Experimental and Numerical Study of the Effect of CO₂ Replacing Part of N₂ present in Air on CH₄ Premixed Flame Characteristics Using a Reduced Mechanism

Ying Chen, Jingfu Wang, Xiaolei Zhang, and Conghao Li

ABSTRACT: The effect of CO₂, which replaces part of N₂ present in air, on flame stability, laminar burning velocities (LBVs), and intermediate radicals (O OH) of CH₄/O₂/N₂/CO₂ premixed flames has been analyzed using detailed experiments and numerical studies. The numerical simulations were conducted using the PREMIX code with a detailed chemical reaction mechanism (GRI-Mech 3.0) and a reduced mechanism (39 species and 205 reactions) based on GRI-Mech 3.0 over a wide range of equivalence ratios (Φ = 0.7−1.3) and CO₂ substitution ratios (0−30%). The reduced mechanism showed a good agreement with the other detailed mechanisms and experimental data. The experimental and numerical results showed that the substitution of CO₂ diminishes the stability of the flame, and the flame blow-out speed is significantly reduced (the substitution ratio is 0−30%, and the corresponding flame blow-out velocity is 5.2−2.5 m/s). In addition, CO₂ inhibits the LBV of the flame owing to the decrease of O and OH mole fractions. It not only accelerates the consumption of these two free radicals but also inhibits the generation of these two free radicals. Further analysis concluded that the substituted CO₂ has the greatest influence on the LBV sensitivity coefficient of the HO₂ + CH₃ = OH + CH₄O reaction.

1. INTRODUCTION

Efficient use of nonrenewable energy and reduction of greenhouse gas and NOₓ emissions have always been a hot topic for research studies.¹ Exhaust gas recirculation (EGR) technology came into being under the dual requirements of this international situation, which is currently being skillfully applied to different engine combustion equipment.²−⁷ EGR technology can simultaneously achieve carbon capture⁸ and pollutant reduction.⁹,¹⁰ In the EGR technology, pure oxygen replaces the traditional air and mixes with the circulating flue gas as the combustion oxidant.¹¹ The combustion atmosphere changes from O₂/N₂ to O₂/CO₂ or O₂/N₂/CO₂ and the corresponding flame combustion characteristics also undergoes conspicuous changes,⁹,¹²−¹⁸ such as laminar burning velocities (LBVs) and flame stability.

Studying the flame propagation mechanism and LBVs in different atmospheres, one can achieve efficient and stable combustion conditions in engineering.¹⁹ Plenty of researchers have carried out countless studies on the flame burning velocity, either experimental or numerical simulation; Chu et al.²⁰ gave a review of the study on the LBV and pollutant emissions. There are many literature studies¹⁵,¹⁷,²¹−²³ on the effect of temperature on adiabatic LBVs. Hassan et al.²¹ used numerical calculations with the GRI-Mech 3.0 mechanism and experimental methods to explore the effect of positive flame stretch rates on the combustion speed of CH₄/air flames. Xie et al.²⁷ Lu et al.²⁵ Hassan et al.²¹ Chen et al.¹⁶ and De Persis et al.²⁷ explored the influence of pressure on the LBV. With the prosperity of EGR technology, the influence of CO₂ as a diluent on multiflame characteristics has attracted the interest of more and more researchers. Hu et al.¹⁴ investigated the flame speed of the CH₄/O₂/CO₂ mixture using a Bunsen burner by varying the O₂ concentration from 25 to 35%. Khan et al.²⁸ carried out an experimental study and numerical simulation with GRI-Mech 3.0 and revealed the influence of N₂ and CO₂ when added as diluents to O₂/CH₄-mixed fuel on LBVs. The range of diluted N₂ and CO₂ percentages were 50−70% and 30−50%, respectively. Results showed that whether it is N₂ or CO₂ diluting the fuel, both will cause the LBV to decrease, but the negative effect of CO₂ is more serious at the same dilution ratio. Wang et al.²¹ studied the LBV of CH₄/O₂/ N₂ and CH₄/O₂/CO₂ flames with varying O₂ mole fractions and equivalence ratios. The emphasis of the experimental and
numerical work was on the elevated pressures. Coh et al.29 conducted an experimental study on \( \text{CH}_4/\text{air}/\text{CO}_2 \) flames using laminar and turbulent Bunsen flames. Ren et al.30 and Xiang et al.31 conducted numerical studies on the \( \text{CO}_2 \) dilution of \( \text{CH}_4/\text{air-mixed fuel}. \) The former focuses on the analysis of \( \text{H}_2 \) intermediates and NO emissions. The main attention of the latter is on the influence of the chemical effect of \( \text{CO}_2 \) on combustion characteristics. While Chu et al.32 investigated the effect of \( \text{N}_2 \) as a diluent on the rich-\( \text{CH}_4/\text{air mixture fuel} \) with the Aramco mechanism, Galmiche et al.33 carried out experiments and numerical studies and characterized the dilution effect of several different diluents (\( \text{N}_2, \text{CO}_2, \text{and H}_2\text{O} \)) by mixing with \( \text{CH}_4/\text{air}. \) The results show that the LBV is negatively correlated with the dilution ratio of the three diluents. Furthermore, this comparison shows that \( \text{CO}_2 \) has the greatest negative impact among the three at the same dilution ratio. There are also plenty of research studies on flame characteristics and NO emissions of adding \( \text{CO}_2 \) as a diluent to \( \text{CH}_4 \) and other mixed fuels, such as \( \text{H}_2,30,33 \text{CO},39 \text{and n-heptane}.40 

From the reference review, the research on adding \( \text{CO}_2 \) as a diluent to \( \text{CH}_4 \) fuel is mainly divided into three mainstream directions, including experimental research and numerical simulation: first, the influence of different parameters (such as pressure, temperature, equivalence ratio, and dilution ratio) on flame combustion characteristics (LBV, AFT, ignition time, NOx emission, etc.) under the condition of \( \text{CO}_2 \) dilution; second, to explore the combustion of \( \text{CH}_4 \) in an \( \text{O}_2/\text{CO}_2 \) (noting that \( \text{CO}_2 \) totally replaced the \( \text{N}_2 \) of the air) atmosphere with oxygen combustion technology as the background; and lastly, direct addition of \( \text{CO}_2 \) to the air. The relative ratio of \( \text{O}_2 \) to \( \text{N}_2 \) in the oxidant is maintained in air, and the corresponding combustion atmosphere is (21% \( \text{O}_2 \) + 79% \( \text{N}_2 \))/\( \text{CO}_2 \). Regarding numerical simulation research, most of the combustion mechanisms directly adopt the earliest and most widely used GRI-Mech 3.0. Throughout the published papers, there is a novel idea that simplify the GRI-Mech 3.0, which is the most widely used and most mature mechanism in the study of hydrocarbon fuel combustion to explore the flame characteristics of the \( \text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2 \) mixture fuel and to reveal the effect of \( \text{CO}_2 \) on the LBV from the perspective of chemical kinetics. At the same time, the author is curious to replace part of \( \text{N}_2 \) present in air with \( \text{CO}_2 \) (the relative ratio of \( \text{O}_2 \) and \( \text{N}_2 \) changes) while fixing the ratio of \( \text{O}_2 \) in the oxidant (keeping at 21%) and note what interesting changes will happen in the flame.

Inspired by the previous analysis, the main purpose of the present work is (1) to simplify GRI-Mech 3.0 using the directed relation graph with error propagation (DRGEP) and sensitivity analysis (SA) methods for \( \text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2 \) flame with specific targets and verify combustion characteristics such as LBVs and main species concentrations with experimental data and detailed mechanism results to determine the adaptability of the reduced mechanism; (2) to carry out experiments to explore the effect of \( \text{CO}_2 \) replacing part of \( \text{N}_2 \) in the air on flame stability; and (3) to make a thorough inquiry of the effect of \( \text{CO}_2 \) on the rate of production (ROP) of \( \text{O} \) and \( \text{OH} \) radicals and the LBV sensitivity coefficient.

### 2. RESULTS AND DISCUSSION

#### 2.1. Validation of the Reduced Mechanism

The reduced mechanism (39 species and 205 reactions) was evaluated over a wide range of conditions by comparing different species concentrations and LBVs with numerical calculation data obtained by other detailed mechanism, respectively. A wide range of conditions are listed in Table 1.

| fuel oxidizer | \( Z_{\text{CO}_2}-Z_{\text{O}_2}-Z_{\text{N}_2} \) | \( \Phi \) | initial temperature (K) |
|--------------|---------------------------------|--------|--------------------------|
| \( \text{CH}_4 \)/\( \text{N}_2/\text{O}_2 \) | 0.0, 0.7, 0.9, 0.21 | 0.7, 1.0, 1.3 | 300, 400, 500, 600 |
| \( \text{CO}_2/\text{N}_2/\text{O}_2 \) | 0.1, 0.6, 0.9, 0.21 | 0.2, 0.5, 0.9, 0.21 | 0.3, 0.4, 0.9, 0.21 |

Figure 1 shows the predicted LBVs using GRI-Mech 3.0, GRI 2.11, Li, and reduced mechanisms with respect to the equivalence ratio over a range of initial temperatures (300–600 K) and \( \text{CO}_2 \) substitution ratios \( Z_{\text{CO}_2} \) (0–30%). It can be obviously observed that the lines have the exactly same shape. Nevertheless, the reduced mechanism slightly understimates the LBV compared with GRI-Mech 3.0, Li mechanism, and experimental data but overestimates the LBV compared with the GRI 2.11 mechanism at \( Z_{\text{CO}_2} \leq 20 \% \) and initial temperature = 300 K. With the increase of initial temperature (\( T \geq 400 \text{ K} \)), the reduced mechanism predicts the LBV slightly better than the Li mechanism and GRI-Mech 3.0 but not the GRI 2.11 mechanism. On further analysis, the reduced mechanism result of LBVs is closest to that of the GRI 2.11 mechanism and farthest from the Li mechanism. The maximum absolute difference between the reduced mechanism and GRI-Mech 3.0 is 7.86 cm/s at \( \Phi = 1.3 \) and \( T = 600 \text{ K} \) and the corresponding relative difference is 7.7%. The maximum relative difference is 9.3% at \( \Phi = 1.3 \) and \( T = 300 \text{ K} \), and the corresponding absolute difference is 2.23 cm/s. Figure 1 also reveals that the increase in the \( \text{CO}_2 \) substitution ratio caused a significant decrease in LBVs, which will be discussed in the following sections.

#### 2.2. Effect of \( \text{CO}_2 \) Replacing Part of \( \text{N}_2 \)

##### 2.2.1. Effect of \( \text{CO}_2 \) on Flame Stability

In this section, the blow-out limits of \( \text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2 \) laminar premixed flames were experimentally measured with different \( \text{CO}_2 \) substitution ratios \( Z_{\text{CO}_2} \). The blow-out limit is used to describe the characteristics of flame extinguishing due to insufficient residence time caused by excessive stretching and is an important parameter to characterize flame stability. The trends of the blow-out limits with different equivalence ratios and increasing \( \text{CO}_2 \) substitution ratios \( Z_{\text{CO}_2} \) are depicted in Figure 2. It is noted that the blow-out limit is significantly reduced with the substitution of \( \text{CO}_2 \). The maximum value read by the gas flow meter for the blow-out limit of the premixed flame of \( \text{CH}_4/\text{O}_2/\text{N}_2 \) is 24.6 L/min, and the corresponding gas flow rate is 5.2 m/s. As the \( \text{CO}_2 \) ratio increases, the maximum gas flow value of the flame blow-out limit is reduced and reaches to 12 L/min at a 30% \( \text{CO}_2 \) substitution ratio, and the corresponding gas flow rate is 2.5 m/s. Moreover, it can be also observed from Figure 2 that the blow-out limits increase with increasing equivalence ratios at the same \( \text{CO}_2 \) substitution ratio. The physical properties (high specific heat and low diffusion coefficient), chemical properties (participating in chemical reactions and affecting the concentration of reactants through the reversible reaction of the combustion mechanism), and radiation properties (three-atom strong radiation gas) of \( \text{CO}_2 \) compared with \( \text{N}_2 \) all contribute to the LBV (as Figure 1),
thereby diminishing the stability of the flame. In addition, the substitution of CO₂ has a negative effect on ignition as well. When the CO₂ concentration is greater than 30%, the ignition hardly succeeds, which is why the maximum value of Z_CO₂ in this paper is 30%.

2.3. Effect of CO₂ on the LBV. The radicals of O, OH, and H possess the characteristics of high energy and strong activity and ensure the continuation of the chain reaction. Plenty of studies found that these three radicals play quite important roles on the LBV estimation. As previously shown in Figure 1, the LBV decreases after CO₂ replaces part of N₂, and hence the effect of CO₂ substitution on LBVs can be revealed from the perspective of chemical kinetics based on the analysis of O, OH, and H radicals.

Figure 3 shows the mole fraction of O, OH, and H radical profiles varying with the distance with different CO₂ substitution ratios (0−30%). The peak value of the OH radical in the CH₄/O₂/N₂/CO₂ mixture fuel with N₂:CO₂ = 0.49:0.3 was about one half of that in the CH₄/O₂/N₂ (without CO₂ substitution) mixture fuel. The peak value of O and H radicals in CH₄/O₂/N₂/CO₂ with N₂:CO₂ = 0.49:0.3 was about one-third of that in CH₄/O₂/N₂ (without CO₂ substitution). This phenomenon reveals that the generation of O, OH, and H radicals is more severely inhibited by the increase of CO₂ substituted, and LBVs decreased simultaneously.

The first-order normalized sensitivity coefficients pertaining to the LBV were calculated using the reduced mechanism as shown in Figure 4, which displays that the change in the
elementary reaction rate has the greatest influence (including positive and negative influence) on the LBV. The three-body chain-terminating reaction \( H + CH_3(+M) = CH_4(+M) \), which has a significant negative effect on the LBV, and the reverse of the three-body chain-branching reaction \( HCO + M = H + CO + M \), which has a positive effect on the LBV, were encouraged due to the increase of substituted CO2. The chain-propagating reaction \( OH + CO=H + CO_2 \) is the most important and final step in the conversion of CH4 to CO2, and the diluted CO2 directly affects the reverse reaction of \( OH + CO_2=H + CO_2 \), thereby slowing down the LBV.

In order to quantitatively explain the degree of influence of the substituted CO2 on the sensitivity coefficient of the elementary reaction, the change rate of the sensitivity coefficient (CASC) was introduced and defined as follows:

\[
\text{CASC}_i = \left| \frac{S_{Z_{CO2},i} - S_{0,i}}{S_{0,i}} \right|
\]

where \( i \) is the elementary reaction number, \( S_{Z_{CO2},i} \) is the sensitivity coefficient of the \( i \)-th elementary reaction when the substitution ratio is \( Z_{CO2} \), and \( S_{0,i} \) is the sensitivity coefficient of the \( i \)-th elementary reaction without CO2 substitution.

Figure 5 shows the degree of influence of the substituted CO2 on the elemental reaction sensitivity coefficient of laminar combustion velocities. The reaction \( H + O_2 = O + OH \) has the greatest LBV sensitivity coefficient, which can be observed from Figure 5. However, the substituted CO2 has the greatest positive (Figure 4) influence on the sensitivity coefficient of the reaction \( HO_2 + CH_3 = OH + CH_3O \) followed by the negative (Figure 4) influence on the sensitivity coefficient of the reactions \( OH + CH_4 = CH_3 + H_2O \) and \( H + HO_2 = O_2 + H_2 \).

2.4. Effect of CO2 on the ROP of OH and H. It can be concluded from the above findings that the molar fraction of \( O, OH, \) and \( H \) radicals decreases with the increase of CO2. There are two explanations for this decrease phenomenon. One is that the addition of CO2 encourages the consumption of unsteady intermediate free radicals, and the other is that the addition of CO2 inhibits the generation of unsteady intermediate free radicals. In order to more profoundly reveal the influence of the floating unsteady intermediate free radicals on the LBV, the production and consumption rate of OH and H under different elementary reactions with improving CO2 substitution are considered (Figure 6). The elementary reactions shown in Figure 6 can be divided into three main categories. \( O + H_2 = H + OH \) and \( H + O_2 = O + OH \) are the main chain-branching reactions, which mainly produce a large amount of highly active free radicals such as OH, H, and O, and this is the first step to ensure that the reactions can proceed as well. However, the elevated CO2 fraction slows down the reaction rate of \( O + H_2 = H + OH \) and \( H + O_2 = O + OH \). We knew that the main reaction path of CH4 oxidative dehydrogenation in an O2/N2 or O2/N2/CO2 atmosphere is \( \text{CH}_4 = \text{CH}_3 = \text{CH}_2O = \text{HCO} = \text{CO}_2 \). The reactions \( O + CH_4 = OH + CH_3, H + CH_4 = CH_3 + H_2O, \) \( OH + CH_4 = CH_3 + H_2O, \) and \( O + CH_3 = H + CH_2O \) are the most...
important chain-propagating reactions; however, CO2 reduces the reaction rate of these reactions, which in turn reduces the reaction rate of the entire oxidation combustion reaction. The reaction OH + CO = H + CO2 has the chain-terminating reaction characteristic and is also the most important exothermic reaction in hydrocarbon fuels. It mainly generates stable intermediate products and final products by consuming free radicals. The suppression of the reaction rate by the addition of CO2 greatly reduced the exothermic heat of the reaction.

3. CONCLUSIONS

In this paper, numerical and experimental investigations on the effect of flame stability, LBVs and the ROP of OH and H radicals on CH4/O2/N2/CO2 laminar premixed flames were conducted. The following conclusions can be drawn based on the systematic results of this study:

1) As CO2 replaces part of N2 present in air, the stability of the flame is diminished. The substitution mole fraction of CO2 increases from 0 to 30%, and the corresponding flame blow-out limit is reduced from 5.2 to 2.5 m/s.

2) The LBV of CH4/O2/N2/CO2 flame decreases with the increase of CO2 substitution ratios owing to the decrease of O and OH radical concentrations. The elementary reaction with the greatest LBV sensitivity coefficient is H + O2 = O + OH, which is an important chain excitation reaction in which the substituted CO2 has the greatest positive influence on the sensitivity coefficient of HO2 + CH3 = OH + CH3O.

3) As the CO2 substitution ratio increases, the ROPs of O and OH radicals are reduced. CO2 not only accelerates the consumption of these two free radicals but also inhibits the generation of these two free radicals.

4. EXPERIMENTAL AND NUMERICAL PARTS

4.1. Experimental Facility. The schematic diagram of the combustion experimental device system used in this work is shown in Figure 7. CH4 (>99.99%, purity), O2 (>99.99%, purity), CO2 (>99.99%, purity), and N2 (>99.99%, purity) needed for this experiment are provided using a 40 L standard seamless steel cylinder containing the corresponding gas in the laboratory. The gas premixing experimental platform is designed with a stainless-steel cylinder. The flame arrester is connected to the nozzle ejector tube, and a partition with holes is installed inside the premixing chamber to play the role of turbulence, so that various gases can be fully mixed in the
premixing chamber. The inner diameter of the Bunsen burner tube selected in this article is 10 mm. In order to ensure fully developed or pure laminar flow in the Bunsen burner without increasing excessive flow resistance, the minimum tube length that depends on the Reynolds number and the tube diameter is expressed in the following equation:

$$L_m = 0.05 R_e \cdot d \approx 150d$$  \hspace{1cm} (2)

The length of the Bunsen tube in this experiment is 2000 mm, and the other parameters of the Bunsen burner are shown in Table 2.

### Table 2. Bunsen Burner Parameters

| parameter      | symbol | value | unit |
|----------------|--------|-------|------|
| ambient temperature | $T$   | 300   | K    |
| ambient pressure | $P$   | 0.1   | MPa  |
| inner diameter  | $d$   | 10    | mm   |
| inner diameter  | $D$   | 12    | mm   |
| length of tube  | $L$   | 2000  | mm   |

The control system is divided into two parts: a gas flow control system and a gas pressure control system, which are mainly completed by a mass flow controller (Brooks, 5850E; 0.03–30 SLPM (m$^3$/h), ±1% FS, 1500 psi (10.432 MPa), and 0–30 L/min) and a pressure reducing valve, respectively.

### 4.2. LBV Measurement

#### 4.2.1. Choosing the Method for LBV Estimation.

There are two different measurement methods for calculating LBVs of the Bunsen burner flames captured using a charge-coupled device (CCD) camera: cone method and full area method. Under stable conditions, the amount of combustible gas flowing out from the lamp in unit time should be equal to the combustible gas burned in the entire inner cone of the flame surface, that is,

$$S \cdot A_f = v \cdot A_o$$  \hspace{1cm} (3)

where $S$ is the LBV of the premixed flame (m/s), $A_f$ is the flame inner cone surface area (m$^2$), $A_o$ is the cross-sectional area of the lamp exit (m$^2$), and $v$ is the average flow velocity at the exit of the lamp port (m/s). The height of the inner cone of the flame and the radius of the outlet tube of the lamp were set to $h$ and $r$, respectively. For the full area method, the LBV can be obtained using the following formulas:

$$A_o = \pi r^2$$  \hspace{1cm} (4)

$$A_f = \pi \sqrt{(r^2 + h^2)}$$  \hspace{1cm} (5)

$$S = \frac{r}{\sqrt{(r^2 + h^2)}} \cdot v$$  \hspace{1cm} (6)

$$S = \frac{Q}{\pi \sqrt{(r^2 + h^2)}}$$  \hspace{1cm} (7)

The flow rate of the mixed fuel $Q = v \pi r^2$ (m$^3$/s) can be read from the MFC.

For the cone method, the LVB can be calculated using the following formulas:

$$S = v \cdot \sin \theta$$  \hspace{1cm} (8)

$$S = v \cdot \sin \left( \arctan \frac{r}{h} \right)$$  \hspace{1cm} (9)

where $\theta$ is the internal angle of the flame.

Figure 8 shows the comparison of the LBVs measured by the full-area method and the cone method with the results simulated by the CHEMKIN premixed code with the GRI-Mech 3.0 kinetic combustion mechanism. It can be clearly seen from the figure that the experimental results measured by the full area method are in good agreement with the numerical calculation, while the LBVs measured by the cone method are significantly above the simulation results. Therefore, the full area method was chosen to calculate the LBV in this work.
4.2.2. Error Analysis. According to the full area method, the measurement error $\delta_l$ is mainly caused by the error of the total flow rate of the mixed gas $\delta_{Q}$ generated by the MFC and the error obtained from the measurement of the height of the flame $\delta_{H}$. The MFC accuracy of CH$_4$, O$_2$, CO$_2$, and N$_2$ is ±1% of the set point. The calculation of the error of the total flow rate of the mixed gas $\delta_{Q}$ is given in

$$\delta_{Q} = \sqrt{\delta_{CH_4}^2 + \delta_{O_2}^2 + \delta_{CO_2}^2 + \delta_{N_2}^2} = 2\% \quad (10)$$

The error of the flame height measurement $\delta_{H}$ calculated according to the reference was about 5.2%.

The overall measurement error $\delta_l$ of the LBV is obtained using the formula $\delta_l = \sqrt{\delta_{Q}^2 + \delta_{H}^2} = 5.57\%$.

4.2.3. Experimental Verification of LBVs. In order to more convincingly verify the accuracy of the full-area method for measuring LBVs, the experimental data were compared with the detailed mechanism and literature data as depicted in Figure 9. The experimental data agree well with the numerical results by GRI-Mech 3.0 at $\Phi = 0.5$–1.6, but it is slightly overestimated compared with other literature data except that of Mitu et al. under lean burn conditions and slightly underestimated under the stoichiometric and rich condition.

4.3. Numerical Simulation. The one-dimensional numerical calculations were conducted using the premixed laminar flame speed code ANSYS CHEMKIN-PRO with the detailed kinetic combustion mechanisms of GRI 2.11, Li, and GRI-Mech 3.0 to simulate the LBV of the CH$_4$/O$_2$/N$_2$/CO$_2$ mixture. Meanwhile, a reduced kinetic reaction mechanism (39 species and 205 reactions) was extracted and developed from GRI-Mech 3.0 (53 species and 325 reactions).

The premixed laminar flame speed calculation model was applied to calculate the adiabatic and unstretched LBVs using mixture-averaged formulation in determining the species ordinary diffusion coefficients and fluxes. For the reactor simulation, the calculated domain was 2.5 cm with an adaptive grid, which is enough to complete all reactions (actually, it is around 0.7 cm to complete all reactions away from the starting position). A user-specified estimated temperature profile was employed for LBV simulation and reduced mechanism validation. The conditions of the simulation were $P = 1$–17 atm, $\Phi = 0.7$–1.3, $T = 300$ K, and $Z_{CO_2} = 0$–30%.

The substitution ratio of CO$_2$ to N$_2$ is defined as $Z_{CO_2}$. Thus, the oxidant composition of the combustion atmosphere is 21% O$_2$ + Z$_{CO_2}$ CO$_2$ + (79% $Z_{CO_2}$) N$_2$.

The reduced mechanism in this work was developed from GRI-Mech 3.0, which is the most popular chemistry mechanism of CH$_4$ and has been validated by numerous research studies. The whole reduced work was accomplished by the DRGEP method to get a skeletal mechanism and the SA method to further reduce the CHEMKIN-PRO reaction workbench. The DRGEP method was extended from the normal DRG method with the same underlying principle in identifying direct species coupling using the immediate error $R_{im}$.

$$R_A(B) = \max_i(r_{ij}) \quad (11)$$

where S is the set of all possible paths leading from species A to species B, and $r_{ij}$ is the chain product of the weights (i.e., the immediate error $r_{ij}$) of the edges along the given path. If A is connected to B through a reaction and B is connected to C through a reaction, there is a path connecting from A to C via B and the R-value of this particular path is $R_{AB} \times R_{BC}$. Based on this definition, a species B must be kept in the mechanism if there is at least one path connecting from A to B whose R-value is larger than the user-specified threshold.

During the reduction, the concentration of CH$_4$, O$_2$, CO$_2$, H$_2$O, CO, and OH and the ignition time of the flame were the target parameters over a range of equivalence ratios, pressures, and CO$_2$ substitution ratios. The criterion for ignition delay is specified using a temperature delta of 400 K. The user-specified relative tolerance is 10% for the maximum of each target species parameter and 10% for the endpoint value of the ignition time.
Actually, in practical applications, the DRGEP method cannot generate the most simplified and effective kinetic mechanism. In some cases, the dramatical induced error will be caused by a group of removed species from the master mechanism during the DRGEP reduction. Within this group, only a few species are responsible for the noticeable amount of error on the targeted parameters, while the rest could have been safely removed. However, DRGEP removes such a group of species simultaneously and cannot distinguish between responsible components and innocent components. As a supplement to the DRGEP method, the sensitivity analysis method further simplifies the skeletal mechanism.

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**Notes**

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