The Effect of CO₂ Dilution on Methane/Air Flames at Elevated Pressures: An Experimental and Modelling Study

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Abstract

This study reports experimental and kinetic modelling results on the effects of CO₂ dilution on laminar premixed methane/air flames, based on spherically propagating flames and one-dimensional-adiabatic planar flame simulations, at elevated pressure. The laminar burning velocities of air mixtures with CH₄ and CO₂ at different dilution ratios were measured. In order to have a comprehensive understanding of the effects of CO₂ dilution both chemically and physically, sensitivity analysis, chemical reaction rate analysis, and mole fraction analysis of active radicals were carried out using the ARAMCO 1.3 kinetic mechanism. The chemical impact of the addition of CO₂ was segregated from its physical effects using fictitious species, FCO₂ with the same thermochemical and transport characteristics as CO₂, but does not participate in any chemical reactions. The CO₂ dilution percentage varied was from 0 to 70% (by volume) to measure $S_L^0$ at 300 K, 1 and 5 bar and equivalence ratios ($\Phi$) of 0.6 to 1.4. Results show that increasing the CO₂ dilution ratio decreases the $S_L^0$ of these CH₄/CO₂/air mixtures. The results simulated using ARAMCO 1.3 illustrate that the chemical effect is less important at elevated pressure than at ambient pressure. The H and OH radical reduction rates are remarkably reduced at elevated pressure, where H radicals are primarily controlling the combustion. Elementary reactions with negative sensitivity coefficient exhibit higher sensitivity towards pressure compared to the dilution effect, while elementary reactions with positive sensitivity coefficient were equally sensitive to both pressure and dilution effects. The increase in initial pressure suppresses the peak net reaction rates for all the elementary reactions, with increasing CO₂ concentration.

1. Introduction
Studying the influence of various gaseous additives on the pollutant emission and combustion characteristics of hydrocarbon fuels is crucial [1]. There is a particular interest in investigating the impact of carbon dioxide, CO₂, as an additive to the combustion system from different perspectives. Exhaust gas recirculation, EGR, is considered to be an adequate methodology to lower the NOₓ emissions from gas turbines and engines [2], where CO₂ is the main component of EGR gas. It has previously been established that the dilution of the hydrocarbon flames with CO₂ addition reduces the soot production tendency [3]. There are still uncertainties regarding the mechanisms of NOₓ or soot reduction with the CO₂ addition from the previous investigations. To ensure a high CO₂ capture rate from flue gasses in the CO₂ capture and storage process, with minimum energy consumption, oxygen enriched combustion coupled with some degree of flow gas recirculation (mainly CO₂) is required [4].

Of direct relevance to the study of the effects of adding CO₂ to methane-air mixtures is the exploration of the East Natuna natural gas field in Indonesia. It is a vast natural gas reservoir with an estimated total gas volume of 222 trillion cubic feet [5]. It contains more than 70% CO₂ and 28% CH₄. The high CO₂ content increases the cost of extraction, which is why the field has not been tapped before now. To determine if this vast resource is viable as a useable energy source, information on these very high CO₂ levels in fuel on the combustion characteristics is necessary.

The thermochemical and biological treatment of biomass and waste yields synthesis gas (syngas). Syngas is as an alternative fuel to natural gas for internal combustion engines [6]. To meet the continuous rise in global energy demand, syngas is also a promising gaseous fuel to diversify the global energy system [6]. The primary constituents of syngas are CO and H₂, with other combustible constituents including CH₄, and some inert gases including CO₂ and N₂. The percentage of CO₂ by volume in syngas varies from 1.6% to 30% [7]. This considerable variation in CO₂ content in the syngas is one of the biggest challenges in designing the syngas burner and combustion systems. The varied CO₂ content in the combustible mixture leads to various flame speeds and, hence, various flame instabilities.

Designing efficient and low-emitting combustion systems requires a comprehensive understanding of the effect of the addition of diluents (CO₂) on hydrocarbon combustion characteristics at conditions close to practical applications (i.e., elevated pressure). The unstretched laminar burning velocity (\(S_L^U\)) is an essential intrinsic feature of the reacting system and is widely used in the literature to determine the characteristics of premixed combustible mixtures for gas
turbines and engines. Many experimental and numerical studies have been performed on the influence of CO\textsubscript{2} addition on the $S_L^o$ of CH\textsubscript{4}/air flames; however, most of the studies were conducted at ambient pressure. Halter \textit{et al.} [8] studied the influence of added CO\textsubscript{2} and N\textsubscript{2} on $S_L^o$ of CH\textsubscript{4}/air and iso-octane/air mixtures under ambient pressure using experiments and CHEMKIN. The $S_L^o$ was seen to decrease with the CO\textsubscript{2} addition to the CH\textsubscript{4}/air mixture [9] [10]. Cao \textit{et al.} [11] experimentally investigated the addition of CO\textsubscript{2} to methane/air mixture at elevated pressure using Schlieren imaging. M. Xie \textit{et al.} [12] conducted a numerical study at elevated pressure to determine the effect of CO\textsubscript{2} addition on $S_L^o$ in a CH\textsubscript{4}- air mixture. Wang \textit{et al.} [13] studied CO\textsubscript{2}–methane dilution in an oxygen-enriched combustion environment. However, there have been limited studies exploring the detailed chemical effects resulting from the addition of CO\textsubscript{2} to methane-air mixtures at elevated pressure, nor have there been sufficient numerical investigations based on experimentally measured values of the primary elementary reactions and reaction rates involved in the observed reduction of $S_L^o$ due to the addition of CO\textsubscript{2}.

As stated by Li \textit{et al.} [14], there are three ways by which the additives can influence the emissions and hydrocarbon combustion characteristics: i) reduction of the concentrations of the reactants due to the dilution effect; ii) thermal impact due to the variation in the flame temperature; and iii) chemical effect due to the participation of the added diluent (CO\textsubscript{2}) in the chemical reactions. The uncertainties in understanding the consequences of CO\textsubscript{2} addition to fuel emissions and combustion are due to the inter-connections between these three factors. The addition of CO\textsubscript{2} dilutes the reactive species' concentrations besides reducing the flame temperature (\textit{i.e.}, thermal effect). Through a chemical reaction, CO\textsubscript{2} addition modifies the temperature of the existing flame. However, the diluent addition's thermal effect is only responsible for the variation of flame temperature due to the diluent’s physical characteristics (\textit{i.e.}, thermal conductivity and specific heat).

Although the chemical effects resulting from the addition of CO\textsubscript{2} are comparably smaller compared with the physical effects, they cannot be ignored. CO\textsubscript{2} dilution has been studied comprehensively at ambient pressure by varying dilution content (as discussed earlier); however, it has not been investigated at elevated pressure with varying equivalence ratios and varying dilution concentrations. This study experimentally and numerically investigates CH\textsubscript{4}/air mixtures dilution with CO\textsubscript{2} at elevated pressure with varying CO\textsubscript{2} concentrations. A comprehensive kinetic study, utilizing the decoupling method, has been carried out to separate the aforementioned effects.
resulting from CO\textsubscript{2} dilution. Outwardly spherical flames were propagated in a Constant Volume Spherical Vessel (CVSV) and corrected for curvature using a linear extrapolation technique, to determine \( S_L^o \) of premixed CH\textsubscript{4} flames at different dilution ratios of CO\textsubscript{2}. Free propagating one-dimensional planar premixed flames were then simulated to understand the kinetic effects of CO\textsubscript{2} dilution on \( S_L^o \) of CH\textsubscript{4}/air mixtures.

2. Experimental Setup, Data Processing, and Flame Conditions

The CVSV at KAUST (shown in Fig. 1) has an inner diameter of 330 mm, with two pairs of orthogonal 120-mm wide quartz windows. These windows provide optical access for photographic (Schlieren) and laser sheet techniques (for flow field and flame structure measurements). The CVSV is designed to withstand the pressures and temperatures generated from flame deflagrations at preliminary pressures and temperatures up to 10 bar and 400 K, respectively. The fuel-air mixture's initial temperature is observed at two points inside the vessel to maintain the thermal homogeneity of the combustible mixture. Chromel-Alumel wire Type-K thermocouples, sheathed in a stainless steel tubing 1.5 mm in diameter, and are employed to measure the internal temperature during mixture preparation and the initial temperature. To ensure mixture homogeneity, the vessel has a stirrer-fan placed centrally inside the CVSV at the top flange. The fan is stopped approximately 5 minutes before mixture ignition to prevent the occurrence of perturbation in the flame propagation.

The reactants are injected into the CVSV based on the gaseous components' partial pressures; a method that depends on the assumption of the gases behave ideally, which they do at these temperatures and pressures. Gaseous fuel mixtures were prepared using their respective partial pressures. Before filling the CVSV with the mixtures, the vessel was flushed twice with air from the lab after the previous combustion events to remove any residual gases remaining inside the vessel. During the experiments, the CVSV was first evacuated using a vacuum pump, and then each reactant was injected into the vessel in the corresponding proportion based on partial pressure.
Two electrodes (1.2 mm in diameter) were used to generate the spark that would ignite the fuel-air mixture. The electrodes were mounted in a V-shaped configuration with a minimum gap of 1 mm and placed at the vessel's center. The average ignition energy of the spark was set to 24 mJ. The pressure rise before and during flame propagation was recorded via a piezoelectric dynamic pressure transducer (Kistler 6045A) mounted within the inner surface of the vessel, whereas the initial pressure of the combustible mixture was measured with a piezoresistive pressure transducer (Keller PAA-33X). With a high-speed imaging camera (Photron, FastCam Ultima APX 120K) in a typical Schlieren setup, the time-sequential images of the propagating flame were recorded at 4000 fps, at a resolution of 512x512 pixels. This led to a spatial resolution of approximately 317 μm/pixel. These recorded images were used to evaluate flame propagation.

For the spherical propagation of laminar flames, the speed of a spherical flame, $S_n$, is measured as $S_n = dr/dt$, where $r$ is the instantaneous average radius of the flame schlieren and $t$ is time. Spherically propagating flames are susceptible to a time-varying flame stretch rate due to curvature [15]; as such, $S_n$ indicates the stretched laminar flame speed. In spherical flames, the stretch rate, $\alpha$, is defined as $(1/A) (dA/dt) = \left(\frac{2}{r}\right) S_n$, where $A$ is the surface area of the flame [15]. The stretch
rate is due to the aerodynamic strain rate and flame stretch resulting from the flame's curvature. For each combustion event, the mean flame radius was determined from the projected flame's surface area and plotted in relation to time. Numerical differentiation was then used for calculating flame speeds by employing central differentiation of five consecutive closely spaced radii.

Values of $S_n$ are indicated by $S$ when there is no influence from instability and perturbation caused by spark ignition or wall-confinement effects. Here, $S$ corresponds to the linear regime in the stretch rate-flame speed relationship. Various correlations between the flame speed, $S$, and $\alpha$ have been suggested to determine the unstretched flame speed, $S_o$, which enables the elimination of the stretch rate effect, by extrapolating $S$ to a zero stretch rate [16]. An asymptotic analysis showed that the difference between the unstretched flame speed, $S_o$, and the stretched flame speed, $S$, is linearly proportional to the flame stretch rate as given by $S_o - S = L_b \alpha$ [17], where the proportionality constant, $L_b$, is the Markstein length of the burned gas. This equation yields values of the stretched flame speed ($S$) and the Markstein length of the burned gas ($L_b$) when extrapolated linearly to a zero stretch rate ($\alpha = 0$), ($r = \infty$), yielding $S_o$. After extraction of $S_o$, the unstretched laminar burning velocity, $S_L^o$, is calculated by the mass balance over $S_e$ as $S_L^o = S_o/\sigma$, where $\sigma$ is the thermal expansion coefficient ($\sigma = \rho_u / \rho_b$, where $\rho_u$ and $\rho_b$ are the unburned and burned density of the mixture, respectively). The CO$_2$ percentages introduced as a mole fraction into the CH$_4$ stream and were varied by 0, 10, 30, 50, and 70%. The mixture equivalence ratio varied from 0.6 to 1.3 at two initial pressures of 1 and 5, while the initial mixture temperature was kept constant at 300 ± 3 K.

Different sources of uncertainty influence the extracted $S_L^o$ one such source is the vessel size. The selection between the extrapolation method (linear or non-linear) for estimating the unstretched flame speed depends on the vessel size. In small vessels where the propagation of the flame reaches the wall region, the confinement effect is pronounced, and a spherical flame will suffer from the curvature in the flame speed-stretch rate relationship [18]. For the small vessel sizes, the non-linear model is more suitable to extract the $S_L^o$ particularly when the flame speed-stretch rate relationship is sensitive (i.e., large $L_b$). In KAUST's CVSV, the results of the two models, called NQ (quasi-steady non-linear model) and LC (Linear model based on curvature) [19], were compared with the results of the linear model. They showed minimal differences in estimating $S_L^o$ [20]. In addition, Elbaz et al. [21, 22], used the Wu et al. [19] methodology, to
investigate the difference between the linear and nonlinear extrapolation on extracting the unstretched flame speed in the current vessel for different ammonia blends with DMM [21] and DEE [22], and they showed a negligible difference between the two methods. Figure 2 shows the flame speed variation with the stretch rate under stoichiometric conditions for $P_o = 1$ and 5 bar, $T_o = 300$ K, and various CO$_2$ dilution ratios. In this plot, the linear and nonlinear extrapolations methods in estimating the unstretched flame propagation speed are included. The results indicate that the linear and nonlinear extrapolations for CH$_4$-air and CH$_4$/CO$_2$-air premixed mixture flames provide the negligible difference with the current large vessel. The results show that the Sn-( relationship follows a linear correlation for most of the cases. Also, the addition of CO$_2$ decreases the flame speed but does not impact the linearity of the $S_n-\alpha$ correlation. Also, the ignition can influence the extracted $S^*_L$; however, with a proper choice of the minimum flame radius used in the extrapolation, the impact of ignition can be avoided. Regarding the impact of spark ignition, the lower limit of the flame radii used in the data processing was selected to be $r_{min} > 10$ mm. The maximum possible radius was 45 mm due to the large vessel size. Any uncertainty due to flame radiation and vessel confinement can be neglected at this maximum flame radius (the maximum flame radius relative to the vessel radius was 0.273). The results of the methane flame speed estimates match the data from the literature well (as shown in Fig. 3). For each condition, 3 to 4 runs were performed to ensure accuracy and to obtain averaged values. Results are shown with error bars to reflect existing uncertainties. Considering variations in the initial temperature and pressure and errors in flame radius determination, the statistical error has a 2.5% confidence level as determined by the Student's t-test and the standard deviation [23]. Chen et al. [24] conducted an extensive study to determine the radiation effect in CO$_2$-diluted methane flames that were outwardly propagating in a constant volume chamber. They concluded that radiation-induced uncertainty is negligible (within 2.5%) at all CO$_2$ dilution levels studied at ambient and elevated pressures.

A detailed description of the evaluation method for uncertainty determination is presented in our previous work [18]. Uncertainties in $S^*_L$ determination are mainly derived from the equivalence ratio caused by variation in pressure and temperature. The range of error in the equivalence ratio based on temperature and pressure was found to be less than 2.5% at $P_o = 1$ bar and $T_o = 300$ K.
Figure 2. Stretched flame speeds of methane/CO$_2$/air mixtures at initial pressures of $P_0 = 1$ and 5 bar, $T_0 = 300$ K. The symbols represent the measured data, while the solid lines are the linear extrapolations of the measurements and the dotted curves show the nonlinear extrapolations at $\Phi = 1$.

3. Chemical Kinetic Simulations

The PREMIX code implemented in the CHEMKIN-PRO software [25] was used to perform simulations of freely propagating one-dimensional (1D) planar flames of methane-air mixtures diluted with CO$_2$. For the initial stage of the chemical kinetic simulations, two reaction mechanisms, ARAMCO 1.3 [26], and GRI 3.0 [27] reaction mechanisms, have been tested versus the experimental data for neat methane flames and the 30% CO$_2$ diluted flames. The results show that ARAMCO 1.3 mechanism simulates the flame speed for both neat methane and CO$_2$ diluted flames better than GRI 3.0 reaction mechanism, see Fig. S1 (in the supplementary material). In addition, the GRI 3.0 reaction mechanism over-predicted the flame speed for the 30% CO$_2$ flames; consequently, in this work, we only presented the simulated flame speed results of ARAMCO 1.3 reaction mechanism. The ARAMCO 1.3 [26] reaction mechanism is a comprehensive combustion reaction mechanism for methane-air combustion. It contains 766 elementary reactions with thermochemical parameters and corresponding rate coefficient expressions for 124 species. The unburned blend's mass flow rate was set to 0.04 g/cm$^2$-s, which is comparable to the estimated...
stoichiometric CH\textsubscript{4}/air flame [28]. The temperature profile for a stoichiometric methane/air flame proposed by Maaren et al. [29] and Uykur et al. [30] was used to initiate the simulation. Then, the produced flame temperature profile was used as the initial temperature for the next simulated iterations. The initial mixture temperature was kept constant at 300 K, while the initial pressure was varied as 1, 3, and 5 bar. A minimum of 500 grids was used to ensure the accuracy of converged solutions with the constraints for GRAD and CURV set to 0.2 and 0.1, respectively. As mentioned earlier, the CO\textsubscript{2} dilution ratio was changed relative to the CH\textsubscript{4} concentration for the complete range of equivalence ratios. To distinguish the chemical effects of CO\textsubscript{2} from its physical effects, we used the proposed fictitious species methodology [14]. The impact of the CO\textsubscript{2} addition on the fuel-air mixture combustion could be divided mainly into physical impact due to the changes in the mixtures' physical properties and chemical impact due to the diluent reactivity [12]. The physical impact has been separated into dilution effect due to the decrease of the fuel and oxidations fractions in the reactants and thermal effect, which considers the variations of the specific heat and thermal diffusivity by Hu et al.[29]. In the current work, the numerical simulation was performed twice, once when normal CO\textsubscript{2} participates in the chemical reactions, and the other when the so-called fictitious CO\textsubscript{2}, FCO\textsubscript{2}. The fictitious CO\textsubscript{2}, FCO\textsubscript{2} has the same thermochemical and transport characteristics as normal CO\textsubscript{2}, but is not allowed to participate in chemical reactions, that is chemically inert. In addition, the carbon dioxide produced by the chemical reactions in the seeded flame is not concerned by the existence of the fictitious CO\textsubscript{2}. Thus, the new FCO\textsubscript{2} causes all the effects of CO\textsubscript{2}, but the chemical effect, which makes the difference between these two simulated conditions' solutions, represents the chemical influences of CO\textsubscript{2} dilution on the flame speed. These decoupling methods have been recently numerically used to investigate the three effects of CO\textsubscript{2} dilution on the premixed methane/air mixture laminar burning velocity [12]. In this work [12], two dilutions have been used, namely N\textsubscript{2}, and CO\textsubscript{2}, where the three effects of the CO\textsubscript{2} were evaluated as the following: dilution effect =\textit{LBV}_{\text{non-diluent}} - \textit{LBV}_{\text{N2}}, thermal effect = \textit{LBV}_{\text{N2}} - \textit{LBV}_{\text{FCO2}}, and chemical effect =\textit{LBV}_{\text{FCO2}} - \textit{LBV}_{\text{CO2}}. In this decoupling methods, the \textit{LBV}_{\text{non-diluent}} is the laminar burning velocity without diluent; \textit{LBV}_{\text{FCO2}} and \textit{LBV}_{\text{CO2}} are the LBVs diluted by N\textsubscript{2} and FCO\textsubscript{2} and CO\textsubscript{2}, respectively.

\textbf{4. Results and discussion}
4.1. Experimental validation

To gain confidence in our data and the methodology utilized in estimating $S_L^o$, the derived $S_L^o$ for methane-air flames at $P_o=1, 5$ bar, and $T_o = 300$K were compared with those in the literature [30, 31] as shown in Fig. 3. They have used different experimental configurations for $S_L^o$ determination, and present data achieved with the linear extrapolation method demonstrates a good agreement with literature data for the wide range of equivalence ratios at 1 bar. This good agreement between the current measurements and those reported in the literature also extended to the high-pressure case ($P_o = 5$ bar), confirming our results' consistency. The simulated $S_L^o$ matches the experimental results at 1 and 5 bar for all of the equivalence ratios investigated.

![Figure 3. $S_L^o$ at varying equivalence ratios for CH$_4$/air premixed flames at $P_o = 1$ and 5 bar and $T_o = 300$ K from the current work and previous studies in the literature. The dashed lines show the simulated results using ARAMCO 1.3 mechanism; the data obtained from the literature were based on CVSV.](image)

4.2 Flame appearance and observation

Figures 4(a) and (b) show schlieren images of stoichiometric methane/air flames with the elapsed time (t) from the ignition at various dilution ratios of CO$_2$ (0, 10, 30, 50, 70%) at 1 bar and 5 bar, respectively. In the cases of the CO$_2$ dilution ratios from 0 to 50%, the flame showed a spherical propagation without noticeable flame. After approximately 29 ms from the ignition, the flame radius with 50% CO$_2$ dilution was smaller than the flame radius of neat methane, as shown in Fig. 4 (a). In addition, the spherically propagating flame was centered close to the end of the spark-
generating electrodes. Figure 4 (a) shows that at 1 bar flames, there are no cracks in the flame front with or without CO₂ dilution, suggesting high flame stability under these conditions. At 5 bar, the flame starts to develop cracks, and the flame radius becomes smaller (right column of Fig.4b). However, as shown in Fig. 4 (b), the flame speed of the mixture with 70% CO₂ dilution is very slow, and the center of the flame moves upward in the vessel (after ~ 192 ms from the ignition, the lower part of the flame is still observed in the quartz window). This movement of the flame's center upward is due to the buoyancy effect. These observations indicate that the flame speed reduces as the CO₂ dilution ratio increases, leading to the flame's upward movement at relatively high CO₂ dilution.

![Schlieren images of the flame fronts at an equivalence ratio of 1 at 1 bar and 5 bar, 300 K and different CO₂ dilution ratios.](image)

**Figure. 4 (a).** Schlieren images of the flame fronts at an equivalence ratio of 1 at 1 bar and 5 bar, 300 K and different CO₂ dilution ratios.
Another feature related to flame appearance and stability is the decrease in the hydrodynamic flame instability with increasing CO\textsubscript{2} dilution ratios. The hydrodynamic flame instability depends on the flame's thermal expansion (\(\sigma\)) and the laminar flame's thickness (\(\delta\)) [32]. The laminar flame's thickness can be evaluated as \(\delta = (T_u - T_b)/(dT/dx)_{\text{max}}\), where \(T_u\) and \(T_b\) are the unburned and burned gas temperatures of the mixture, respectively; here, \((dT/dx)_{\text{max}}\) is the maximum temperature gradient [32]. The CHEMKIN simulation results (ARAMCO 1.3) of one-dimensional planar flames were used to determine \((dT/dx)_{\text{max}}\). As stated earlier, the thermal expansion is based on the ratio of the unburned density to the burned density of the mixture. The higher the thermal expansion ratio, the greater the flame tendency toward hydrodynamic instability [33]. On the contrary, the thinner the laminar flame's thickness, the higher the hydrodynamic instability.

Figure 5 (a) shows \(\sigma\), while 5 (b) and 5 (c) show \(\delta\) versus \(\Phi\) for different CO\textsubscript{2} dilution ratios at 1 bar and 5 bar, respectively. Fig. 5 (a) demonstrates that the thermal expansion increases as \(\Phi\) changes from lean to the stoichiometric mixture and then decreases as the mixture gets richer. At 5 bar, the thermal expansion ratio is slightly higher compared to 1 bar. The opposite trend is observed in Figs. 5(b) and (c) for \(\delta\) versus \(\Phi\). This trend suggests that the hydrodynamic instability increases as \(\Phi\) changes from lean to stoichiometric mixtures; however, it resists instability with the richest mixtures. Moreover, as the CO\textsubscript{2} dilution ratio increases, the flame thickness increases while its thermal expansion ratio decreases. This suggests that as the CO\textsubscript{2} percentage increases in the mixture, there is less tendency that the flame's hydrodynamic instability will be observed. Also, at 5 bar, the hydrodynamic instability is suppressed due to a considerable increase in the laminar flame thickness at high dilution ratios. However, at 5 bar, neat CH\textsubscript{4}, along with 10% and 30% CO\textsubscript{2} dilution ratios, experiences a decrease in flame thickness compared to flame thickness at ambient
pressure for the corresponding CO$_2$ dilution ratios. It is to be noted at elevated pressure that higher dilution ratios of CO$_2$ yield thicker flame thickness, increasing their stability. Since both flame thickness and the thermal expansion, were calculated based on the one-dimensional planar simulated flames, the highly observed buoyancy effect at high CO$_2$ dilution ratio (70%) has no roles on these simulated parameters.
Figure. 5. (a) Thermal expansion ratios at 1 and 5 bar, 300K; (b) laminar flame thicknesses at 1 bar, 300 K; (c) laminar flame thickness at 5 bar, 300 K of CH₄/air mixtures at various equivalence ratios and dilution ratio of CO₂.

The $S_L^o$ follows a positive correlation with adiabatic flame temperature $T_{ad}$, where the overall reaction rate is influenced by chemical reactions occurring near the adiabatic flame temperature [15]. Figures 6(a) and (b) show the adiabatic flame temperature at 1 and 5 bar with varying equivalence ratios and CO₂ dilution ratios. Higher CO₂ dilution ratio results in a decreased adiabatic flame temperature, as expected. However, $T_{ad}$ is higher at elevated pressure than at lower pressure for the same CO₂ dilution ratio. The variation in $T_{ad}$ reflects the thermal effect on the $S_L^o$ [34]. Studying the chemical and physical effects resulting from CO₂ dilution methane/air mixture is therefore essential. The laminar flame speed is directly proportional to the thermal diffusivity times of the chemical reaction rate [21]. The Arrhenius equation indicates that the chemical reaction rate depends on the reacting temperature, and mainly the chemical reactions controlling the overall oxidation rate react at nearby the adiabatic flame temperature (presented in Fig. 6a-6b). The impact of the CO₂ addition on the mixture thermal diffusivity could be understood via the close inspection of the variation of the thermal diffusivity with CO₂ at Φ = 1 at 1 and 5 bar presented in Fig. 6c. It is observed that the mixture thermal diffusivity of the mixture is decreased with increasing the CO₂ dilution ratio at 1 bar; however, at 5 bar it shows less sensitivity to the CO₂%.
Figure 6. The adiabatic flame temperature of CH₄/air mixtures at (a) P₀ = 1 bar, (b) P₀ = 5 bar, at various equivalence ratios, and dilution ratio of CO₂, (c) mixture thermal diffusivity at Φ = 1 with CO₂ dilution ratio at 1 and 5 bar.

4.3. CH₄/air/CO₂ premixed mixtures and $S_L^o$

Figure 7 presents $S_L^o$ of CH₄/air mixtures at various dilution ratios of CO₂ with varying equivalence ratios at initial pressure and temperature of 1 bar and T=300K, respectively. The symbols indicate the experimental data. As shown in Fig. 7, increasing the CO₂ dilution ratios limits the flame propagation after the ignition with the richest and leanest mixtures leading to extinguished flames. For instance, at 10% and 30% CO₂ dilution ratios, the flame was extinguished at 0.6 > Φ > 1.2, and these limits were further limited to 0.8 > Φ > 1 for the 50% CO₂ dilution ratio. A few milliseconds after ignition, the boundaries of the flame kernel become unobservable. Under these conditions, the flame kernel tends to become readily quenched due to low heat release from the chemical reaction. In the 1-bar case, $S_L^o$ of the CH₄/air/CO₂ mixture increases and reaches its peak flame velocity at ~ Φ=1.1 and then decreases with Φ in the rich mixtures, as expected. The same behaviors were observed for the flames at 5 bar initial pressure. The effect of the CO₂ dilution ratio at Φ = 1 on the flame speed at the three initial pressure of 1, 3, and 5 bar are presented in Fig. S2 of the supplementary material, however for the sake of concision in the rest of the manuscript we will present only the 1 and 5 bar data.
Figure 7. $S_L^0$ plotted for CH$_4$–CO$_2$–air blends at $P_o = 1$ bar and $T_o = 300$ K.

Figures 8 (a) and (b) demonstrate the excellent agreement between the simulated and experimental flame speeds over the wide range of $\Phi$ and for the different CO$_2$ dilution ratios, at initial pressures and temperature of 1 and 5 bar, 300K, respectively. Figure 9 shows the variation of $S_L^0$ with CO$_2$ dilution ratios for 1 and 5 bar and $\Phi = 0.8$, 1, and 1.2. As shown in Fig. 9, the flame speed decreases with increasing CO$_2$ dilution ratio and shows an approximately linear decrease for the stoichiometric condition; however, it indicates a non-linear decline in the $S_L^0$ with CO$_2$ for the lean and rich mixtures ($\Phi = 0.6$ and 1.2) at 1 bar.
Figure. 8. $S_L^o$ of CH$_4$/air mixtures with equivalence ratios for different CO$_2$ dilution ratios at (a) 1 bar and (b) 5 bar and 300 K initial temperature. The symbols refer to the experimental results and lines indicate the predicted values of $S_L^o$ using ARAMCO 1.3 mechanism.

Figure. 9. $S_L^o$ for the different ratio of CO$_2$ at (a) 1 bar and (b) 5 bar and temperature up to 300 ± 2 K. Symbols represents experimental results. The solid line represents simulated $S_L^o$ using ARAMCO 1.3 mechanism.

To clearly observe the variation of the $S_L^o$ with pressure at different CO$_2$ dilution ratios, another set of data at 3 bar was collected. The effects of pressure on the burning velocity are presented in Fig. 10. In this plot, the normalized $S_L^o/S_L^o$ is plotted in relation to $P/P_o$, where the subscript o indicates...
the datum values of $S_L$ at 1 bar and 300 K and by assuming the empirical correlation at 300 K between 1 and 5 bar as $S_L/S_L^o = (P/P_o)^\beta$. The pressure power exponent ($\beta$) is extracted from the measured values of $S_L^o$ for different CO$_2$ dilution ratios. $\beta$ is related to the overall reaction order as $\beta = n/2 - 1$[35]. Under a condition of constant CO$_2$ dilution ratios, as illustrated in Fig.10, the variation in $S_L/S_L^o$ in relation to $P/P_o$ is very sensitive to the lower range of pressure. In addition, the negativity of the $\beta$ exponent increases as the CO$_2$ dilution ratio increases and the most significant $S_L/S_L^o$ pressure dependence is found at 50% CO$_2$ dilution ratio where $\beta = -0.505$ (see Fig. 10 (a)). As indicated in Figure 10 (b), the variation of the simulated values of the pressure power exponent $\beta$, show a reasonable quantitative agreement with the experimental values and that at the various dilution CO$_2$ ratio. The advantage of evaluating $\beta$ is that it facilitates the extrapolation of $S_L^o$ at elevated pressure, which cannot be obtained experimentally due to safety and test rig limitations.

![Figure 10](image_url)

**Figure. 10.** (a) Variations in $S_L/S_L^o$ with $P/P_o$ indicated by curved lines for dilution ratios of CO$_2$ under stoichiometric conditions at 300 K and the respective fitting curves. Symbols represent present results; lines represent fitting curves. (b) Calculated and predicted values of $\beta$ under stoichiometric conditions.

### 4.4. Effects of the CO$_2$ dilution ratio on physical and chemical parameters

As noted above, to distinguish between the physical and chemical effects of the CO$_2$ dilution ratios, we used the fictitious CO$_2$ (FCO$_2$) strategy in the chemical kinetic models. Figure 11 shows the neat CH$_4$/air premixed mixture's simulated flame speed at 1 bar, and 5 bar together with 50% CO$_2$ diluted flame speeds with and without FCO$_2$ for $\Phi$ =1. As shown in Fig. 11, the difference between the simulated results for the neat CH$_4$/air premixed mixture and those for 50% CO$_2$ captures the
total effect of CO$_2$ on the flame speed (the physical and chemical effects). The difference between the simulated data with CO$_2$ and FCO$_2$ dilution shows the chemical effect, as shown in Fig.11. For 1 and 5 bar, the chemical and physical influences lead to slow down the flame speed over a wide range of $\Phi$. In general, the physical effect impacts the flame speed more than the chemical effect, and the chemical effect is seen to be reduced with increasing pressure. Moreover, the significant reduction in flame speed is seen to occur in the slightly rich mixture between $\Phi = 1.05$ and 1.1 at atmospheric and elevated pressure.

**Figure. 11.** Chemical and physical effects on the $S_L^0$ with 50% CO$_2$ dilution ratios of CH$_4$/air stoichiometric mixtures at (a) $P_o = 1$ bar and (b) $P_o = 5$ bar.

Figure 12 demonstrates the consequence of the CO$_2$ addition on both the chemical and physical behavior of the CH$_4$/air mixture flame speed at $\Phi=1$. Relative to the neat CH$_4$/air flame speed (shown as a horizontal line in the plot), both the chemical and physical effects increase with increasing CO$_2$ dilution ratio at both pressures. To quantify the degree of the reduction in the flame speed due to the chemical effect from CO$_2$ dilution, we used the normalized contribution factor, $\xi_{CO2}$, which is defined as:

$$
\xi_{CO2} = \frac{[S_L(FCO2)-S_L(CO2)]}{[S_L(0)-S_L(CO2)]}
$$

Here, $S_L(FCO2)$ and $S_L(CO2)$ are laminar burning velocity with fictitious CO$_2$ and CO$_2$, respectively, while $S_L(0)$ is the laminar burning velocity for neat CH$_4$/air mixtures. Figure 13 shows the contribution factor $\xi_{CO2}$ versus the CO$_2$ dilution ratio for $\Phi = 1$ and $P_o = 1$ and 5 bar.
The chemical effect of CO$_2$ dilution is more notable in flames at 1 bar than at 5 bar. The contribution factor, $\xi_{CO_2}$, experiences significant reductions with increasing dilution of CO$_2$ at 1 bar flames. In addition, the lower the CO$_2$ addition ratio, the less the influence of the pressure on the flame speed reduction due to the chemical effect (see the difference in $\xi_{CO_2}$ factor between the 1 and 5 bar cases at 10% CO$_2$ dilution and the corresponding difference at 50% CO$_2$ dilution).

Figure. 12. Effect of FCO$_2$ and CO$_2$ addition on the $S_L^0$ under stoichiometric conditions. Experimental results from the present study are also presented.

Figure. 13. Contribution of CO$_2$ dilution at 1 and 5 bar for $\phi = 1$ using Aramco 1.3.
4.5. Sensitivity analysis

To better investigate the physical and chemical effects of CO\textsubscript{2} dilution ratios on the $S_L^o$ of stoichiometric CH\textsubscript{4}/air mixtures, the sensitivity analysis of the top 20 reactions for $S_L^o$ with 30% and 50% CO\textsubscript{2} dilution ratios at 1 and 5 bar are presented in Fig. 14a and 14b, respectively. For the sake of comparison, the sensitivity reactions of neat CH\textsubscript{4}-air mixtures are also presented. Regardless of CO\textsubscript{2} ratio, $S_L^o$ is sensitive to chain branching/propagation reactions and chain termination reactions, including H, O, OH radicals. In all cases, the dominant chain branching reaction is R1 (H+O\textsubscript{2} = O+OH), which produces a great amount of O and OH radicals. In addition, three reactions, R30 (HCO+M =H+CO +M), R27 (CO+OH = CO\textsubscript{2} +H), and R135 (CH\textsubscript{3}+OH = CH\textsubscript{2}O +H), have the most positive sensitivity coefficients after reaction R1 (see Fig. 14a and Fig. 14b for 30 and 50% CO\textsubscript{2} dilution ratios respectively). On the other hand, reactions R127 (CH\textsubscript{3} +H (+M) =CH\textsubscript{4} (+M)), R8 (H+OH+M=H\textsubscript{2}O+M), and R9 (H+O\textsubscript{2} (+M) = HO\textsubscript{2} (+M)) show the most negative influence on the $S_L^o$ (terminating reactions with negative sensitivity coefficients).

As shown in Fig. 14, the reactions as mentioned above, are chain branching reactions that produce H atoms (R30, R27, and R135) or chain termination reactions consuming the active H radicals (R127, R8, R9). The primary chain branching reaction R1 consumes one H atom and forms O and OH radicals. As the pressure for the neat CH\textsubscript{4}/air mixture rises, the sensitivity factors of the most strong termination reactions (R127, R8, R9) show a more considerable increase compared to those of the primary branching reaction R1, at the same time, the positive sensitivity coefficient of the reaction R30 is suppressed with increasing the pressure. These reactions lead to a decline in the flame speed with increasing pressure. A comparison of the sensitivity plots in Fig. 14a and 14b under the same pressure show that as the CO\textsubscript{2} dilution ratio increases from 30 to 50%, the sensitivity coefficient of R1 has the maximum increase among the chain branching reactions. However, reaction R30 shows a strong sensitivity to the pressure and a little change with CO\textsubscript{2} increase. A close inspection of R27 (CO+OH= CO\textsubscript{2} +H) indicates the direct effect of dilution on the flame speed. This reaction does not show sensitivity to pressure for neat methane-air mixture; however, with CO\textsubscript{2} addition, a slight increase in pressure sensitivity is noticeable. This means this reaction (R27) competes with reaction R1 in consuming H atoms, which suppresses the positive impact of this reaction on the flame speed by increasing the mixture's CO\textsubscript{2} concentration. Similarly, R30 (R30: HCO + (M)$\leftrightarrow$H + CO + M) also shows appreciable sensitivity to pressure
compared to CO\textsubscript{2} addition. Reaction R135 (\textit{CH}_3+\textit{OH}=\textit{CH}_2\textit{OH}+\textit{H}) exhibits a higher sensitivity to pressure, and the CO\textsubscript{2} dilution ratio by providing more H atoms and formaldehyde radicals. The positive influence of reaction R135 on the flame speed is attenuated with increasing the pressure and/or CO\textsubscript{2} dilution ratio. This indirectly impacts the positive result of reaction R30 by reducing the HCO formation's main chain via CH\textsubscript{2}OH route.

On the other hand, the sensitivity coefficient of the two termination reactions, R127 (\textit{CH}_3+\textit{H}(+M)=\textit{CH}_4(+M) and R9 (\textit{H}+\textit{O}_2(+M)=\textit{HO}_2(+M)), exhibit maximum growth with increases in pressure (\textit{i.e.}, a greater consumption of the H radical). Thus, these two reactions (R127 and R9) show a keen sensitivity to pressure increases compared to the CO\textsubscript{2} dilution ratio increases. This suggests that the net amount of H radicals will govern the overall combustion rate, which is controlled by the net amount of chain branching of reactions R1 and R135. These reactions compete for H atoms with the termination reactions R127, R9 and the backward reaction R27 with increasing CO\textsubscript{2} or pressure. This sensitivity analysis explains why the main reactions lead to reducing the flame speed with the CO\textsubscript{2} dilution ratios or with pressure.
Figure. 14(a). Sensitivity analysis of the $S_L^p$ at 30% CO$_2$ dilution ratio for the stoichiometric methane/air mixture.

Figure. 14(b). Sensitivity analysis of the $S_L^p$ at 50% CO$_2$ dilution ratio for the stoichiometric methane/air mixture.

4.6. Molar fraction of intermediate and small molecules

Sensitivity analysis in Figs. 14(a) and 14(b) shows that primary elementary reactions with positive sensitivity coefficient (R1, R30 and R27) and negative sensitivity coefficient (R8, R9 and R127) are controlled by intermediate and small molecules. We can conclude that CO, CO$_2$, H$_2$O, and intermediate radicals (HO$_2$ and CH$_3$) strongly influence the $S_L^p$ based on the sensitivity analysis. Thus, it is essential to determine this product’s behavior with varying initial pressures and CO$_2$ dilution ratios.

From the sensitivity analysis, R8: H+ OH + (M)$\leftrightarrow$H$_2$O + M and R30: HCO + (M)$\leftrightarrow$H + CO + M involve three-body reactions. At elevated pressure, these three-body reactions have significant effects on $S_L^p$. As H$_2$O and CO are involved in these three-body reactions, it is essential
to study the chemical effect on these species' molar fractions at elevated pressure. Figure 15(a) shows FCO₂ and CO₂ molar fractions with 30% CO₂ dilution at 1 and 5 bar initial pressure. The resultant molar fractions of CO₂ and CO decrease with FCO₂ dilution as compared to CO₂ dilution, indicating the chemical effects from higher CO₂ and CO dilution. However, the reverse trend is observed in the molar fraction of H₂O. The addition of FCO₂ results in a slight increase in the H₂O molar fraction. At elevated pressure, the CO₂ molar fraction reduction decreases while the reduction in the CO molar fraction increases at elevated pressure. The CO molar fraction's peak position resembles the peak position of the net reaction rate of R27: CO + OH →CO₂ + H, which means the profile of R27 reaches the peak when CO starts to decline. This indicates that the R27 reaction causes the CO molar fraction to decrease and that at elevated pressure, this effect reduces due to a reduced chemical effect. Thus, the inhibiting impact of R27 plays a primary role in the effect of pressure versus the chemical impact. The chemical impact produces a much stronger influence on CH₃ as compared to HO₂, as shown in Fig. 15(b). However, at the elevated pressure of 5 bar, the chemical effect is reduced with significant variation in the CH₃ radical molar fraction compared to at 1 bar.
Figure 15. The effects of CO$_2$ addition on the flame structure of a stoichiometric methane/air mixture at $T = 300$ K, $P = 1$ and 5 bar for CO$_2$ dilution ratio of 30%: (a) molar fractions of intermediates, (b) molar fractions of small molecules

Figures 16(a) and (b) show H and OH radicals' main consumption and production rates, respectively. In these plots, the contribution of the main chain branching (R1, R3, R12, R27, R30, R135 and R144) and the chain termination (R8, R9, R35 and R127) reactions under stoichiometric conditions with 30 percent CO$_2$ dilution (1 and 5 bar, 300 K). As shown in Fig. 16 (a), R1 is the primary reaction responsible for OH and H radicals' production and consumption, respectively. This correlates with the sensitivity coefficient of R1 at elevated pressure shown in Figs. 14(a) and 14(b). From Fig. 16(a) it can be concluded H radicals production rate reaches at peak following R30 while R3 and R27 attain peak in the downward phase of R30 at elevated pressure. The ROP of the OH radicals is significantly increased at elevated pressure compared to at 1 bar, as shown
in Fig. 16(b). Production of H radicals is primarily influenced by R3, R27 and R30, reactions with positive sensitivity coefficient. Contrary to this, OH radical consumption rate is mainly controlled by R3 and 27. Thus, it can be concluded that R3 and R27 are exhibiting a significant influence on active radical pool concentration. Besides, R3 and R27 sensitivity reduce at elevated pressure with an increase in CO\textsubscript{2} dilution ratio, as shown in Fig. 14(a) and (b), resulting in the observed reduction in $S_L^O$ at elevated pressure. The primary reactions responsible for the consumption of the OH radicals (R3 and R27) have much higher ROP at 5 bar compared to 1 bar due to the increased reaction rate of R1 at elevated pressure. Reactions R3 and R27 attained their peak values after OH approached its maximum ROP.

Figure. 16. ROP of H and OH radicals at 30% CO\textsubscript{2}, 1 and 5 bar, 300 K. (a) $\phi = 1$, H radical; (b) $\phi = 1$, OH radical.

The flame temperature has a prevailing influence on $S_L^O$, as discussed in previous studies [32]. Molar fractions of active radicals such as H and OH can also reveal the nature of $S_L^O$. Figure 17(a) shows molar fractions of H and OH at 300 K, 1 and 5 bar pressure in the presence of CO\textsubscript{2} and FCO\textsubscript{2}. The CO\textsubscript{2} dilution ratio increase results in a reduced H and OH molar fractions concentration. The difference between non-dilution and FCO\textsubscript{2}-containing flames reveals the impact of the physical effect. The difference between non-dilution and CO\textsubscript{2}-containing flames shows the physical and chemical effects, and the difference between FCO\textsubscript{2}- and CO\textsubscript{2}-containing flames reveal the chemical impact. FCO\textsubscript{2}-containing flames have higher concentrations of H and OH molar fractions and flame temperatures compared with CO\textsubscript{2}-containing flames. The impact of dilution is considerable on flame temperature, as revealed by the largest gap. The chemical effect
gap is the smallest, illustrating less influence on flame temperature compared to the dilution effect. This is consistent with the behaviors of CO₂ dilution shown in Fig. 11. From Figs. 17 (a) and (b), the increase in the dilution ratio leads to an increase in the flame thickness. Mole fraction of H radicals reduces as the CO₂ dilution ratio increases, similar to the OH molar fractions' trend at the stoichiometric condition. An increase in the dilution ratio of CO₂ also results in increased chemical effects, as shown in Figs. 17(a) and 17(b). The physical and chemical effects of CO₂ dilution on flame temperatures are also shown in Fig. 17 at \( \phi = 1 \). Dilution with CO₂ reduces the final flame temperature, and at elevated pressure, the flame temperature is comparatively higher than 1 bar. With an increase in the dilution ratio of CO₂, the slope of the corresponding flame temperature reduces, indicating an enhancement in flame thickness. At elevated pressure, the peak of active radicals reduces, and H radicals undergo significant reduction compared to OH radicals at elevated pressure. From Fig. 17 (b) and 17(d), it can be noted the depletion of H and OH radicals occurs faster than at 1 bar. This finding is validated with the ratio of production analysis discussed in Fig. 16, where the consumption of active radicals (H and OH) is significantly pronounced at 1 bar. Further, at elevated pressure, third body reaction \( R9(H+O_2 (+M) = HO_2 (+M)) \), becomes dominant, leading to high consumption of H radicals.
4.7. Reaction rate analysis

The influences of the radical species on the $S_L^o$ are obtained via the elementary reactions. As per the sensitivity analysis of the $S_L^o$, the effect of CO$_2$ addition and pressure includes six main reactions (three with positive sensitivity coefficients and three with negative sensitivity coefficients). For these reactions, Fig. 18 shows the net reaction rates at 1 and 5 bar initial pressure with a 30% addition of FCO$_2$ and CO$_2$. As seen in Fig. 18, in general, regardless of the dilution ratio or pressure, the peak of the net reaction rates for the reactions with the positive sensitivity coefficients is higher than those reactions with the negative sensitivity coefficients. This sustains the flame even at a higher CO$_2$ dilution ratio. The addition of CO$_2$ leads to a remarkable decrease
in the net elementary reactions, where the peaks of the all net reaction rates are attenuated and shifted downstream. It is evident that the decrease in the peak net reaction rates is observed for reactions R1 and R27. Increasing the initial pressure to 5 bar leads to an increase in the peaks' values of the net reaction rates for all reactions. However, the reduction in peak value at elevated pressure was markedly high compared to 1 bar at reaction rate for all the cases except R127, where the net reaction rate at 1 bar experienced quite a high reduction. At 1 bar, the addition of CO$_2$ resulted in a slowing R1 net reaction rate, as shown in Fig. 18 (a). For example, in Fig. 18(a), the net reaction rate of R1 at elevated pressure is much higher as compared to 1 bar. At elevated pressure, the reaction rates of R1 and R27 are much higher compared with those for neat and diluted mixtures. This significant increase in reaction rates at elevated pressure is attributed to the higher adiabatic flame temperature at 5 bar ($\phi = 1$) compared with at 1 bar ($\phi = 1$). Dilution with CO$_2$ as compared to FCO$_2$ resulted in reducing the CO conversion to CO$_2$ by reaction R27. Figs. 18 (a) and 18 (b) show that the chemical effects are significantly greater at elevated pressure as compared with net reaction rates at 1 bar. The primary branching reaction R1 exhibits a reaction rate peak difference of 7.65E-03 mol/cm$^3$-sec between CO$_2$ and FCO$_2$ at 5 bar, whereas it is 8.69E-04 mol/cm$^3$-sec at 1 bar. The difference in peaks captures the chemical effects. For terminating reactions R8, R9, R35, and R127, shown in Fig 18 (e, f, g, and h), the net reaction rates at ambient pressure are remarkably slow compared with the reaction rates at 5 bar. Moreover, the chemical impacts of the CO$_2$ addition on the elementary reactions R8, R9, R27, and R135 improves at elevated pressure. At both 1 and 5 bar initial pressures, the physical effect is dominant compared to the chemical effect, shown in Figs. 18 (a-h).
Figure 18. The net reaction rates of the main elementary reactions for $\phi = 1$ methane/air mixture diluted with CO$_2$ and FCO$_2$ at $P_o = 1$ and 5 bar, 300 K.
Figures 19 (a) and (b) show maximum reaction rates of R1 and R27 with the addition of CO$_2$ and FCO$_2$. Figures. 19 (a) and (b) show that the increase in dilution with CO$_2$ results in more substantial suppression of the maximum reaction rates, and this suppression increases with pressure. The influence of physical and chemical effects with increased CO$_2$ dilution is more significant at elevated pressure than at 1 bar for both R1 and R27.

![Graph](image)

**Figure. 19.** The effect of the addition of CO$_2$ and FCO$_2$ on the maximum reaction rates of (a) R1 and (b) R27 with varying CO$_2$ dilution ratios at 1 and 5 bar, 300 K for $\phi = 1$.

**Conclusion**

In the current work, the laminar flame characteristics of CH$_4$/air mixtures diluted with CO$_2$ (from 0 to 70% by volume) at initial pressure and temperature of 1-5 bar and 300K, and equivalence ratio varied over (0.6 -1.3) were experimentally investigated using an outwardly propagating spherical flame. A detailed Aramco 1.3 oxidation mechanism was used to simulate one dimensional planar CH$_4$/air/CO$_2$ flames. In the simulated flames, the chemical and physical effects of CO$_2$ dilution on the laminar flame speed were segregated by using the fictitious CO$_2$ species, FCO$_2$.

The conclusions of this study are as follows:

- The $S'_L$ decreases as the CO$_2$ dilution ratio increases. The experimental results are in reasonable agreement with Aramco 1.3 reaction mechanism simulation results. At 70% CO$_2$ dilution ratio, spherical flame experienced strong buoyancy effect, and the propagating flame was no longer spherical.
The thermal expansion ratio at elevated pressure increases slightly as the CO₂ dilution ratio increases, particularly near the stoichiometric region. Increased CO₂ dilution resulted in a reduction of hydrodynamic instability; however, at elevated pressure, hydrodynamic instability increased for the neat CH₄, 10 and 30% of CO₂ dilution ratio, due to the combined effect of an increase in the thermal expansion ratio and a decrease in the laminar flame thickness. At elevated pressure with high CO₂ dilution ratios (50 and 70% CO₂), the flame experiences a reduction in hydrodynamic instability due to increased flame thickness compared to ambient pressure. The increase in flame thickness with increased CO₂ dilution is also evident in H and OH radical molar fraction analysis. When CO₂ dilution increases, the spread of H and OH radical concentrations widen.

The pressure dependence exponent \( \beta \) shows that an increase in the CO₂ dilution ratio increases the sensitivity to pressure. Dilution with 50% CO₂ exhibits the highest sensitivity to pressure (\( \beta = -0.505 \)). The normalized contribution factor (\( \xi_{\text{CO}_2} \)) shows that at lower CO₂ addition ratio, there is less influence of the pressure on the flame speed reduction due to the chemical effect.

Among the intermediate radicals, reactions involving the consumption of CH₃ radicals (R127, R135, R144, and R206) experience primary sensitivity to pressure as compared to the dilution effect. At elevated pressure, reduction in the chemical effect experienced by HO₂ radicals is much less compared with that of CH₃.

Increased CO₂ dilution ratios suppress the primary branching reaction's peak reaction rates, and this suppression is much stronger at elevated pressure. The chemical effect is more prominent in elementary reactions exhibiting positive sensitive coefficients. R27: CO + OH \( \leftrightarrow \) CO₂ + H, exhibits no sensitivity to pressure for neat methane-air mixture; however, the addition of CO₂ imparts pressure sensitivity. Based on sensitivity analysis, the positive influence of R30 (HCO+M \( \leftrightarrow \) H+CO+M) and R3 (OH+H₂ \( \leftrightarrow \) H+H₂O) suppresses at elevated pressure; where R3 and R30 are the primary reactions with the maximum rate of production of H radicals. This results in increasing the consumption rate of H radicals at elevated pressure, evident in H radicals mole fraction analysis. Elementary branching reactions with positive sensitivity coefficient exhibits sensitivity to both pressure and CO₂ dilution while terminating reactions with negative sensitivity coefficients were keen towards pressure effect.

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