Effects of CO$_2$ Dilution and CH$_4$ Addition on Laminar Burning Velocities of Syngas at Elevated
Pressures: An Experimental and Modeling Study

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Abstract

Variations in biomass-derived syngas composition can be a challenge to efficient combustion and low emissions. A study on the effects of CO₂ dilution and CH₄ addition on flame propagating characteristics of syngas at high pressure was conducted using the heat flux method and kinetic simulations. This paper presents the laminar burning velocity, $S_L$, of H₂/CO/CO₂/O₂/diluent mixtures and H₂/CO/CH₄/O₂/diluent at $\phi = 0.5 - 2.5$, elevated pressures one-11 atm and H₂:CO mole fraction ratios 0.25: 0.75 to 0.75: 0.25. The effects of CO₂ mole fraction dilution in the fuel (from 0.0 to 0.4), CH₄/(CH₄+CO) (from 0.0 to 1.0), and pressure dependence on $S_L$ were experimentally investigated and compared to the simulated results from three kinetic mechanisms. The increase of the hydrogen mole fraction, or the decrease of the CO₂ mole fraction in the fuel, both lead to an increase of $S_L$; the decreased mole fraction enhanced $S_L$ significantly more in over-rich conditions. The dilution, thermal-diffusion and chemical effects (including the direct reaction and three-body effects) of CO₂ dilution were quantitatively distinguished at different pressures and H₂ contents. The results showed that increasing the pressure and CO₂ mole fraction in the fuel enhanced the competition of H consuming reactions, and the retarding effect of CO₂ dilution was found to be favored at high hydrogen content syngas conditions. Both CO₂ dilution and CH₄ addition decreased the overall reaction order of the syngas flames by decreasing the adiabatic flame temperature. Increasing the pressure and H₂ content increased the syngas heat release rate by enhancing three-body collision reactions and enrichment of H radical, and their effects were reversed on syngas flame speed.

Keywords: Laminar burning velocity, high pressure, heat flux method, CO₂ dilution, biomass, syngas.
1. Introduction

Synthetic gas--syngas--as an alternative fuel has drawn wide interest to Gas Turbines manufacturers and applied to integrated gasification combined cycle (IGCC) because hydrogen is ubiquitous and burns without emitting unburned hydrocarbon, CO₂, and CO [1]. Furthermore, the gasification technology employed in the IGCC power plant allows a wide range of feedstocks such as coal or biomass [2, 3], municipal solid waste [4], agriculture residues [5, 6], herbaceous energy crops [7, 8], and others to be converted into syngas. There is a potential to realize non-carbon emission from IGCC power plants by implementing carbon capture and storage (CCS) techniques [9].

Syngas composition may vary considerably depending on the gasification process and is important affecting the design of IGCC system [10, 11]. Its composition is mostly in combustible hydrogen (H₂) and carbon monoxide (CO), together with some levels of methane (CH₄), dilutions as carbon dioxide (CO₂), nitrogen (N₂) and some other species. To maintain the same power output for gas turbines, the low heat value of syngas requires a higher flow rate than traditional fossil fuels [12]. High reactivity and availability make syngas promising for the development of clean, high-efficiency combustion technologies with low emissions. At the same time, the significant variation of its composition is accompanied by important challenges to practical combustors and furnaces, which might take advantage of its combustion stability and emission control. Lean-premixed or dry-low NOx combustion technologies have advanced to solve syngas combustion emissions, but increasing pressure also changes reactivity and emission characteristics, making it crucial to understand the fundamental combustion characteristics of syngas over a wide range of diverse components. Although practical combustors are operated at high pressures, unlike atmospheric pressure research, basic investigation of syngas combustion at high pressure is rarely reported.

Laminar burning velocity ($S_L$) is an essential parameter of the fuel/oxidizer, related to phenomena such as blow-off, flashback and flame stability; it is the basis for study of turbulent flame speed. It is also essential to
represent diffusion probability, heat release rate and the overall reaction rate that can be used to develop kinetic mechanisms. Various methods have been utilized to measure laminar burning velocities of syngas at atmospheric [3, 13-17] and elevated pressures [18-30] for diverse syngas composition and impurity content. Because of the availability of a vast database of syngas/air flame speed, Table 1 lists only syngas with CO₂ dilution, or CH₄ addition, at elevated pressures, which is the concern of this study. Previous studies have shown that dilution gases like N₂, He, Ar, CO₂ and H₂O have a significant effect on radiation and thermal-diffusion properties and the chemical reaction rate of syngas, impacting its flammability limits and laminar burning velocity. Previous works [31, 32] compared the reduction in S_L with different diluents and ranked the order as He< Ar< N₂ <CO₂ , with CO₂ being the inhibitor most effective in decreasing flame temperature and S_L. The effects of CO₂ addition on the S_L of syngas and hydrocarbon fuels include the dilution effect; thermal-diffusion and chemical effects are investigated under atmospheric and elevated pressures [13, 25, 28, 32-35]. CO₂ gas is also used as an exhaust gas in recirculation to suppress thermal-NOₓ formation in oxy-fuel combustion [26, 34]. Han et al. [28] reported that the chemical retarding effect of CO₂ addition increased as pressure increased and the direct reaction effect through CO₂ + H = CO + OH always dominated the decrease of adiabatic flame temperature. Due to the strong three-body collision effect (H + O₂ (+M) = HO₂ (+M)), especially at elevated pressures, CO₂ dilution increases the pressure dependence of the mass burning rate [21], bringing greater uncertainty to predicting S_L by using different kinetic mechanisms. However, a review of the literature found that the S_L of syngas with a high hydrogen content diluted by CO₂ --especially at elevated pressures--was rarely reported. And a systematic and consistent investigation of the effect of CO₂ addition on S_L of syngas, with continuous change in fuel composition and initial pressure, is still necessary to validate the kinetic mechanism and practical combustor design.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>H₂: CO (mol.)</th>
<th>Oxidizer</th>
<th>Impurities</th>
<th>P (atm)</th>
<th>φ</th>
</tr>
</thead>
</table>
Aside from H₂ and CO, syngas composition from various gasifier processes also includes CH₄, ranging from 0% to 9.3% [36]. Increasing CH₄ content increases the heat value of the syngas, but it decreases overall reactivity. Many studies have investigated the SL of biomass or coal-derived syngas under atmospheric pressures [37-42] and found that increasing the CH₄ content in syngas/CH₄ fuel mixtures decreased the overall SL values and shifted the peak SL to the leaner side, due to the change of adiabatic flame temperature. Wu et al. [41] and Cheng et al. [42] used the opposed-jet flame method to investigate the effect of CO content on the SL of CH₄/CO/air...
and CH₄/H₂/CO/air mixtures under atmospheric pressures. They found that by increasing the CO content to 80% in the CH₄/CO fuel mixture, the $S_L$ and heat release rate increased to the maximum and decreased by further increasing CO, due to the enhanced reaction $CO + OH = CO₂ + H$. The addition of hydrogen to the fuel mixture (up to 50%) removed the non-monotonic variation of $S_L$, because of the increase in the OH radical pool, and enhanced the chain-branching reactions $H + O₂ = O + OH$. This was confirmed by He et al. [40]. However, this non-monotonic behavior of $S_L$ with H₂, and the effect of adding CH₄ to a CH₄/CO/H₂ fuel mixture was never investigated at elevated pressures. Experimental data for the $S_L$ of a CH₄/CO/H₂ fuel mixture--especially at elevated pressures--is urgently needed to fill this gap. Zhou et al. [29] reported on the $S_L$ of H₂/CO/CH₄/O₂/He mixtures at pressures up to 0.5 MPa and found that the kinetic mechanism both respectively overpredicted and underpredicted the experimental results, at lean and rich sides. Most of the high-pressure $S_L$ data obtained are based on a spherical propagating flame method that requires cross-validation. The recently established heat flux burner under elevated pressures could provide reliable $S_L$ measurements on H₂/CO/CH₄/O₂/diluent mixtures [30, 34].

Therefore, the goals of the present study are: 1) To provide $S_L$ data on H₂/CO/CO₂/O₂/diluent flames at different H₂-CO ratios and pressures and to distinguish the thermal-diffusion and chemical effect of CO₂ dilution at elevated pressures. 2) To offer $S_L$ data on H₂/CO/CH₄/O₂/diluent flames at different CH₄/CO ratios and pressures. 3) To compare the prediction accuracy of different kinetic mechanisms and investigate the effects of CO₂ and CH₄ addition on the pressure dependence of $S_L$.

2. Experiment

Experiments were conducted in a high-pressure chamber fitted with a specially designed heat flux burner in order to establish a planar, adiabatic and stretchless flame on a perforated burner plate under high pressures. The principle of the heat flux method is that heat loss from the flame to the burner can be compensated by heat gain by the unburnt gas flowing through the burner plate. When the radial temperature gradient equaled zero,
the adiabatic laminar burning velocity was determined from the feeding gas velocity [43, 44]. The heat flux method was applied to measure $S_L$ at high pressures by other authors [45, 46]. Detailed experimental setup and uncertainty analyses can be found in [30, 34, 47]; a brief introduction appears below.

The high-pressure chamber was designed to sustain pressures up to 50 atm; it was equipped with a burner plate 20 mm in diameter, with perforated holes of 0.3 mm diameter and 0.4 mm pitch. Gas flow rates supplied to the chamber were measured by high pressure mass flow controllers (HMFC, Brooks Instrument Co. Ltd.). The accuracy of the mass flow controller was 1% full scale. A controller guided the pressure via a manually operated valve and an electrical PID valve, both of which were installed in the exhaust gas pipeline. Exhaust gases released from the top of the chamber were directed to a heat exchanger and condenser to collect the water vapor prior to feeding it to the pressure control valves. The heat flux burner plenum chamber and burner plate were maintained separately at 298 K and 353 K by two thermostatic water baths. Jingong Gas provided the cylinders of H\textsubscript{2} (with purity = 99.999%), CO (99.99%), CH\textsubscript{4} (99.95%), O\textsubscript{2} (99.995%), N\textsubscript{2} (99.999%), CO\textsubscript{2} (99.999%) and He (99.999%). Synthetic air was produced from volume fractions of 79% N\textsubscript{2} and 21% O\textsubscript{2}. The equivalence ratio was defined as $\phi = (F/A)/(F/A)_{stoichiometry}$, and the mole fraction of the component M in the fuel mixture was defined as $X_M = V_M/V_{fuel\ mixture}$. As discussed earlier [30, 34], the uncertainty of the measured $S_L$ using the heat flux method included three aspects: 1) uncertainty associated with the temperature of the burner plate, which was measured by multiple thermocouples; 2) uncertainty associated with the inlet flow velocities of gases controlled by the mass flow controllers; 3) uncertainty associated with pressure measurements by the pressure controller. These uncertainties were revealed as error bars associated with the reported experimental laminar burning velocity; they showed a maximum uncertainty of $\pm 1.0$ cm/s.

Detailed experimental conditions of this work are listed in Table 2. The experimental conditions include four aspects of parameter variation: firstly, investigate the effect of H\textsubscript{2}: CO and dilution content of CO\textsubscript{2} variation in a wide range of equivalence ratios; secondly, investigate the effect of pressure variation; thirdly, investigate the
effect of CO₂ dilution; finally, investigate the effect of CH₄ addition. Due to the measuring limitation of heat flux method of 60~80 cm/s and our Mass flow meters’ maximum flowrate at high pressures, the following sections 4.2-4.4 choose the equivalence ratio follows the principle as: the variation range of parameters to be examined is as wide as possible within the measuring limitation. Although the equivalence ratio is changed, due to there is no cellular flame instability, they do not affect the flame speed variation trend as a function of the parameters to be examined.

Table 2: Experimental conditions of CO₂ dilution and CH₄ addition on laminar burning velocities of syngas/O₂/diluent flames.

<table>
<thead>
<tr>
<th>φ</th>
<th>P (atm)</th>
<th>Fuel (mol.)</th>
<th>Oxidizer (mol.)</th>
<th>Tad (K)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8-2.8</td>
<td>1</td>
<td>H₂: CO: CO₂ = 39: 21: 40</td>
<td>O₂: N₂ = 21: 79</td>
<td>1260-2080</td>
<td>Change H₂: CO</td>
</tr>
<tr>
<td>0.8-2.8</td>
<td>1</td>
<td>H₂: CO: CO₂ = 30: 30: 40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8-2.8</td>
<td>1</td>
<td>H₂: CO: CO₂ = 15: 45: 40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8-2.8</td>
<td>1</td>
<td>H₂: CO: CO₂ = 32.5: 32.5: 35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8-2.8</td>
<td>1</td>
<td>H₂: CO: CO₂ = 27.5: 27.5: 45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>1-11</td>
<td>H₂: CO = 75: 25</td>
<td>O₂: He = 1: 9</td>
<td>1490</td>
<td>Change pressure</td>
</tr>
<tr>
<td>0.73</td>
<td>1-11</td>
<td>H₂: CO: CO₂ = 45: 15: 40</td>
<td></td>
<td>1490</td>
<td>Change pressure</td>
</tr>
<tr>
<td>0.6</td>
<td>1,4</td>
<td>H₂: CO: CO₂ = 65: 35: 0 ~39:</td>
<td>O₂: He = 12: 88</td>
<td>1690-1480</td>
<td>Change CO₂ dilution</td>
</tr>
<tr>
<td>0.6</td>
<td>1,4</td>
<td>H₂: CO: CO₂ = 50: 50: 0 ~30:</td>
<td></td>
<td>1710-1500</td>
<td>Change CO₂ dilution</td>
</tr>
<tr>
<td>1.0</td>
<td>1,3</td>
<td>CH₄: CO = 100: 0 ~3: 97</td>
<td>O₂: He = 1: 7</td>
<td>2100-2240</td>
<td>Change CH₄ content</td>
</tr>
<tr>
<td>1.0</td>
<td>1,3</td>
<td>CH₄: CO: H₂ = 75: 0 ~22.5: 52.5: 25</td>
<td></td>
<td>1990-2080</td>
<td>Change CH₄ content</td>
</tr>
<tr>
<td>1.0</td>
<td>1,3</td>
<td>CH₄: CO: H₂ = 22.5: 52.5: 25</td>
<td>O₂: He = 1: 10</td>
<td>2080-2170</td>
<td>Change CH₄ content</td>
</tr>
</tbody>
</table>

3. Numerical simulations
The 1-D, freely-propagating laminar flame speed model, PREMIX in CHEMKIN Pro [48] was used to model the CH₄/H₂/CO/O₂/diluent flames. Three kinetic mechanisms (the USC mechanism [49], ELTE mechanism [50] and the mechanism developed by Burke et al. [51]) were used here; hereafter they will be referred to as USC-Mech, ELTE-Mech and Burke-Mech. The USC Mech, containing 111 species and 784 reactions, was optimized for high temperature oxidation of H₂/CO/C₁–C₄ hydrocarbons in a series of studies over the last decade. The Burke-Mech updated the rate constants of HO₂ formation and consumption reactions of the H₂/O₂ system based on high pressure flame speed measurements; it has 22 species and 106 reactions and can predict high pressure CH₄/H₂/CO/O₂/diluent flame speed. The ELTE-mech was developed based on an optimization approach in a comprehensive set of experimental data of syngas combustion with pressure up to 50 bar and it performed well in reproducing these experimental results. It has 15 species and 44 reactions. Those conditions with CH₄ addition were modeled only by the USC-Mech and Burke-Mech due to the inclusion of a methane sub-mechanism. An adaptive re-gridding method with convergence conditions of GRAD and CURV values set at 0.02 (ensuring at least 500 grid points), was used for each test condition. Thermal diffusion (Soret effect) and a mixture-averaged transport formulation were included in the computations.

4. Results and discussion

4.1. Effect of equivalence ratio on $S_L$

To investigate the effects of H₂-CO ratios in the syngas composition, and CO₂ dilution proportions on the $S_L$ at different equivalence ratios, results at one and three atm are presented in Figure 1. In the same figure, the numerical simulation results of three mechanisms are also shown for comparison. It was found that both increasing the hydrogen content and decreasing the CO₂ content significantly increased the $S_L$ values at one and three atm. The $S_L$ of all conditions reached maximum at the moderately rich side, which is $\phi \approx 1.5$. In Figures 1(a) and (c), for a given CO₂ content, the maximum enhancement of $S_L$ due to the increase of the hydrogen content occurred at $\phi = 1.5$; for lean ($\phi < 1.0$) and over-rich ($\phi > 2.0$) conditions, the enhancement in $S_L$ decreased.
This indicates that the change of H₂- CO ratio only had an obvious effect on $S_L$ values on the moderately rich side ($\phi$ around 1.5) at different pressures. Figures 1(b) and (d) show that at a given H₂- CO ratio, the maximum enhancement of $S_L$ caused by decreased carbon dioxide content also occurred at $\phi = 1.5$. In lean ($\phi < 1.0$) conditions, the dilution effect of CO₂ decreased, while a significant impact from CO₂ was observed in the over-rich ($\phi > 2.0$) mixtures. It was found that decreasing CO₂ content enhanced $S_L$ values from the lean to the moderately-rich side (a reaction much like increasing the hydrogen content), while the divergent trend of the mixtures’ $S_L$ with different CO₂ ranges was more evident than with different hydrogen content in the over-rich side. In Figs. 1(a) and (c), it can be seen that the peak $S_L$ shifted to the leaner side as the hydrogen content increased, however, it shifted to the richer side when the CO₂ content increased (Figs. 1(b) and (d)); this trend was more obvious at elevated pressures. Elevated pressures decreased the overall $S_L$ values and shifted the peak $S_L$ to the leaner side with all H₂- CO ratios and CO₂ dilution proportions. The numerical simulations from all three mechanisms agreed well with the present experimental results at one and three atm. Specifically, the USC-Mech and ELTE-Mech predicted low pressure and lean conditions better, while the Burke-Mech predicted the elevated pressure and rich conditions better.
According to the laminar flame theory, $S_L$ is proportional to $(\alpha RR)^{1/2}$ [52], where $\alpha$ is the thermal diffusivity, and $RR$ is the overall reaction rate. The $RR$ depends on adiabatic flame temperature, $T_{ad}$. The thermal diffusivity, peak H radical mole fraction and adiabatic flame temperature are calculated using the CHEMKIN EQUIL and PREMIX modules [48] with the transport data using the ELTE-mechanism [50]. To investigate the effects of $H_2$-CO ratios and $CO_2$ dilution on the $S_L$ of the conditions presented in Fig. 1, $\alpha$, $T_{ad}$ and the peak mole fraction of $H$ of $H_2/CO/CO_2/air$ mixtures, as a function of $\phi$ at one and three atm, are presented in Fig. 2. Figure 2(a) shows that $T_{ad}$ had a maximum at stoichiometry mixtures for all blend ratios and pressures. Fig. 2(b) shows that $\alpha$ increases monotonically as $\phi$ increases at 1 atm but decreases monotonically as $\phi$ increases at 3 atm. Take the fuel composition with molar ratio of $H_2$: $CO$: $CO_2$ of 0.3: 0.3: 0.4 for example, at 1 atm and 298 K, the thermal
diffusivity is \( \alpha_{\text{fuel}} = 0.3418 \text{ cm}^2/\text{s} \); the thermal diffusivity of oxidizer with molar ratio of O2: He of 0.1: 0.9 is \( \alpha_{\text{O2/He}} = 1.4155 \text{ cm}^2/\text{s} \); and the thermal diffusivity of air is 0.2209 \( \text{ cm}^2/\text{s} \). Thus, \( \alpha_{\text{O2/N2}} < \alpha_{\text{fuel}} < \alpha_{\text{O2/He}} \) which means the increase of equivalence ratio will lead to the increase of the thermal diffusivity of fuel/O\(_2\)/N\(_2\) mixtures while decrease the thermal diffusivity of fuel/O\(_2\)/He mixtures. The thermal diffusivity, \( \alpha = \lambda/(\rho \cdot C_p) \) (where \( \lambda \) is the thermal conductivity, \( \rho \) is the density and \( C_p \) is the heat capacity), is reversely proportional to the pressure variation, but with helium dilution, the \( \alpha \) of fuel/oxidizer at 3 atm even achieves the same level as the \( \alpha \) of N\(_2\) diluted fuel/oxidizer. Thus, helium is used at 3 atm to increase the Lewis number (\( Le = \alpha/D \) where \( D \) is the species diffusivity) and suppress the thermal-diffusion and hydrodynamic cellular flame instability. \[53\]. The steep decrease of thermal diffusivity at the rich side of three atm lead to early reduction in \( S_L \) at the rich side (Fig. 1). It was also found that increasing the hydrogen content decreased the \( T_{ad} \) but increased the \( \alpha \), e.g., when the CO\(_2\) dilution content was fixed at 0.4, the case of H\(_2\): CO: CO\(_2\) = 0.15: 0.45: 0.4 had higher \( T_{ad} \), but lower \( \alpha \) than in the case of H\(_2\): CO: CO\(_2\) = 0.3: 0.3: 0.4 (Fig. 2). Reducing the CO\(_2\) dilution content increased both \( T_{ad} \) and \( \alpha \) more significantly in \( T_{ad} \), e.g., when fixed, the H\(_2\): CO = 1: 1, the case of H\(_2\): CO: CO\(_2\) = 0.275: 0.275: 0.45 had lower \( T_{ad} \) and \( \alpha \) than those of H\(_2\): CO: CO\(_2\) = 0.3: 0.3: 0.4, shown in Fig. 2. Considering that the peak \( S_L \) occurred at the moderately rich side for all syngas mixtures (although \( T_{ad} \) and \( \alpha \) tended to decrease, at three atm of this range), it is the chemical reaction effect led to this phenomenon. Figure 2(c) shows that the peak H radical mole fraction correlated well with the trend of \( S_L \), shown in Fig. 1.
Thus, increasing the H₂ content increased the $S_L$ mainly through enrichment of the active H radical pool, and the increase of $\alpha$. In the same context, lowering the CO₂ content increased the $S_L$ (primarily by reducing the CO₂ dilution effect), and raised the adiabatic flame temperature.

The following discussion compares and summarizes the results from changing the H₂-CO ratio and the CO₂ dilution on $S_L$ at different equivalence ratios. In Figure 2, on the fuel-lean side, the flame speeds of all fuel mixture types were similar, because of the closeness of their three parameters: $T_{ad}$ (thermal effect), $\alpha$ values
(diffusion effect) and H radical concentration (chemical effect). When the equivalence ratio moved to the moderately rich side, all the fuel types achieved peak $S_L$ values at $\phi = 1.5$, rather than at $\phi = 1.0$, because the maximum of the H radical occurred at $\phi = 1.5$, although the $T_{ad}$ achieved their maximum at $\phi = 1.0$. When the equivalence ratio moved further to the over-rich side, changing the $H_2$-CO ratio significantly altered the thermal-diffusivity of the mixtures, but changing the $CO_2$ dilution significantly changed $T_{ad}$ and H radical concentration of all cases. Thus, changing the $CO_2$ dilution resulted in a more notable difference in the $S_L$ of the mixture than changing the $H_2$-CO ratios.

4.2. Effect of pressure on $S_L$

To investigate the effects of pressure on the $S_L$ of lean $H_2/CO/CO_2/O_2/He$ mixtures, with or without $CO_2$ dilution, the adiabatic flame temperature, $T_{ad}$ was maintained constant at 1490K by increasing the $\phi = 0.6$ to 0.73 for the diluted mixture (40% $CO_2$). The results are presented in Fig. 3. Thus, the effect of $T_{ad}$ on $S_L$ was excluded from the present comparison. It is seen that the sensitivity of the flame speed to pressure was high at the low mixture pressure, and this sensitivity decreased as the pressure increased. Despite the constant adiabatic flame temperature, the $CO_2$ dilution reduced the $S_L$, as shown by the comparison between the mixture with/without $CO_2$ dilution. This difference was caused by the dilution and the chemical reaction effects of $CO_2$. To distinguish between the dilution and the chemical effect, the fictitious $CO_2$ species was introduced into the mixture. The fictitious $CO_2$, FCO$_2$ has the same thermal and transport properties of $CO_2$, but it does not participate in the chemical reactions [33]. In Fig. 3, 40% volumetric ratio of FCO$_2$ dilution is presented for comparison. Taking no dilution condition as the baseline, the difference in $S_L$ between no dilution and FCO$_2$ dilution conditions was the result of the dilution effect. The difference in $S_L$ between FCO$_2$ dilution and $CO_2$ dilution conditions was attributed solely to the chemical reaction effect. It was found that, over all pressures, the dilution effect was far greater than the chemical reaction effect.
The chemical reaction effect includes a direct reaction effect, through CO₂ participation in reaction CO₂ + H = CO + OH, and a three-body effect. Dilution by different impurities also causes a change in the thermal diffusivity of the fuel mixture, for this reason, an inert artificial species (TCO₂) was introduced, which participated in the three-body termination reactions. For the same dilution content in the fuel mixture, 40% volumetric ratio of N₂ dilution and 40% volumetric ratio of TCO₂ dilution are also presented for comparison in Fig. 3. Taking the N₂ dilution condition as the baseline, the difference in $S_L$ between N₂ dilution and FCO₂ dilution conditions was caused by the thermal-diffusion effect, the dimensional contribution factor is

$$\frac{S_L(N_2) - S_L(FCO_2)}{S_L(N_2) - S_L(CO_2)}$$

In the chemical reaction effects, the difference in $S_L$ between the FCO₂ dilution and the TCO₂ dilution conditions was caused by the three-body effect. The dimensional contribution factor is

$$\frac{S_L(FCO_2) - S_L(TCO_2)}{S_L(N_2) - S_L(CO_2)}$$

and the direct reaction effect is expressed as

$$\frac{S_L(TCO_2) - S_L(CO_2)}{S_L(N_2) - S_L(CO_2)}.$$  

It was found that the total chemical reaction effects of CO₂ played a more minor role than the thermal-diffusion effects. The absolute difference caused by thermal diffusivity effects was nearly independent of pressure variation in a fixed CO₂ dilution proportion. Figure 4 further illustrates the individual role of the direct reaction effect and the three-body effect of CO₂ addition. As pressure increased, the total chemical effect decreased, and the direct reaction effect was greater than the three-body effect at the initial stage, but it gradually decreased. The three-body effect had a maximum of around six to eight atm. The total chemical effect decreased due to elevated pressure, which
exhausted the active radicals and reduced the overall reaction rate and the laminar burning velocity. However, the three-body result was favored as the pressure increased, unlike the direct reaction effect.

![Diagram](Fig. 4: Dimensional contribution factor of chemical effects of $X_{\text{H}_2}$: $X_{\text{CO}}$: $X_{\text{CO}_2} = 0.45$: 0.15: 0.4 in the oxidizer of $\text{O}_2$: $\text{He} = 1$: 9 at $\phi = 0.73$ along with pressure.

Previous studies have shown that as pressure increases, the decrease in laminar burning velocity is mainly attributable to increased density, so the mass burning rate is more directly related to the pressure dependence of the overall reaction rate [21, 54]. Figure 5 shows the mass burning rate of $\text{CO}_2$ in the diluted condition in Fig. 3, along with pressure (i.e., $X_{\text{H}_2}$: $X_{\text{CO}}$: $X_{\text{CO}_2} = 0.45$: 0.15: 0.4) in the oxidizer of $\text{O}_2$: $\text{He} = 1$: 9 at $\phi = 0.73$. Numerical simulation results are presented in the same figure. It was found that the mass burning rate first increased and then decreased with increasing pressure, because the overall reaction order decreased from positive to negative as the pressure approached the second explosion limit [21, 30]. Thus, the three-body collision effect shown in Fig. 4 also maximized at the peak mass burning rate. It was also found that the Burke-Mech predicted the overall pressure range results better than the USC-Mech. The discrepancy between the experimental and numerical results seemed to grow as the pressure and mass burning rate increased. According to the mass burning rate: $f^0 = p^n/2 \exp(-E_a/2R\theta T_{ad})$ [54], the overall reaction order $n$ was also calculated and shown in Fig. 6. It was found that the $n$ showed a quasi-linear decreasing trend with pressure, and $n$ without dilution was consistently higher than with $\text{CO}_2$ dilution. Their overall reaction orders were close to 1.5 at lower pressures and became slightly divergent as the pressure increased. The previous study showed that the adiabatic flame temperature controlled the overall reaction order [21, 30], so that the $n$ of the three conditions ($\text{CO}_2$
dilution, FCO₂ dilution and no dilution) were always close to each other due to their similar $T_{ad}$, while the $n$ in the N₂ diluted condition was always higher than the rest due to its relatively high $T_{ad}$. As the pressure increased further, the enhanced three-body termination reactions which decreased the overall reaction rate--as well as the overall reaction order--were more favored in CO₂ diluted conditions. Therefore, due to chemical reaction effects, their differences grew with increased pressure.

![Fig. 5](image)

**Fig. 5**: Mass burning rate of $X_{H₂} : X_{CO} : X_{CO₂} = 0.45 : 0.15 : 0.4$ in the oxidizer of O₂: He = 1:9 at $\phi = 0.73$, with pressure.

![Fig. 6](image)

**Fig. 6**: Overall reaction order of syngas without dilution ($X_{H₂} : X_{CO} = 0.75 : 0.25$, $\phi = 0.6$) and with CO₂ dilution ($X_{H₂} : X_{CO} : X_{CO₂} = 0.45 : 0.15 : 0.4$, $\phi = 0.73$) in the oxidizer of O₂: He = 1:9 and $T_{ad} = 1490K$.

### 4.3. Effect of CO₂ dilution on $S_L$

Figure 7 shows the $S_L$ of $X_{H₂} : X_{CO} = 0.65 : 0.35$ and 0.5 : 0.5 as a function of the mole fraction of CO₂ in the fuel in the oxidizer of O₂: He = 0.12: 0.88 and $\phi = 0.6$. The decreased rate of $S_L$ was not sensitive to the initial increase of CO₂ mole fraction, but gradually became aggravated as the CO₂ mole fraction increased further in
all conditions. It was also discovered that the difference in $S_L$ between $X_{\text{H}_2}: X_{\text{CO}} = 0.65: 0.35$ and $0.5: 0.5$ decreased as CO$_2$ the mole fraction increased at all pressures. Simulated results from the USC-Mech accurately predicted the decreasing trend of $S_L$ in comparison with the present experimental results. To distinguish the chemical effects of CO$_2$ dilution, simulated $S_L$ results (replacing CO$_2$ with FCO$_2$) are also presented for comparison. The chemical effects of CO$_2$ increased as its mole fraction grew, but the effect was still minor at all pressures.

![Figure 7: Laminar burning velocity of $X_{\text{H}_2}: X_{\text{CO}} = 0.65: 0.35$ and $0.5: 0.5$ as a function of mole fraction CO$_2$ in fuel in the oxidizer of O$_2$: He = 12: 88 and $\phi = 0.6$.](image)

The normalized value of $S_L$-CO$_2$ dilution /$S_L$-no dilution is also presented in Fig. 8; there was no obvious change in the drop rate of $S_L$ as a function of the CO$_2$ mole fraction when the hydrogen content increased, and the pressure rise notably increased the drop rate of $S_L$ as a function of the CO$_2$ mole fraction when the H$_2$-CO ratios were fixed. The drop rate was aggravated much more by increasing the pressure than by increasing the hydrogen content. This analysis shows that, because of the similarity in the $T_{ad}$ of syngas with different H$_2$-CO ratios, the drop rates in their $S_L$ as the CO$_2$ mole fraction increased were very similar, this also means the effect of thermal diffusivity on the drop rate was excluded. When the H$_2$-CO ratio was fixed, and as the pressure increased from one to four atm, the $T_{ad}$ remained unchanged, so the effect of the $T_{ad}$ on different drop rate was excluded. Thus, the effect of increasing pressure on the greatly increased drop rate was caused by chemical reaction effects.
Fig. 8: Normalized laminar burning velocity of $X_{H2} \times X_{CO} = 0.65: 0.35$ and $0.5: 0.5$ as a function of mole fraction of CO$_2$ in fuel in the oxidizer of O$_2$: He = 0.12: 0.88 and $\phi = 0.6$.

To further examine the chemical reaction effect of different CO$_2$ dilution proportions and different pressures on $S_L$ of syngas mixtures, a sensitivity analysis of $S_L$ by the USC-Mech is presented in Fig. 9. It was found that the five top sensitive reactions were all enhanced as CO$_2$ dilution content--or pressure--increased. When the CO$_2$ dilution content increased, the reaction $CO + OH = CO_2 + H$ was enhanced most, which was attributable to the enrichment of CO$_2$ favoring the reverse reaction. Thus, the most important chain-branching reaction ($H + O_2 = O + OH$), was also enhanced because of the competition with reverse reaction $CO + OH = CO_2 + H$ for consuming the H radical. Increased pressure also enhanced the three-body termination reactions ($i.e., H + O_2 (+M) = HO_2 (+M)$ and $H + OH + M = H_2O + M$). More CO$_2$ content in the fuel mixtures also strengthened the three-body role, resulting in a more rapidly decreasing rate of $S_L$ at elevated pressures, shown in Fig. 8.

Fig. 9: Sensitivity coefficients of $S_L$ of $X_{H2} \times X_{CO} = 0.5: 0.5$ with and without CO$_2$ dilution in the oxidizer of O$_2$: 
He = 0.12: 0.88 at $\phi = 0.6$, $P = \text{one}$, four atm.

Figure 10 further displays the net reaction rates of the three main H producing and consuming reactions at different pressures; FCO$_2$ diluted conditions are also presented for comparison. Figures 10 (a)(b) show that the reaction CO + OH = CO$_2$ + H always possessed the highest reaction rate, followed by H + O$_2$ = O + OH and H + O$_2$ (+M) = HO$_2$ (+M). However, as CO$_2$ dilution content decreased, or hydrogen content increased, their order reversed (Figs. 10 (c)(d)). In comparing FCO$_2$ and CO$_2$ diluted conditions, it was found that replacing FCO$_2$ with CO$_2$ did not significantly change the adiabatic flame temperature. In contrast, the CO$_2$ addition enhanced the reverse reaction of CO + OH = CO$_2$ + H, decreasing its net reaction rates. The other two H consuming reactions were also weakened in comparison to FCO$_2$ dilution conditions. Comparing Figs. 10 (a) and (b), it can be seen that as the pressure increased, all the reaction rates were enhanced, with three-body termination reactions improved most. The difference between CO$_2$ diluted conditions and FCO$_2$ diluted conditions grew as the pressure increased from one atm to four atm, so that the chemical reaction effect of CO$_2$ was enhanced as the pressure increased. Figure 9 shows that the addition of CO$_2$ increased the sensitivity of the two competing reactions, which shared the same reactants (H + O$_2$), one is a three-body termination reaction and another is the chain-branching reaction. Thus, the overall reaction rates of syngas with higher H$_2$ content were more likely to be affected by CO$_2$ dilution. The difference between FCO$_2$ and CO$_2$ dilution is more apparent in Fig. 10(d) than in Fig. 10(b), confirming this point. The previous study also showed that adding CO$_2$ decreased the thermal diffusivity in the fuel mixture with a higher hydrogen content more obviously than in the lower hydrogen content [13]. These two factors lead to a slightly higher drop rate in the $S_L$ of syngas with a higher hydrogen content (Fig. 8).
Fig. 10: Reaction flux of H producing and consuming reactions of H2/CO/CO2/O2/He mixtures at (a) \(X_{\text{H2}}: X_{\text{CO}}: X_{\text{CO2}} = 0.3: 0.3: 0.4\), 1 atm; (b) \(X_{\text{H2}}: X_{\text{CO}}: X_{\text{CO2}} = 0.3: 0.3: 0.4\), 4 atm; (c) \(X_{\text{H2}}: X_{\text{CO}}: X_{\text{CO2}} = 0.5: 0.5: 0\), 4 atm; (d) \(X_{\text{H2}}: X_{\text{CO}}: X_{\text{CO2}} = 0.39: 0.21: 0.4\), 4 atm. (Solid line is CO2 dilution, dashed line is FCO2 dilution.)

4.4. Effect of CH4 addition on \(S_L\)

To investigate the effect of CH4 addition on the \(S_L\) of H2/CO mixtures, the \(S_L\) of CH4/CO/H2/O2/He with \(X_{\text{H2}}/(X_{\text{H2}} + X_{\text{CO}} + X_{\text{CH4}}) = 0\) and 0.25 as a function of mole fraction ratios CH4/(CH4+CO) at one and three atm. Due to the measuring limit (below 80 cm/s in the heat flux method), in cases with CH4/(CH4+CO) less than 0.3, the oxidizer of O2: He = 1: 8 was replaced by an oxidizer of O2: He = 1: 10. In Fig. 11(a), it can be seen that increasing the CH4/(CH4+CO) increased the \(S_L\) first, while decreasing the \(S_L\) primarily when CH4/(CH4+CO) was beyond 0.2, regardless of pressures. In Fig. 11(b), with a 25% volume fraction of H2 in the fuel, the variation trend of \(S_L\) changed to monotonically decrease as CH4/(CH4+CO) increased in the fuel at all pressures. It was found that the USC-Mech and Burke-Mech predicted the \(S_L\) well at elevated pressures, compared to the experimental
results. The non-monotonic behavior of $S_L$ of CH$_4$/CO mixtures was attributed to the first increase of H radical with CH$_4$ addition, which speeded up the overall reaction rate; then the subsequent decrease of $T_{ad}$ as the CH$_4$ content increased further, limited the overall reaction rate and decreased the $S_L$ [40, 41]. While with a 25% volume fraction of H$_2$ in the fuel, the large H radical pool removed the restriction and the $S_L$ decreased monotonically as CH$_4$/(CH$_4$+CO) increased.

Fig. 11: Laminar burning velocity of CH$_4$/CO/H$_2$/O$_2$/He mixtures as a function of CO mole fraction in CH$_4$/CO with (a) $X_{H2} = 0$ and (b) $X_{H2} = 0.25$ in the fuel mixture at one and three atm.

Following the empirical correlation of the pressure dependence of $S_L$: $S_L/S_{L0} = (P/P_0)\beta$, where $\beta = n/2-1$. The numerical simulations of pressure exponents $\beta$ of CH$_4$/CO/H$_2$/air mixtures as a function of mole fraction ratios CO/(CH$_4$+CO), with $X_{H2} = 0.1$-0.5 in the fuel mixture. Although the overall reaction order depended on pressure change, as shown in Fig. 6, it could be thought of as being constant over the range of one to five atm for stoichiometric CH$_4$/CO/H$_2$/air mixtures. It was found that the pressure exponents increased as the CO mole
fraction increased. Although the $S_l$ of CH$_4$/CO/O$_2$/He mixtures (Fig. 11(a)) showed non-monotonic variation behavior, the pressure exponents in Fig. 12 show a monotonically increasing trend against the CO/(CH$_4$+CO) variation. $\beta$ values of different $X_{H_2}$ conditions were similar and their difference slightly augmented as the CO mole fraction decreased or increased. The similarity of $\beta$ in different $X_{H_2}$ was caused by their similar adiabatic flame temperature; both additions of H$_2$ and CO could increase the $T_{ad}$ of CH$_4$, but the CO had a more significantly enhancing effect.

![Pressure exponents of CH$_4$/CO/H$_2$/air mixtures as a function of CO mole fraction in CO/CH$_4$ with $X_{H_2} = 0.1-0.5$ in the fuel mixture at $\phi = 1.0$.](image)

Fig. 12: Pressure exponents $\beta$ of CH$_4$/CO/H$_2$/air mixtures as a function of CO mole fraction in CO/CH$_4$ with $X_{H_2} = 0.1-0.5$ in the fuel mixture at $\phi = 1.0$.

Figure 13 further displays the species mole fraction of the main reactants, products and intermediate radicals of CH$_4$/H$_2$/CO/air flames at 1 atm by the USC-Mech. In all cases, it was found that hydrogen was always the first to oxidize, or form at the initial stage, and methane always decreased to near zero earlier than H$_2$ and CO at a lower temperature, with substantial CH$_3$ formation. H$_2$O formed earlier than CO$_2$ at a lower temperature and significantly increased by increasing the initial CH$_4$, or H$_2$ mole fraction. Comparing Figs.13 (a)(b), it can be seen that the increase of CH$_4$ content increased the peak OH and CH$_3$ concentration, but it decreased the peak values of O, while the peak values of H were similar in the two cases, which lead to an inconspicuous decrease of $S_l$, as shown in Fig. 11(a). Comparing Figs. 13(c)(d), where hydrogen is added to the fuel mixture, it was found that increasing the CH$_4$ content significantly decreased the peak values of H and O, while the peak values of OH remained the same, leading to the apparent decrease of $S_l$, as shown in Fig. 11(b). It was also found that-
- although increasing the CH\textsubscript{4} content decreased the \( T_{ad} \)-the peak location of H, O and OH shifted downstream to a higher temperature region, indicating the increase of activation energy in the fuel mixture. This means that the radical peak levels dominated the \( S_L \) of stoichiometric CH\textsubscript{4}/H\textsubscript{2}/CO/air mixtures.

Fig. 13: Species mole fraction of main reactants, products and intermediate radicals of CH\textsubscript{4}/H\textsubscript{2}/CO/air flames at one atm and \( \phi = 1.0 \). (a) CH\textsubscript{4}/(CO+CH\textsubscript{4}) = 0.1, \( X_{H_2} = 0 \); (b) CH\textsubscript{4}/(CO+CH\textsubscript{4}) = 0.9, \( X_{H_2} = 0 \); (c) CH\textsubscript{4}/(CO+CH\textsubscript{4}) = 0.1, \( X_{H_2} = 0.5 \); (d) CH\textsubscript{4}/(CO+CH\textsubscript{4}) = 0.9, \( X_{H_2} = 0.5 \).

Figure 14 shows the heat release rate of CH\textsubscript{4}/H\textsubscript{2}/CO/air flames at CO/(CO+CH\textsubscript{4}) = 0.5, \( \phi = 1.0 \), \( X_{H_2} = 0 \) and 0.5, \( P = \) one and five atm. It was found that in all cases, the positive heat release rate originated mainly from the CH\textsubscript{4} oxidation: CH\textsubscript{3} + O = CH\textsubscript{2}O + H and CH\textsubscript{3} + H (+M) = CH\textsubscript{4} (+M), and the negative heat release rate was mainly from the chain-branching reaction H + O\textsubscript{2} = O + OH. Comparing Figs. 14(a)(b), it can be seen that, as the hydrogen content increased, the heating value of the CH\textsubscript{4}/H\textsubscript{2}/CO/air mixtures decreased. The total heat release rate increased due to the enrichment of H radicals and the enhancement of chain propagating reactions,
leading to the increase of $S_l$. Reactions \( \text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H} \), \( \text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M}) \) replaced the \( \text{CH}_3 + \text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M}) \), \( \text{CO} + \text{OH} = \text{CO}_2 + \text{H} \) and contributed to the positive heat release rate. Comparing Figs. 14(a) (c) or (b) (d), as the pressure increased, all the chain termination reactions were enhanced, including R88, R104, R9 and R12. All the heat release processes shifted downstream to the higher temperature window, increasing the activation energy and causing the decrease of $S_l$. Thus, the elevated pressure increased the total heat release rate. The overall chain propagating reactions were more reliable in the high temperature region, and the overall reaction rate decreased due to enhanced chain termination reactions.

Fig. 14: Heat release rate of \( \text{CH}_4/\text{H}_2/\text{CO/air} \) flames at \( \text{CH}_4/(\text{CO}+\text{CH}_4) = 0.5, \phi = 1.0 \), (a) $X_{\text{H}_2} = 0$, one atm; (b) $X_{\text{H}_2} = 0.5$, one atm; (c) $X_{\text{H}_2} = 0$, five atm; (d) $X_{\text{H}_2} = 0.5$, five atm.
5. Conclusions

This work presented the laminar burning velocities of H₂/CO/CH₄/O₂/diluent mixtures at \( \phi = 0.5 - 2.5 \), elevated pressures one to 11 atm and H₂-CO mole fraction ratios 0.25: 0.75 to 0.75: 0.25 measured using a high-pressure heat flux burner. The effects of CO₂ dilution in the fuel from 0.0 to 0.4 and CH₄/(CH₄+CO) from 0.0 to 1.0 on \( S_L \), and the pressure dependence, were experimentally investigated and compared to the simulated results using three kinetic mechanisms. The main conclusions of this study are:

1. Increasing H₂: CO ratios increased the \( S_L \), mainly through enhancement of the H radical and thermal diffusivity. Increasing the CO₂ dilution decreased the \( S_L \) mainly through a decrease in the adiabatic flame temperature. Reducing CO₂ dilution content in the fuel more significantly enhanced flame propagating speed in the over-rich side.

2. Increasing pressure shifted the peak \( S_L \) to the leaner side due to a decrease in thermal diffusivity. The total chemical effect of CO₂ dilution decreased as the pressure increased, caused mainly by the reduction of the direct reaction effect, while the three-body effect showed a maximum at the peak mass burning rate. The difference in the overall reaction order between flames with and without CO₂ dilution grew as pressure increased, due to the enhanced three-body effect. The Burke-Mech predicted \( S_L \) better for elevated pressure and rich conditions.

3. Increasing pressure and CO₂ dilution content in the fuel enhanced the competition of H consuming reactions, i.e., three-body termination reactions and CO₂ reduction reactions in competition with chain-branching reaction. Thus, CO₂ dilution had a more significant reduction effect on \( S_L \) at high hydrogen content and elevated pressure conditions.

4. The replacement of CO by CH₄ decreased the pressure exponents of CH₄/CO/H₂/air mixtures dominated by the adiabatic flame temperature, although the peak H radicals dominated the non-monotonic variation of \( S_L \). The USC-Mech predicted the \( S_L \) for high CH₄ content and low-pressure conditions better. Increasing
the hydrogen content and the pressure increased the total heat release rate separately by enriching the H radical and enhancing three-body termination reactions.

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References

The effects of CO\textsubscript{2} dilution and methane addition on S\textsubscript{e} of syngas.