Experimental and modeling study on effects of N$_2$ and CO$_2$ on ignition characteristics of methane/air mixture

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ABSTRACT

The ignition delay times of methane/air mixture diluted by N$_2$ and CO$_2$ were experimentally measured in a chemical shock tube. The experiments were performed over the temperature range of 1300–2100 K, pressure range of 0.1–1.0 MPa, equivalence ratio range of 0.5–2.0 and for the dilution coefficients of 0%, 20% and 50%. The results suggest that a linear relationship exists between the reciprocal of temperature and the logarithm of the ignition delay times. Meanwhile, with ignition temperature and pressure increasing, the measured ignition delay times of methane/air mixture are decreasing. Furthermore, an increase in the dilution coefficient of N$_2$ or CO$_2$ results in increasing ignition delays and the inhibition effect of CO$_2$ on methane/air mixture ignition is stronger than that of N$_2$. Simulated ignition delays of methane/air mixture using three kinetic models were compared to the experimental data. Results show that GRI_3.0 mechanism gives the best prediction on ignition delays of methane/air mixture and it was selected to identify the effects of N$_2$ and CO$_2$ on ignition delays and the key elementary reactions in the ignition chemistry of methane/air mixture. Comparisons of the calculated ignition delays with the experimental data of methane/air mixture diluted by N$_2$ and CO$_2$ show excellent agreement, and sensitivity coefficients of chain branching reactions which promote mixture ignition decrease with increasing dilution coefficient of N$_2$ or CO$_2$.

Introduction

Gas explosion always exists in the coal mining. Gas explosion will form a detonation wave and produce a large amount of catastrophic gases, which will damage the roadway and equipment and cause a large number of miners’ casualties [1–6]. The reaction kinetics of gas explosion has been experimental and numerical studied [7–11] and the effects of inert gas on the combustion characteristics of the methane/air mixture in
gas explosion have been reported recently [12–14]. Hu et al. [15] numerically studied the effects of diluents (N₂ and CO₂) on the laminar burning velocity of the premixed methane/air flames. Stone et al. [16] investigated the effects of CO₂ on the laminar-burning velocity of methane/air mixtures for variations in unburnt gas temperature (within the range of 293–454 K) and pressures (within the range of 0.5–10.4 bar). Konnov and Dyakov [17] experimentally measured the propagation speed of adiabatic flames of methane/oxygen/CO₂, and the effects of CO₂ on the propagation speed of methane/air mixtures were presented. The effects of N₂ on the combustion characteristics of methane/air mixture in gas explosion were reported by Liang et al. [18]. They found that the laminar flame propagation velocity, laminar combustion velocity, markstein length, flame stability and the maximum combustion pressure decreased distinctly with the dilution coefficient of N₂ increasing. Furthermore, when the dilution coefficient of N₂ in the gas mixture was over 20%, the flame would be unstable and was easy to extinguish. However, as the first stage in the process of gas explosion (which consists of four stages: ignition, laminar burning, explosive burning and deflagration), the effect of inert gas on the ignition characteristics of the methane/air mixture in gas explosion is little reported.

The shock tube is an ideal device for investigating the ignition delays of hydrocarbon fuels although there are many other experimental devices [19,20]. Lifshitz et al. [21] examined the ignition of methane/oxygen mixtures highly diluted with argon in a reflected shock tube. Their measurements covered a temperature range of 1500–2150 K at pressure varying from 2 to 10 atm for mixture equivalence ratios of 0.5–2.0. Huang et al. [22] conducted a series of shock tube experiments to measure the ignition delays of homogeneous methane/air mixtures at moderate temperatures (1000–1350 K) and elevated pressures (16–40 atm). The equivalence ratios of their test mixtures were varied from 0.7 to 1.3. Zhang et al. [23] experimentally studied the ignition delays of methane/hydrogen mixtures with the mole fraction of hydrogen in this mixture varying from 0% to 100% in a chemical shock tube.

This work presents the effects of N₂ and CO₂ on the ignition characteristics of methane/air mixture in a chemical shock tube over the temperature range of 1300–2100 K, pressure range of 0.1–1.0 MPa and equivalence ratio range of 0.5–2.0 through experiment and simulation. Meanwhile, sensitivity analysis is made to identify the effects of N₂ and CO₂ on the key elementary reactions in the ignition chemistry of methane/air mixture. Experimental and simulated results are used to explain the inhibition mechanism of inert gas on methane/air mixture ignition in gas explosion.

Experimental

Fig. 1 shows the experimental apparatus of the chemical shock tube. This chemical shock tube has been detailed described in the previous studies [24,25]. Zhang et al. [24] used this facility to measure the ignition delays of methane/air/argon mixtures, and comparisons show good agreement between their studies and the previous experimental studies [21,26]. The cross section of the main body of this chemical shock tube is 130 mm × 80 mm, and the wall thickness is 10 mm. Double PET diaphragms separate the shock tube into a 4 m long driver section and a 5.3 m long driven section. PET diaphragms are burst by pressurizing the driver with He (> 99.99% purity)/N₂ (> 99.99% purity) mixed gas to generate shock waves. The detailed descriptions of this experimental
device and the experimental principle have been presented by Zhang et al. [24]. The uncertainty of experimental temperature behind the reflected shock waves is about 30 K in this study, and the effect of the boundary layer on the typical pressure rise rate is 4%/ms ($\frac{dp}{dt}$).

The ignition delay time ($t_{\text{ign}}$) in this study is defined as the time interval between the arrival of the reflected shock wave and the onset of ignition at the side-wall observation location (20 mm from the end-wall). The arrival of the reflected shock wave is marked by the step rise in pressure, while the onset of ignition is defined using the extrapolation of the maximum slope in observed CH$^+$ chemiluminescence signal to the baseline. Example pressure and CH$^+$ chemiluminescence profiles are shown in Fig. 2a. At this condition ($p = 0.1$ MPa, $T = 1735$ K and $\phi = 1.0$), $t_{\text{ign}}$ of methane/air mixture is 178 $\mu$s.

Results and discussion

Ignition delays of methane/air mixtures diluted with N$_2$ and CO$_2$ (the dilution coefficient is 0%, 20% and 50%, respectively) are measured. Detailed compositions of test mixtures in this study are given in Table 1.

The formula of dilution coefficient ($\phi_r$) is

$$\phi_r = \frac{V_{\text{diluent}}}{V_{\text{fuel}} + V_{(O_2+3.762N_2)}} + V_{\text{diluent}}$$ (1)

Ignition delays of methane/air mixture

In this paper, ignition delay times of methane/air mixture are measured over the temperature range of 1300–2100 K, pressure range of 0.1–1.0 MPa and equivalence ratio range of 0.5–2.0. The maximum and minimum measured ignition delay times of this mixture at each condition are presented in Table 2.

Fig. 2b illustrates the measured ignition delays of methane/air mixture over pressure range of 0.1–1.0 MPa and for equivalence ratios of 0.5, 1.0 and 2.0.

From Fig. 2b we can see that a linear relationship exists between the reciprocal of temperature and the logarithm of the ignition delay times, according with the Arrhenius-type correlation, and an increase in ignition temperature results in a decrease in the measured ignition delay time. Fig. 2b also illustrates ignition delays of this mixture are decreasing with
increasing ignition pressure. This can be explained by using the Arrhenius-type correlation,

$$
\tau_{\text{ign}} = A \cdot p^{\alpha} \phi X_{O_2} \exp \left( \frac{E_a}{RT} \right)
$$

(2)

Generally, the pressure exponential $\alpha$ gives the negative value for the typical hydrocarbon fuel, which indicates that ignition delay decreases with the increase in pressure. For validation, correlation formulas for the ignition delays and pressure at $\phi = 0.5, 1.0$ and $2.0$ are obtained by linear regression analysis and the results are shown as follows:

$$
\begin{align*}
\phi = 0.5 : \quad \tau_{\text{ign}} &= 1.31 \times 10^{-3} \times p^{-0.68} \times e^{(167.945)/(RT)} \\
\phi = 1.0 : \quad \tau_{\text{ign}} &= 1.28 \times 10^{-3} \times p^{-0.65} \times e^{(169.690)/(RT)} \\
\phi = 2.0 : \quad \tau_{\text{ign}} &= 1.03 \times 10^{-3} \times p^{-0.7} \times e^{(171.020)/(RT)}
\end{align*}
$$

Table 1 Compositions of the test mixtures in this study.

| Mixtures | Dilution coefficient | XCH\(_4\) (%) | XO\(_2\) (%) | XN\(_2\) (%) | XCO\(_2\) (%) | $\phi$ |
|----------|----------------------|---------------|-------------|-------------|-------------|------|
| 1        | 0%                   | 4.99          | 19.95       | 75.06       | 0.0         | 0.5  |
| 2        | 9.50                 | 19.00         | 71.5        | 0.0         | 1.0         |
| 3        | 17.36                | 17.36         | 65.28       | 0.0         | 2.0         |
| 4        | 20% (N\(_2\))       | 3.99          | 15.96       | 80.05       | 0.0         | 0.5  |
| 5        | 7.60                 | 15.20         | 77.2        | 0.0         | 1.0         |
| 6        | 13.89                | 13.89         | 72.22       | 0.0         | 2.0         |
| 7        | 20% (CO\(_2\))      | 3.99          | 15.96       | 60.05       | 20          | 0.5  |
| 8        | 7.60                 | 15.20         | 57.2        | 20          | 1.0         |
| 9        | 13.89                | 13.89         | 52.22       | 20          | 2.0         |
| 10       | 50% (N\(_2\))       | 2.49          | 9.98        | 87.53       | 0.0         | 0.5  |
| 11       | 4.75                 | 9.50          | 85.75       | 0.0         | 1.0         |
| 12       | 8.68                 | 8.68          | 82.64       | 0.0         | 2.0         |
| 13       | 50% (CO\(_2\))      | 2.49          | 9.98        | 37.53       | 50          | 0.5  |
| 14       | 4.75                 | 9.50          | 35.75       | 50          | 1.0         |
| 15       | 8.68                 | 8.68          | 32.64       | 50          | 2.0         |

Table 2 Max and min ignition delay times of methane/air mixture ($p = 0.1–1.0$ MPa, $\phi = 0.5–2.0$).

| $\phi$ | $P$ (atm) | $T$ (K) | $\tau_{\text{ign}}$ (\text{\micro s}) | $\phi$ | $P$ (atm) | $T$ (K) | $\tau_{\text{ign}}$ (\text{\micro s}) | $\phi$ | $P$ (atm) | $T$ (K) | $\tau_{\text{ign}}$ (\text{\micro s}) |
|--------|-----------|---------|--------------------------------------|--------|-----------|---------|--------------------------------------|--------|-----------|---------|--------------------------------------|
| 1.0    | 1.1       | 1924.0  | 47                                   | 0.5    | 1.04      | 1897.2  | 55                                   | 2.0    | 1.11      | 1830.1  | 70                                   |
| 1.0    | 1.04      | 1513.4  | 937                                  | 0.5    | 0.92      | 1490.8  | 919                                  | 2.0    | 0.97      | 1556.3  | 597                                  |
| 1.0    | 2.78      | 1821.1  | 45                                   | 0.5    | 2.99      | 1751.8  | 56                                   | 2.0    | 3.11      | 1728.6  | 60                                   |
| 1.0    | 2.8       | 1461.0  | 788                                  | 0.5    | 2.88      | 1384.8  | 1163                                  | 2.0    | 3.03      | 1460.0  | 763                                  |
| 1.0    | 5.01      | 1756.3  | 49                                   | 0.5    | 4.97      | 1822.0  | 29                                   | 2.0    | 5.19      | 1765.9  | 41                                   |
| 1.0    | 4.81      | 1443.0  | 681                                  | 0.5    | 4.8       | 1406.8  | 809                                  | 2.0    | 5.11      | 1412.4  | 653                                  |
| 1.0    | 10.06     | 1718.3  | 38                                   | 0.5    | 9.8       | 1662.4  | 50                                   | 2.0    | 10.5      | 1661.6  | 43                                   |
| 1.0    | 9.21      | 1351.2  | 873                                  | 0.5    | 9.2       | 1334.9  | 941                                  | 2.0    | 9.92      | 1326.2  | 967                                  |

Fig. 3a Pressure and CH\^{*} chemiluminescence signals in the ignition process of methane/air mixture diluted by N\(_2\).
Eqs. (3)–(5) show that $\tau_{\text{ign}}$ has pressure dependence of $p^{-0.68}$, $p^{-0.65}$ and $p^{-0.7}$ at $\phi = 0.5$, 1.0 and 2.0, respectively, and all of the exponents of $p$ are negative. Meanwhile, the global activation energy of the mixture is $167.95 \cdot 10^3$, $169.69 \cdot 10^3$ and $171.02 \cdot 10^3$ (J/mol) at $\phi = 0.5$, 1.0 and 2.0, respectively, indicating that increasing $\phi$ has little effect on the global activation energy of this mixture.

Ignition delays of methane/air mixture diluted by N$_2$

The typical pressure and CH$^*$ chemiluminescence signals in the ignition process of methane/air mixture diluted by N$_2$ ($\phi_r = 20\%$ and 50\%) at $p = 0.1$ MPa and $\phi = 1.0$ are shown in Fig. 3a. The maximum and minimum measured ignition delay times of this mixture with $\phi_r = 50\%$ are also presented in Table 3.

Table 3 Max and min ignition delay times of methane/air mixture diluted by N$_2$ ($\phi_r = 50\%$).

| $\phi$ | $P$ (atm) | $T$ (K) | $\tau_{\text{ign}}$ (us) | $\phi$ | $P$ (atm) | $T$ (K) | $\tau_{\text{ign}}$ (us) | $\phi$ | $P$ (atm) | $T$ (K) | $\tau_{\text{ign}}$ (us) |
|-------|-----------|--------|--------------------------|-------|-----------|--------|--------------------------|-------|-----------|--------|--------------------------|
| 1.0   | 1.06      | 2027.7 | 45                       | 1.0   | 9.48      | 1737.2 | 42                       |
| 1.0   | 0.95      | 1587.5 | 892                      | 0.5   | 1.01      | 1966.8 | 50                       |
| 1.0   | 4.85      | 1784.0 | 63                       | 0.5   | 0.98      | 1508.9 | 1324                     |
| 1.0   | 4.72      | 1495.5 | 748                      | 0.5   | 4.8       | 1798.1 | 41                       |
| 1.0   | 9.54      | 1734.0 | 64                       | 0.5   | 4.95      | 1469.7 | 801                      |

Effects of N$_2$ and CO$_2$ on methane/air mixture ignition
Fig. 4a  Pressure and CH<sup>+</sup> chemiluminescence signals in ignition process of methane/air mixture diluted by CO<sub>2</sub>.

Fig. 4b  Ignition delays of methane/air mixture diluted by CO<sub>2</sub>.
The typical pressure and CH\(^{+}\) chemiluminescence signals in the ignition process of methane/air mixture diluted by CO\(_{2}\) (\(\phi_r = 20\%\) and 50\%) at \(p = 0.1\) MPa and \(\phi = 1.0\) are shown in Fig. 4a. The maximum and minimum measured ignition delay times of this mixture with \(\phi_r = 50\%\) are also presented in Table 4.

**Table 4 Max and min ignition delay times of methane/air mixture diluted by CO\(_{2}\) (\(\phi_r = 50\%).**

| \(\phi_r\) | \(P\) (atm) | \(T\) (K) | \(\tau_{ign}\) (\(\mu\)s) | \(\phi\) | \(P\) (atm) | \(T\) (K) | \(\tau_{ign}\) (\(\mu\)s) | \(\phi\) | \(P\) (atm) | \(T\) (K) | \(\tau_{ign}\) (\(\mu\)s) |
|----------|-----------|-----|----------------|-----|-----------|-----|----------------|-----|-----------|-----|----------------|
| 1.0      | 1.2       | 1985.1 | 70  | 1.0 | 9.88      | 1491.5 | 829  | 0.5 | 10.19 | 1726.1 | 63 |
| 1.0      | 1.06      | 1686.9 | 558 | 0.5 | 1.16      | 2070.0 | 47   | 0.5 | 9.62  | 1456.1 | 582 |
| 1.0      | 5.47      | 1797.9 | 66  | 0.5 | 0.97      | 1667.7 | 537  | 2.0 | 1.32  | 1984.1 | 80 |
| 1.0      | 4.94      | 1499.2 | 1082 | 0.5 | 5.37      | 1912.4 | 29   | 2.0 | 1.28  | 1701.8 | 476 |
| 1.0      | 10.74     | 1798.1 | 51  | 0.5 | 4.96      | 1497.7 | 634  |     |       |        |    |

\(\phi_r = 0\%: \quad \tau_{ign} = 1.36 \times 10^{-3} \times p^{-0.68} \times \phi^{0.01} \times e^{(168.028/RT)}\)\(\quad (6)\)

\(\phi_r = 20\%: \quad \tau_{ign} = 0.91 \times 10^{-3} \times p^{-0.71} \times \phi^{0.32} \times e^{(178.499/RT)}\)\(\quad (7)\)

\(\phi_r = 50\%: \quad \tau_{ign} = 0.72 \times 10^{-3} \times p^{-0.69} \times \phi^{0.43} \times e^{(186.568/RT)}\)\(\quad (8)\)

Eq. (6) shows that the exponents of \(\phi\) is 0.01, which indicates \(\tau_{ign}\) has little dependence on equivalence ratio at \(\phi_r = 0\%\). With \(\phi_r\) increasing from 0\% to 50\%, the exponent of \(\phi\) is increasing, indicating that the dependence of the ignition delays on \(\phi\) becomes stronger with \(\phi_r\) increasing. Meanwhile, the global activation energy of the mixture is 168.03 \(\times 10^{3}\), 178.5 \(\times 10^{3}\) and 186.56 \(\times 10^{3}\) (J/mol) at \(\phi_r = 0\%, 20\%\) and 50\%, respectively, indicating that an increase in the dilution coefficient results in increasing of the global activation energy of this mixture.

**Fig. 5** Comparisons of the effect of N\(_{2}\) and CO\(_{2}\) on ignition delays of methane/air mixture (\(\phi_r = 50\%).**
Fig. 4b illustrates the measured ignition delays of methane/air mixture diluted by CO$_2$ with $\phi_r$ is 20% and 50%, respectively. A linear relationship also exists between the ignition temperature and the ignition delay times of methane/air mixture diluted by CO$_2$. Meanwhile, an increase in the dilution coefficient of CO$_2$ from 0% to 20%, then to 50%, also results an increase in the ignition delays of methane/air mixture.

Correlation formulas for the ignition delay time with $p$ and $\phi$ at $\phi_r = 20\%$ and 50% are obtained by linear regression analysis and the results are shown as follows:

$$\phi_r = 20\%: \quad \tau_{ign} = 1.71 \times 10^{-3} \times p^{-0.74} \times \phi^{0.26} \times e^{(171.851/(RT))}$$

$$\phi_r = 50\%: \quad \tau_{ign} = 1.84 \times 10^{-3} \times p^{-0.71} \times \phi^{0.29} \times e^{(177.003/(RT))}$$

Comparisons of the effects of N$_2$ and CO$_2$ on ignition delays of methane/air mixture

Fig. 5 illustrates comparisons of the effects of N$_2$ and CO$_2$ on ignition delays of methane/air mixture with the dilution coefficients of N$_2$ and CO$_2$ are 50%. From Fig. 5 we can see that ignition delays of methane/air mixture diluted by CO$_2$ are longer than that of N$_2$ diluted at $\phi_r = 50\%$. However, with the equivalence ratio of methane/air mixture increases from 0.5 to 1.0, the discrepancy of the effects of N$_2$ and CO$_2$ on ignition delays of methane/air mixture becomes smaller. Furthermore, it is noteworthy that the lines for methane/air mixture diluted by N$_2$ and CO$_2$ ($\phi_r = 50\%$) at $\phi = 0.5$ will be crossed at low ignition temperatures, which suggests that the discrepancy of the effects of N$_2$ and CO$_2$ on ignition delays also becomes smaller at low ignition temperatures and lean mixture.

Numerical predictions

The ignition delay times of the methane/air mixture calculated by different reaction mechanisms are different although at the same conditions, as described by Zhang et al. [23]. Therefore, in this paper, the ignition delay times of the methane/air mixture calculated by different reaction mechanisms are compared firstly, and a reasonable reaction mechanism is selected to analyze the effect of inert gas on ignition delays of the methane/air mixture.
Mechanism selection

The ignition delay times of the methane/air mixture calculated by three reaction mechanisms e.g. GRI_3.0 mechanism [27], USC_2.0 mechanism [28], and NUI_Galway mechanism (includes 118 species and 663 reactions) [29] are compared with the experimental data at the same conditions, as shown in Fig. 6. All calculated ignition delays are made using the CHEMKIN-PRO program. GRI_3.0 mechanism includes 53 species and 325 reactions, and applied ranges of this reaction mechanism are $T = 1000–2500 \text{ K}$, $p = 0.1–1.0 \text{ MPa}$ and $\phi = 0.1–5.0$. USC_2.0 mechanism was developed from GRI_3.0 mechanism, and extra includes H$_2$/CO optimal model [30], C-2 reaction model [31], C-3 reaction model based on oxidation and pyrolysis of C$_3$H$_6$ [32], and C-4 reaction model based on oxidation and pyrolysis of 1,3-C$_4$H$_6$. This reaction mechanism includes 111 species and 784 reactions.

From Fig. 6, we can see that GRI_3.0 mechanism can well predict the ignition delays of methane/air mixture at $\phi = 0.5$, 1.0 and $p = 0.1, 1.0 \text{ MPa}$, while the calculated results by the other two kinetic models are different from experimental data. It is noteworthy that all kinetic models over-predict the ignition delays at $\phi = 2.0$ and $p = 0.1 \text{ MPa}$. Recent studies [33] showed that the discrepancy between experiments and simulations was from the uncertain elementary reaction rate constant, and the ignition delay was limited by local ignition and different facility. This suggests that the current kinetic models need further modifications under wide conditions to simulate the ignition delays of rich methane/air mixture.

Comparison with experiments

Through the above comparative analyses, the GRI_3.0 reaction mechanism is selected to analyze the ignition delay times of the methane/air mixture diluted by N$_2$ and CO$_2$.

Comparisons of calculated ignition delays of methane/air mixture diluted by N$_2$ and CO$_2$ and the measured data are shown in Figs. 7a and 7b. From these two figures we can see that the calculated ignition delays of methane/air mixture diluted by N$_2$ and CO$_2$ with $\phi_r = 50\%$ agree well with experimental data. When the dilution coefficients of N$_2$ and CO$_2$ are 20\%, discrepancies exist between the calculated ignition delays and experimental data at some conditions. However, this discrepancy is within the experimental uncertainty limits ($\pm 10\%$).
Fig. 7b  Measured and calculated ignition delays for methane/air mixture diluted by CO₂.

Fig. 8a  Effects of N₂ on the sensitivity coefficients of the key reactions (a: φᵣ = 0%, b: φᵣ = 50%).
**Sensitivity analysis**

Sensitivity analysis is always used to illustrate the key reactions in the reaction mechanism which will promote or inhibit the combustible mixture ignition, and it also helps to further understand the chemical kinetic characteristics in the process of ignition. The detailed descriptions of sensitivity analysis have been presented by Vlachos [34].

The sensitivity analysis is conducted for methane/air mixture diluted by N$_2$ and CO$_2$ using the GRI_3.0 mechanism to analyze the effect of inert gas on ignition delays in this study.

Fig. 8a shows the sensitivity coefficients of some key reactions in the ignition process of methane/air mixture at $\phi = 1.0$, $p = 0.1$ MPa and $T = 1540$ K. The dominant reactions promoting methane/air mixture ignition are:

- R155: \( \text{CH}_3 + \text{O}_2 \leftrightarrow \text{O} + \text{CH}_3\text{O} \)
- R38: \( \text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH} \)
- R156: \( \text{CH}_3 + \text{O}_2 \leftrightarrow \text{OH} + \text{CH}_2\text{O} \)
- R119: \( \text{HO}_2 + \text{CH}_3 \leftrightarrow \text{OH} + \text{CH}_3\text{O} \)

The dominant reactions inhibiting methane/air mixture ignition are:

- R158: \( \text{CH}_3 + \text{CH}_3(+)\text{M} \leftrightarrow \text{C}_2\text{H}_6(+)\text{M} \)
- R53: \( \text{H} + \text{CH}_4 \leftrightarrow \text{CH}_3 + \text{H}_2 \)

Generally, the auto-ignition of combustible mixture is more sensitive to small radicals because the fuel and large radicals are mainly consumed to form small radicals by dissociation. The free radicals such as H, O and OH are extremely active and short-lived during the process of ignition. The chain-branching and chain-propagating reactions initiated by the free radicals play the most important role in the chemical reaction, as described by Zhang et al. [24,25]. There is O or OH radical formed in R155, R38, R156 and R119, so these reactions will promote methane/air mixture to ignition.

In addition, the key ignition promotion reactions are the chain termination reaction R158 and the consumption reactions of methane R53.

Figs. 8a and 8b shows the effects of N$_2$ and CO$_2$ on the sensitivity coefficients of these key reactions at $\phi = 1.0$, $p = 0.1$ MPa, $T = 1540$ K and $\phi_r = 50\%$. The sensitivity coefficients of these key reactions promoting ignition decrease greatly as methane/air mixture diluted by N$_2$ and CO$_2$, leading to the weakening on accelerated ignition tendency. Furthermore, with methane/air mixture diluted by CO$_2$, the sensitivity coefficients of these key ignition promotion reactions decrease greater than that of the mixture diluted by N$_2$. That is to say, comprised with N$_2$, the inhibition effect of CO$_2$ on methane/air mixture ignition is greater and this is consistent to the experimental results in Fig. 5. N$_2$ and CO$_2$ are chemically passive agents, and they have passive influences on methane/air mixture ignition at two aspects: thermal effect and chemical kinetic effect. With the dilution coefficients of N$_2$ and CO$_2$ increasing, the concentration of the fuel will be decreased (as shown in Table 1), leading to the decrease in the total heat value, and will prolong the ignition delay time of methane/air mixture at the same $p$, $T$ and $\phi$ (compared the results in Figs. 3a and 3b of this paper with the results in Fig. 3 of Zhang et al. [24]). N$_2$ has been constantly treated as non reactive bulk gas which does not participate in ignition and combustion. However, CO$_2$ is a major product of combustion while it is chemically passive as well. Adding CO$_2$ into fuel/air system may possibly influence the chemical kinetics and thus the ignition delay. CO$_2$ modifies the ignition kinetics in two main ways. First, the reverse of the reaction, \( \text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H} \), decreases the H atom concentration and weakens the ignition. Second, dilution with CO$_2$ results in an overall stronger third-body efficiency of the mixture than dilution with N$_2$.

Fig. 8c gives the effects of N$_2$ and CO$_2$ on the sensitivity coefficients of these key reactions at $p = 0.1$ MPa, $T = 1540$ K and $\phi = 0.5$, 1.0, 2.0, respectively. From Fig. 8c we can see that the values of sensitivity coefficients of these key ignition promotion reactions reach maximum at $\phi = 1.0$, which implies the strongest promotion effect on ignition at the stoichiometric equivalence ratio. Furthermore, at
each equivalence ratio, the sensitivity coefficients of these key ignition promotion reactions decrease as methane/air mixture diluted by N₂ and CO₂, and the inhibition effect of CO₂ on methane/air mixture ignition is greater than that of N₂, and this is also consistent to the experimental results in Fig. 5.

Conclusions

The ignition delays of methane/air mixture diluted by N₂ and CO₂ with dilution coefficients varying from 0% to 50% were experimentally measured and simulated in a chemical shock tube over the temperature range of 1300–2100 K, the pressure range of 0.1–1.0 MPa, and for equivalence ratios of 0.5, 1.0 and 2.0. Following conclusions are summarized.

(1) A linear relationship exists between the reciprocal of temperature and the logarithm of the ignition delay times, and an increase in ignition temperature or pressure results in a decrease in ignition delay time of methane/air mixture.

(2) An increase in the dilution coefficient of N₂ or CO₂ results in increasing ignition delays and the inhibition effect of CO₂ on methane/air mixture ignition is stronger than that of N₂.

(3) Simulated ignition delays of methane/air mixture using three kinetic models including USC_2.0 mechanism, GRI_3.0 mechanism and NUIGalway mechanism were compared to the experimental data show that GRI_3.0 mechanism gives the best prediction on ignition delay times of the methane/air mixture.

(4) Comparisons of the calculated ignition delays with the experimental data of methane/air mixture diluted by N₂ and CO₂ show excellent agreement, and sensitivity analysis shows that ignition delays of methane/air mixture are more sensitive to the small radicals such as H, O and OH. Sensitivity coefficients of ignition promotion reactions decrease with increasing dilution coefficients of N₂ and CO₂. This inhibits the total reaction rate and increases the ignition delays of methane/air mixture.

As discussed above, the inhibition effects of N₂ and CO₂ on methane/air mixture ignition (as the first stage in gas explosion) are greater, and the inhibition effect becomes significant with dilution coefficient increased.

Conflict of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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