilution, preheat temperature, and pressure. Combust Flame 2007;151:104–19.
- Natarajan J, Kochar Y, Lieuwen T, Seitzman J. Pressure and preheat dependence of laminar flame speeds of H<sub>2</sub>/CO/CO<sub>2</sub>/O<sub>2</sub>/He mixtures. Proc Combust Inst 2009;32:1261–8.
- Burke MP, Qin X, Ju Y, Dryer FL. Measurements of hydrogen syngas flame speeds at elevated pressures. In: 5th US Combustion Meeting. California: San Diego; March 2007.
- Burke MP, Chaos M, Dryer FL, Ju Y. Negative pressure dependence of mass burning rates of H<sub>2</sub>/CO/O<sub>2</sub>/diluent flames at low flame temperatures. Combust Flame 2010;157:618–31.
- Sun H, Yang S, Jomaas G, Law C. High-pressure laminar flame speeds and kinetic modeling of carbon monoxide/hydrogen combustion. Proc Combust Inst 2007;31:439–46.
- Prathap C, Ray A, Ravi MR. Investigation of nitrogen dilution effects on the laminar burning velocity and flame stability of syngas fuel at atmospheric condition. Combust Flame 2008;155:145–60.
- Prathap C, Ray A, Ravi M. Laminar flame speeds of H<sub>2</sub>/CO mixtures: effect of CO<sub>2</sub> dilution, preheat temperature, and pressure condition. Combust Flame 2012;159:482–92.
- Kéromnès A, Metcalfe WK, Heufer KA, Donohoe N, Das AK, Sung CJ, et al. An experimental and detailed chemical kinetic modeling study of hydrogen and syngas mixture oxidation at elevated pressures. Combust Flame 2013;160:995–1011.
- Krejci M, Vissotski A, Ravi S, Metcalfe W, Keromnes A, Curran H, et al. Laminar flame speed measurements of moist syngas fuel blends at elevated pressures and temperatures. In: Spr tech meeting (CSSCI). Ohio: Dayton; April 2012.
- Burbano HJ, Pareja J, Amell AA. Laminar burning velocities and flame stability analysis of H<sub>2</sub>/CO/air mixtures with dilution of N<sub>2</sub> and CO<sub>2</sub>. Int J Hydrogen Energy 2011;36:3232–42.
- Wang J, Huang Z, Kobayashi H, Ogami Y. Laminar burning velocities and flame characteristics of CO–H<sub>2</sub>–CO<sub>2</sub>–O<sub>2</sub> mixtures. Int J Hydrogen Energy 2012;37:19158–67.
- Singh D, Nishiie T, Tanvir S, Qiao L. An experimental and kinetic study of syngas/air combustion at elevated temperatures and the effect of water addition. Fuel 2012;94:448–56.
- Liu F, Guo H, Smallwood GJ. The chemical effect of CO<sub>2</sub> replacement of N<sub>2</sub> in air on the burning velocity of CH<sub>4</sub> and H<sub>2</sub> premixed flames. Combust Flame 2003;133:495–7.
- Chen Z, Qin X, Xu B, Ju Y, Liu F. Studies of radiation absorption on flame speed and flammability limit of CO<sub>2</sub> diluted methane flames at elevated pressures. Proc Combust Inst 2007;31:2693–700.
- Halter F, Foucher F, Landry L, Mounaïm-Rousselle C. Effect of dilution by nitrogen and/or carbon dioxide on methane and iso-octane air flames. Combust Sci Technol 2009;181:813–27.
- Xie Y, Wang J, Zhang M, Gong J, Jin W, Huang Z. Experimental and numerical study on laminar flame characteristics of methane oxy–fuel mixtures highly diluted with CO<sub>2</sub>. Energy Fuels 2013;27:6231–7.
- Qiao L, Gu Y, Dahm WJA, Oran ES, Faeth GM. A study of the effects of diluents on near-limit H<sub>2</sub>–air flames in microgravity at normal and reduced pressures. Combust Flame 2007;151:196–208.
- Zhang W, Chen Z, Kong W. Effects of diluents on the ignition of premixed H<sub>2</sub>/air mixtures. Combust Flame 2012;159:151–60.
- Zhou Z, Tao ZQ, Lin BY, Kong WJ. Numerical investigation on effects of high initial temperatures and pressures on flame behavior of CO/H<sub>2</sub>/Air mixtures near the dilution limit. Int J Hydrogen Energy 2013;38:274–81.
- Davis SG, Joshi AV, Wang H, Egolfopoulos F. An optimized kinetic model of H<sub>2</sub>/CO combustion. Proc Combust Inst 2005;30:1283–92.
- Li J, Zhao Z, Kazakov A, Chaos M, Dryer FL, Scire JJ. A comprehensive kinetic mechanism for CO, CH<sub>2</sub>O, and CH<sub>3</sub>OH combustion. Int J Chem Kinet 2007;39:109–36.
- Ai Y, Zhou Z, Chen Z, Kong W. Laminar flame speed and Markstein length of syngas at normal and elevated pressures and temperatures. Fuel 2014;137:339–45.
- Chen Z, Burke MP, Ju Y. Effects of Lewis number and ignition energy on the determination of laminar flame speed using propagating spherical flames. Proc Combust Inst 2009;32:1253–60.
- Chen Z. Effects of radiation and compression on propagating spherical flames of methane/air mixtures near the lean flammability limit. Combust Flame 2010;157:2267–76.
- Clavin P. Dynamic behavior of premixed flame fronts in laminar and turbulent flows. Prog Energy Combust Sci 1985;11:1–59.
- Yu H, Han W, Santner J, Gou X, Sohn CH, Ju Y, et al. Radiation-induced uncertainty in laminar flame speed measured from propagating spherical flames. Combust Flame 2014;161:2815–24.
- Chen Z. On the extraction of laminar flame speed and Markstein length from outwardly propagating spherical flames. Combust Flame 2011;158:291–300.
- Kee RJ, Grcar JF, Smooke M, Miller J. PREMIX: a Fortran program for modeling steady laminar one-dimensional premixed flames. Sandia National Laboratories Report 1985.
- Chen Z, Burke MP, Ju Y. Effects of compression and stretch on the determination of laminar flame speeds using propagating spherical flames. Combust Theor Model 2009;13:343–64.
- Zhang H, Guo P, Chen Z. Critical condition for the ignition of reactant mixture by radical deposition. Proc Combust Inst 2013;34:3267–75.
- Liu F, Smallwood GJ, Gülder ÖL. Application of the statistical narrow-band correlated-k method to non-grey gas radiation in CO<sub>2</sub>–H<sub>2</sub>O mixtures: approximate treatments of overlapping bands. J Quant Spectrosc Radiat Transfer 2001;68:401–17.
- McLean IC, Smith DB, Taylor SC. The use of carbon monoxide/hydrogen burning velocities to examine the rate of the CO + OH reaction. Proc Combust Inst 1994;25:749–57.
- Bouvet N, Halter F, Chauveau C, Yoon Y. On the effective Lewis number formulations for lean hydrogen/hydrocarbon/air mixtures. Int J Hydrogen Energy 2013;38:5949–60.
- Liu F, Guo H, Smallwood GJ, Gülder ÖL. The chemical effects of carbon dioxide as an additive in an ethylene diffusion flame: implications for soot and NO<sub>x</sub> formation. Combust Flame 2001;125:778–87.
- Qiao L, Kim C, Faeth G. Suppression effects of diluents on laminar premixed hydrogen/oxygen/nitrogen flames. Combust Flame 2005;143:79–96.