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The chemical effect of CO₂ on the methane laminar flame speed in O₂/CO₂ atmosphere

Wang Feng, Liu Shibo, He Yizhuo, Jia Huiqiao

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, 430074, China

Abstract. This paper studied in detail the chemical effects of CO₂ on methane laminar flame speed in O₂/CO₂ atmosphere both experimentally and numerically. Experimentally, flames were established in the counterflow configuration at atmosphere pressure with inlet temperature (Tu) of 293K and the methane laminar flame speed (S_u^0) in O₂/CO₂ atmosphere was measured with the help of PIV technique. Numerically, A comprehensive comparison between the flame speeds in O₂/CO₂ atmosphere and O₂/N₂ atmosphere with an identical mole fraction of O₂ is established by introducing the artificial materials U, V, W, X, Y, Z to gradually isolate the effects of chemical properties and specific heat, mass diffusivity, radiation, thermal conductivity and density. A detailed sensitivity analysis is conducted for C₁-C₃ so that a overall effect of the elementary reactions is given. Then combined with the path analysis especially for the target elementary reactions, the ways of how they influence the methane flame speed can be obtained. The results showed that the reasons of the decline in speed in O₂/CO₂ atmosphere were mainly chemical properties and specific heat of CO₂. The chemical effects of CO₂ on the methane laminar flame speed led to a tremendous reduction in the reaction rate of CO+OH \rightleftharpoons CO₂+H in O₂/CO₂ atmospheres as compared to those in O₂/N₂ atmospheres. Among the 3 reactions including CO+OH \rightleftharpoons CO₂+H that are both significant in methane flame speed sensitivity and path analysis, high concentration in CO₂ reduced the pathways of the positive ones and increased those of the negative ones.

1. Introduction

Public awareness of the increase in greenhouse gas emissions is increasing. Approximately one-third of all CO₂ emissions resulting from human activity come from fossil fuels used to generate electricity. Currently, a promising technology for carbon capture and storage is oxy-fuel combustion ^[1].

Oxy-combustion is a technology where air is replaced with highly-purified oxygen and thus a high concentration of CO₂ gathers in the gas downstream. In this way, it facilitates separation of CO₂ for utilization and in turn creates CO₂-rich combustion conditions. Finally, the carbon emission reduction can be achieved ^[2]. In recent years, the oxy-combustion is in heated-debate in the coal combustion area^[3]. Among the many factors in the development of this technology, CO₂ is being focused for its significant effect on combustion characteristics.

Laminar flame speed is one of the key characteristics that determines the propagation of one-dimensional, planar, and adiabatic premixed flames, and thus it is used to evaluate detailed kinetic models. Furthermore, it is also the basic unit for describing the turbulent flame, and predicting flame extinction ^[4].

There is an extensive body of experimental and theoretical studies^[5-8] on the laminar flame speeds of alkanes. The key to measuring the laminar flame speed accurately is to model a perfectly flat adiabatic flame as closely as possible. It can be learned that the laminar flame speed of alkanes



declined dramatically under oxy-fuel condition compared to that using a conventional combustion mode but the effects of high concentrations of CO₂ were not fully illustrated.

The main purpose of the present study is to perform a mechanism analysis to show how the chemical characteristics of CO₂ affect the laminar flame speed of methane.

2. System configuration

A schematic description of the premixed flame is displayed in Figure 1. The experimental setup was laboratory-scale counterflow burners designed to measure flame velocity. Experiments were conducted at atmospheric pressure with methane at the inlet temperatures ($T_u = 293$ K), under oxy-fuel combustion mode. This system provided a one-dimensional or quasi-one-dimensional flame structure, resulting in more efficient modeling with the help of well-defined initial conditions and governing equations than could be obtained with a two-dimensional flame. The apparatus comprised two nozzles 14 mm in diameter. The burner was arranged vertically and the distance between the two nozzles was also 14 mm. The fuel and oxidizer streams were supplied from the bottom nozzle, whereas the inert gas (N₂) was supplied from the upper nozzle. The co-flow gas was N₂. The flat flame was stabilized by balancing the upper main N₂ flow rate and the co-flow rate.

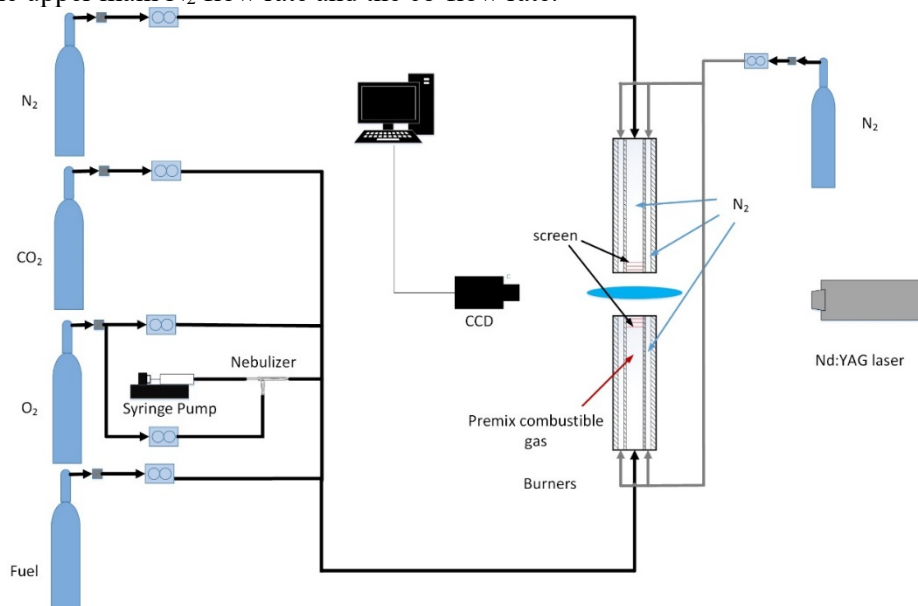


Fig. 1. Schematic of the experimental configuration.

The flow rates were controlled by the digital mass flow controllers (EL-FLOW®, Bronkhorst). All the fuel gases (CH₄, C₂H₆, and C₃H₈) used in the experiments were of high purity (99.99%). All tubing was made of stainless steel. A syringe system was placed in the middle of the tubing system. Silicone oil was used as the trace particle, which was automatically controlled by the syringe system to have an average flow rate 0.15 μ L/min. A bypass channel was designed to change the total flow rate before entering the main tube.

For the PIV measurement, a Vlite-200 (Beamtech) dual-pulse Q-switched nanosecond laser was used to produce a maximum 200 mJ/pulse light beam at 532 nm with a 6–8 ns pulse width and 7 mm beam diameter. An intense PIV system (TSI) was used to capture the image. The system contained a 12-bit charge-coupled device (CCD) with a 2352 \times 1768 pixel resolution at 16 fps. The system was also equipped with an AF 200 mm f/4D IF-ED Nikkor lens and a synchronizer that associated the CCD with the laser and could be controlled by computer. Insight 4G software was used to record image data and process flow calculations based on the cross-correlation technique. During the measurements, a 32 \times 32 pixel interrogate field was set to ensure the accuracy. The time between two exposures varied from 50 to 100 μ s according to the burner exit velocities.

3. A modified mechanism

In this study, the simulations were conducted with both CHEMKIN-III and CHEMKIN Pro^[9]. Thermal diffusion was accounted for, and the mixture-averaged case was determined in the transport equation. The radiation model was considered based on the optical thin approximation. S_u^0 was calculated using the PREMIX code^[10].

The mechanism used in this study was hierarchically structured based on the comprehensive oxidation mechanism previously developed for hydrogen, C₁-C₂ hydrocarbons, and nitrogen-containing species (HCN, NH₃), as well as for the interactions of these components. The mechanism consisted of 170 species and 1208 reactions^[11-12].

A proper chemical kinetic mechanism is of paramount value to understand and evaluate oxy-fuel combustion. Mazas et al., Xie et al., and Oh and Noh adopted the GRI 3.0 mechanism to model the laminar burning velocity. Konnov and Dyakov updated their mechanism to simulate the ethane oxy-fuel flame speed. In this study, we investigated the detailed chemical kinetic mechanism for the oxy-fuel combustion mode, in which four detailed kinetic mechanisms were used to determine the experimental laminar flame speed: the updated, USC-Mech II, and GRI 3.0 mechanisms and Konnov's mechanism. The updated present mechanism resulted in better predictions than the USC-Mech II and GRI 3.0 mechanisms and Konnov's mechanism^[13]. The updated mechanism was therefore adopted for the further modeling in this study.

4. Experimental results

Figure 2 depicts the experimental and computed S_u^0 values for methane-O₂/CO₂ at 293 K using the updated mechanism. The simulation results are in good agreement with the experimental data from equivalence ratio 0.7 to equivalence ratio 1.0. It overestimated the experimental results at equivalence ratios higher than 1.0.

The laminar flame speed in methane-O₂/CO₂ gradually increased from 18.13 cm/s ($\Phi = 0.7$) to the peak laminar flame speed of 25.86 cm/s ($\Phi = 1.0$). It then gradually decreased to 18.11 cm/s ($\Phi = 1.3$).

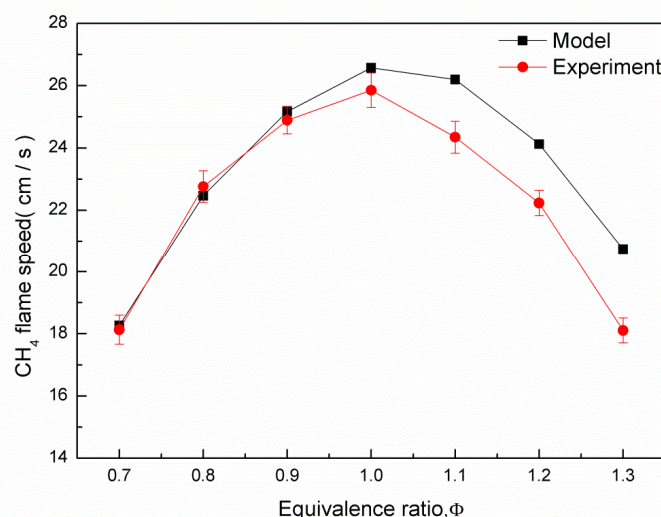


Fig.2. Experimentally and numerically determined S_u^0 of methane-O₂/CO₂ (35:65) flame at 285 K.

5. Isolation of chemical effects

Now that the overall effect is known, an isolation method is in need to divide the chemical effect apart so as to perform further investigations on the chemical effect.

Here a comprehensive comparison between the flame speeds in O₂/CO₂ atmosphere and O₂/N₂ atmosphere with an identical mole fraction of O₂ is established by introducing the artificial materials X, Y, Z, U, V, W to gradually isolate the effects of chemical properties and specific heat, mass diffusivity, radiation, thermal conductivity and density. This comparison modifies every characteristic to turn the O₂/CO₂ atmosphere finally into N₂/CO₂ atmosphere. So the chemical characteristics of the six artificial materials are as same as N₂, while their physical characteristics are as displayed in Table 1

In this way, the difference between X and CO₂ compared to that between CO₂ and N₂ represents the share of chemical effect, as shown in Figure 3.

Table 1. The physical characteristics of the six artificial materials at 1000K, 0.1Mpa

Material	N ₂	CO ₂	X	Y	Z	U	V	W
C _p (J/mol K)	32.7	54.32	CO ₂	N ₂	N ₂	N ₂	N ₂	N ₂
Mass diffusivity(m ² /s)	4.37e-4	2.97e-4	CO ₂	CO ₂	N ₂	N ₂	N ₂	N ₂
Absorption(l/m)	0	0.43	CO ₂	CO ₂	CO ₂	N ₂	N ₂	N ₂
Heat conductivity(W/(m K))	0.066	0.071	CO ₂	CO ₂	CO ₂	CO ₂	N ₂	N ₂
Density(kg/m ³)	0.336	0.529	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	N ₂

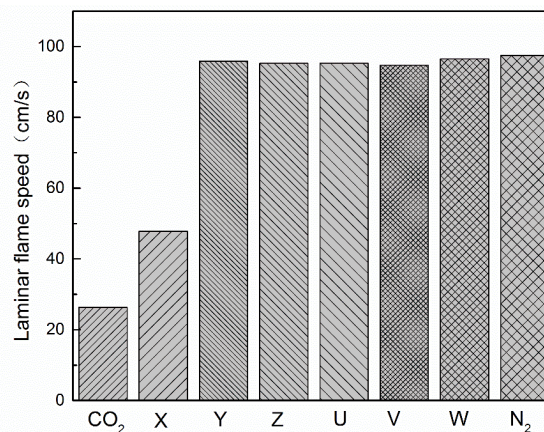


Fig. 3. The computational laminar flame speed in O₂/CO₂, O₂/U, O₂/V, O₂/W, O₂/X, O₂/Y, O₂/Z and O₂/N₂ of 35% O₂ flame at 293K

6. Chemical effect of CO₂ on methane laminar flame speed

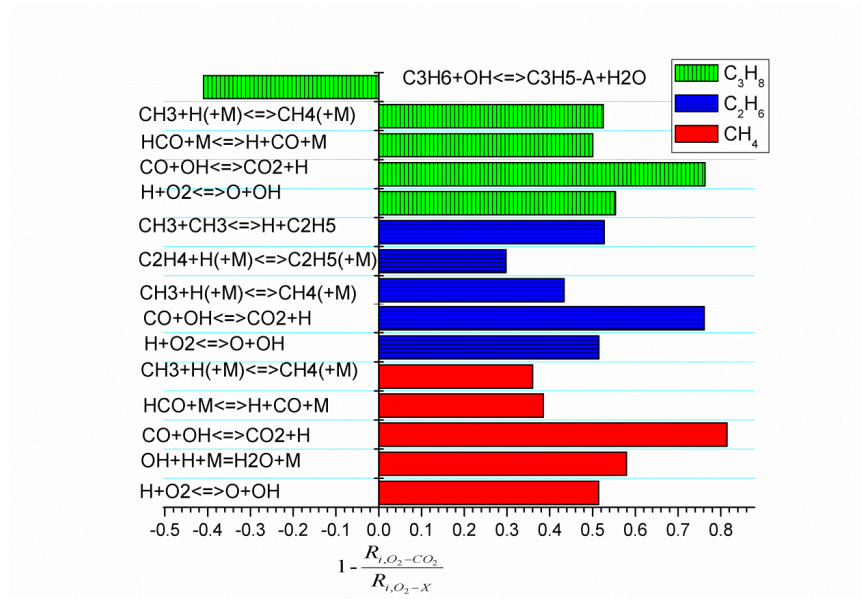
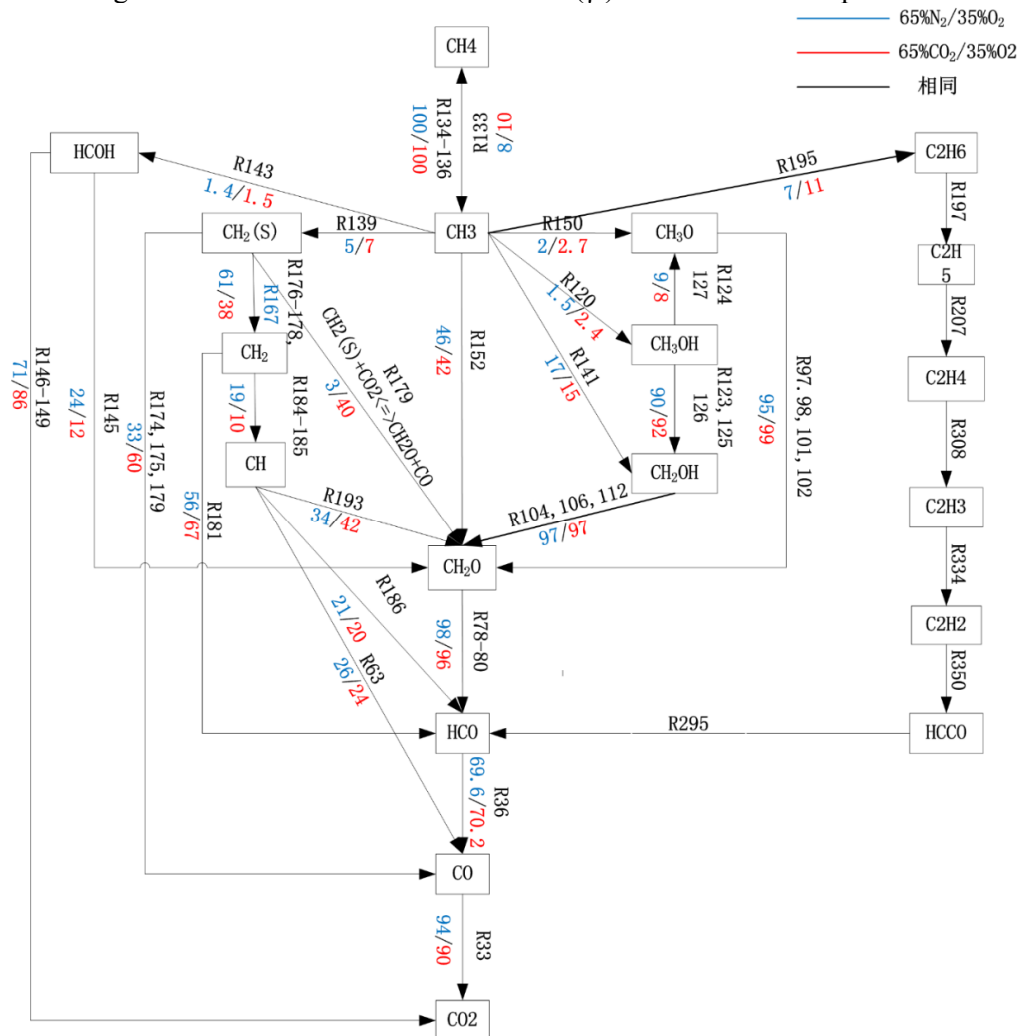
From the above, it can be seen that the chemical effect contributes most except for the C_p. Obviously a further investigation is essential to figure out the cause.

The chemical effect index of CO₂ (γ_i) can be defined as

$$\gamma_i = 1 - \frac{R_{i,O_2-CO_2}}{R_{i,O_2-X}} \quad (1)$$

Where R_{i,O_2-CO_2} is the i reaction rate in O₂-CO₂ conditions and R_{i,O_2-X} is the i reaction rate in O₂-X conditions. The chemical effect indexes of reactions significantly contributing to flame speed chosen by sensitivity analysis are shown in Figure 4.

In methane-O₂/CO₂ conditions, the first two positive sensitive reactions are H+O₂⇌O+OH and HCO+M⇌H+CO+M. As shown in Figure 4, their reaction rates decreased by 51% and 38%, respectively. In addition, the reaction rates of the first two negative sensitive reactions, CH₃+H(+M)⇌CH₄(+M) and OH+H+M=H₂O+M, decreased by 58% and 36%, respectively, because of the chemical effect of CO₂. So these four reactions on top seem to exemplify nothing. But at least we have marked 3 target reactions from the 5 above (only reactions including element C have been considered in path analysis) to study in the path analysis as shown in Figure 5.

Fig. 4. The chemical effect index of CO₂ (γ_i) on laminar flame speedFig.5. The path analysis of methane-O₂/CO₂ (35:65) flame at 285 K

The two numbers beneath each series number of the reaction represents the share by percentage, the left one for O₂/CO₂ atmosphere while the right one for O₂/N₂ atmosphere. From this perspective, it can be seen that the path of HCO+M \rightleftharpoons H+CO+M stays the same, while R33 (CO+OH \rightleftharpoons CO₂+H) whose sensitivity is positive declines from 94% to 90%, R133 (CH₃+H(+M) \rightleftharpoons CH₄(+M)) whose sensitivity is negative rises from 8% to 10%, both agreeable with the decline of flame speed. What's more, it means that the oxy-atmosphere may enhance the path of some negative reactions and weaken those positive ones.

The top-10 ranking reactions in both atmospheres are listed in Figure 6. If they mostly comply with the trend above, then the chemical effect can be explained.

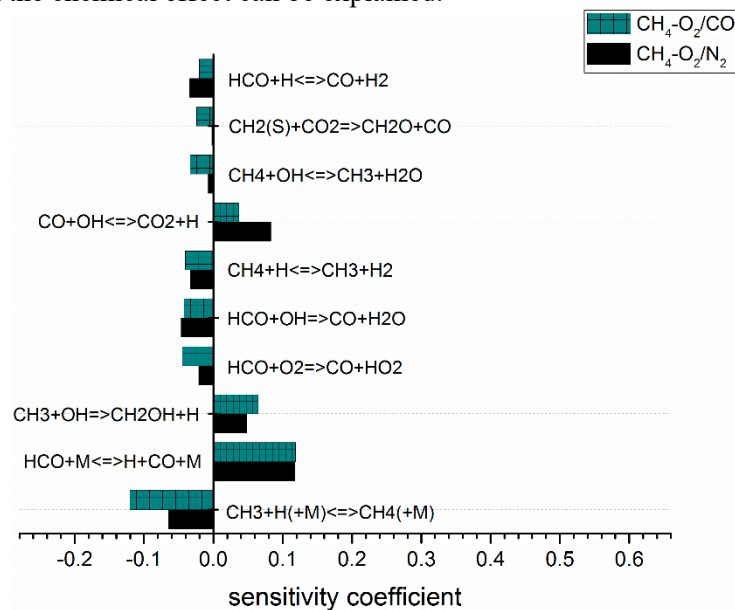


Fig. 6. The top-10 ranking reactions in sensitivity analysis in methane-O₂/CO₂ (35:65) flame at 285 K

Among all the other reactions that change in path, R141 (CH₃+OH \rightleftharpoons CH₂OH+H, positive from 17% to 16%), R179 (CH₂(S)+CO₂ \rightleftharpoons CH₂O+CO, negative from 3% to 40%), R135 (CH₄+H \rightleftharpoons CH₃+H₂, negative from 26% to 37%) R37 (HCO+O₂ \rightleftharpoons CO+HO₂, negative from 12.5% to 14%) fit well and are consequently agreeable with the decline of flame speed. Meanwhile, R38 (HCO+H \rightleftharpoons CO+H₂, negative from 8% to 2.5%) and R41 (HCO+OH \rightleftharpoons CO+H₂O, 9%-6%) break the rule. However, these 2 paths are really inferior compared to R36 and R37 in the path of HCO \rightarrow CO.

It's noteworthy that the path of R179 (CH₂(S)+CO₂ \rightleftharpoons CH₂O+CO) whose sensitivity and path share are negligible under O₂/N₂ atmosphere rises from 3% to 40%, convincingly exemplify how the chemical effect of CO₂ influences the laminar flame speed.

7. Comparison of each CO₂ effect

As previously depicted in Figure 3, the effect factor of C_p on laminar flame speed can be defined as

$$\theta_{C_p} = \frac{V_Y - V_X}{V_{N_2} - V_{CO_2}} \quad (2)$$

Similarly, we can have the effect factor of other characteristics, as displayed in Table 2.

Table 2. Comparison of each CO₂ effect on laminar flame speed

CH ₄ Φ = 1	Chemical (%)	C _p	Mass diffusivity	Radiation	Heat conductivity
θ_i (%)	30.9	69.5	-0.8	0	0.4

We can see that the mass diffusivity, thermal conductivity contribute a small share whereas the radiation takes little effect besides the chemical effect and C_p .

8. Conclusion

The laminar flame speeds of various alkanes (methane, ethane, propane) in O_2/CO_2 atmospheres were measured in the counterflow configuration at atmospheric pressure with inlet temperatures (T_u) of 293 K for methane and 285 K for ethane and propane. A modified mechanism consisting of 170 species and 1208 reactions was used to calculate the laminar flame speed. The agreement between experimental results and numerical work was satisfactory.

The major effect of CO_2 on laminar flame speed is C_p but not a dominant factor. The chemical effect is comparable to that of C_p . Besides, the mass diffusivity and thermal conductivity contribute a small share whereas the radiation takes little effect.

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