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Experimental and modeling study on effects of N₂ and CO₂ on ignition characteristics of methane/air mixture



Wen Zeng ^{a,*}, Hongan Ma ^a, Yuntao Liang ^b, Erjiang Hu ^c

^a School of Aerospace Engineering, Shenyang Aerospace University, Liaoning, Shenyang 110136, PR China

^b State Key Laboratory of Coal Mine Safety Technology, Shenyang Branch of China Coal Research Institute, Liaoning, Shenyang 110016, PR China

^c State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Shanxi, Xi'an 710049, PR China

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ABSTRACT

The ignition delay times of methane/air mixture diluted by N₂ and CO₂ 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 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. 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 N₂ and CO₂ 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 N₂ and CO₂ show excellent agreement, and sensitivity coefficients of chain branching reactions which promote mixture ignition decrease with increasing dilution coefficient of N₂ or CO₂.

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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 equipments 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

* Corresponding author. Tel.: +86 2489723722; fax: +86 2489723720.

E-mail address: zengwen928@sohu.com (W. Zeng).

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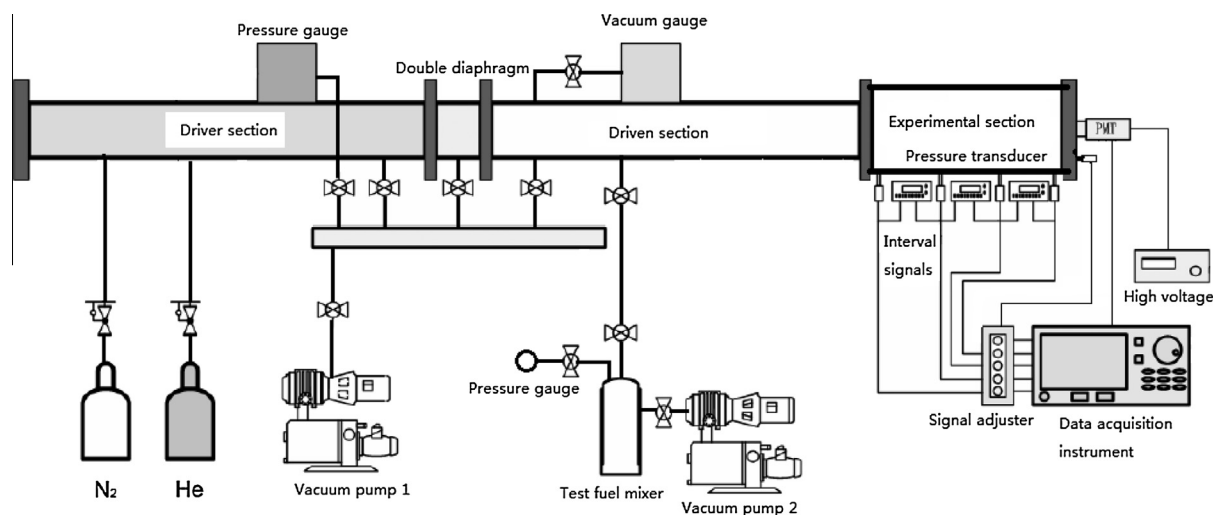


Fig. 1 Experimental apparatus of the chemical shock tube.

gas explosion have been reported recently [12–14]. Hu et al. [15] numerically studied the effects of diluents (N_2 and CO_2) on the laminar burning velocity of the premixed methane/air flames. Stone et al. [16] investigated the effects of CO_2 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/ CO_2 , and the effects of CO_2 on the propagation speed of methane/air mixtures were presented. The effects of N_2 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 N_2 increasing. Furthermore, when the dilution coefficient of N_2 in the gas mixture was over 20%, the flame would be unstable and was easy to exterminate. 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 N_2 and CO_2 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 N_2 and CO_2 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)/ N_2 (> 99.99% purity) mixed gas to generate shock waves. The detailed descriptions of this experimental

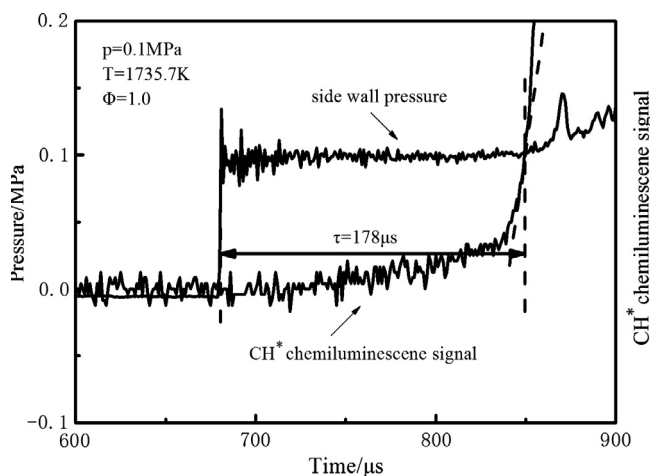


Fig. 2a Pressure and CH^* chemiluminescence signals in the ignition process of methane/air mixture.

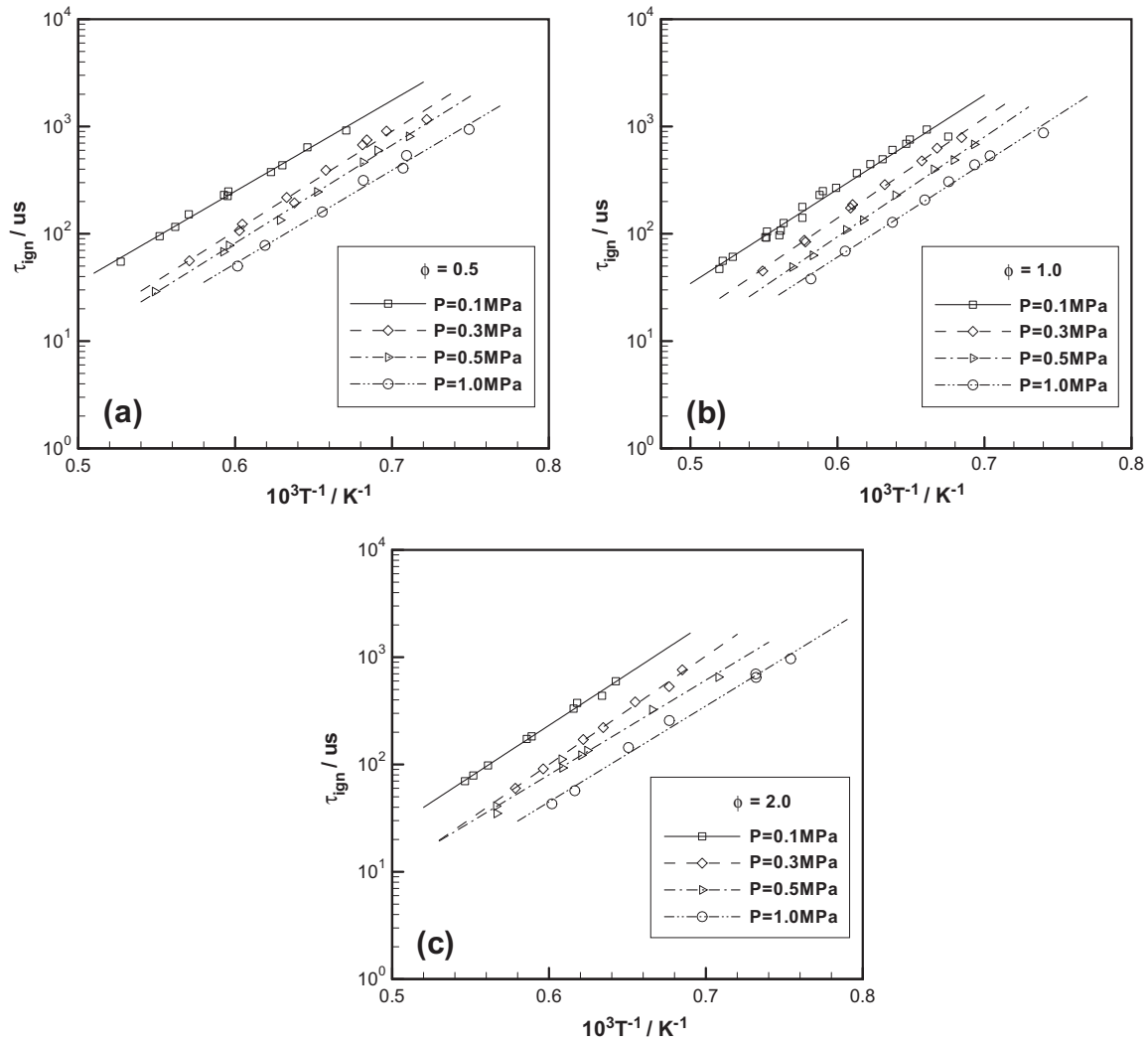


Fig. 2b Ignition delay times of methane/air mixture.

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 (dp/dt).

The ignition delay time (τ_{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 $\phi = 1.0$), τ_{ign} of methane/air mixture is 178 μ s.

Results and discussion

Ignition delays of methane/air mixtures diluted with N₂ and CO₂ (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 (ϕ_r) is

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

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.

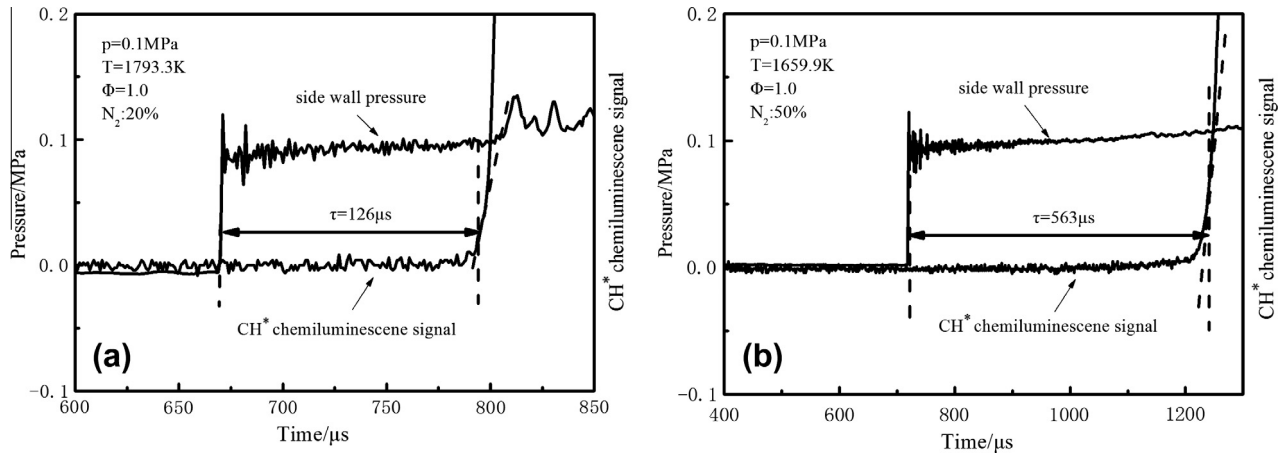
From Fig. 2b we can see that a linear relationship exists between the reciprocal of temperature and the logarithm of the ignition delay times, according with the Arrhenius-type correlation, and an increase in ignition temperature results in a decrease in the measured ignition delay time. Fig. 2b also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

Table 1 Compositions of the test mixtures in this study.

Mixtures	Dilution coefficient	XCH ₄ (%)	XO ₂ (%)	XN ₂ (%)	XCO ₂ (%)	ϕ
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 ($p = 0.1\text{--}1.0$ MPa, $\phi = 0.5\text{--}2.0$).

ϕ	P (atm)	T (K)	τ_{ign} (μ s)	ϕ	P (atm)	T (K)	τ_{ign} (μ s)	ϕ	P (atm)	T (K)	τ_{ign} (μ 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 N₂.

increasing ignition pressure. This can be explained by using the Arrhenius-type correlation,

$$\tau_{ign} = A \cdot p^a \phi^b X_{O_2}^c \exp \frac{E_a}{RT} \quad (2)$$

Generally, the pressure exponential a 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:

$$\phi = 0.5: \tau_{ign} = 1.31 \times 10^{-3} \times p^{-0.68} \times e^{(167,945/(RT))} \quad (3)$$

$$\phi = 1.0: \tau_{ign} = 1.28 \times 10^{-3} \times p^{-0.65} \times e^{(169,690/(RT))} \quad (4)$$

$$\phi = 2.0: \tau_{ign} = 1.03 \times 10^{-3} \times p^{-0.7} \times e^{(171,020/(RT))} \quad (5)$$

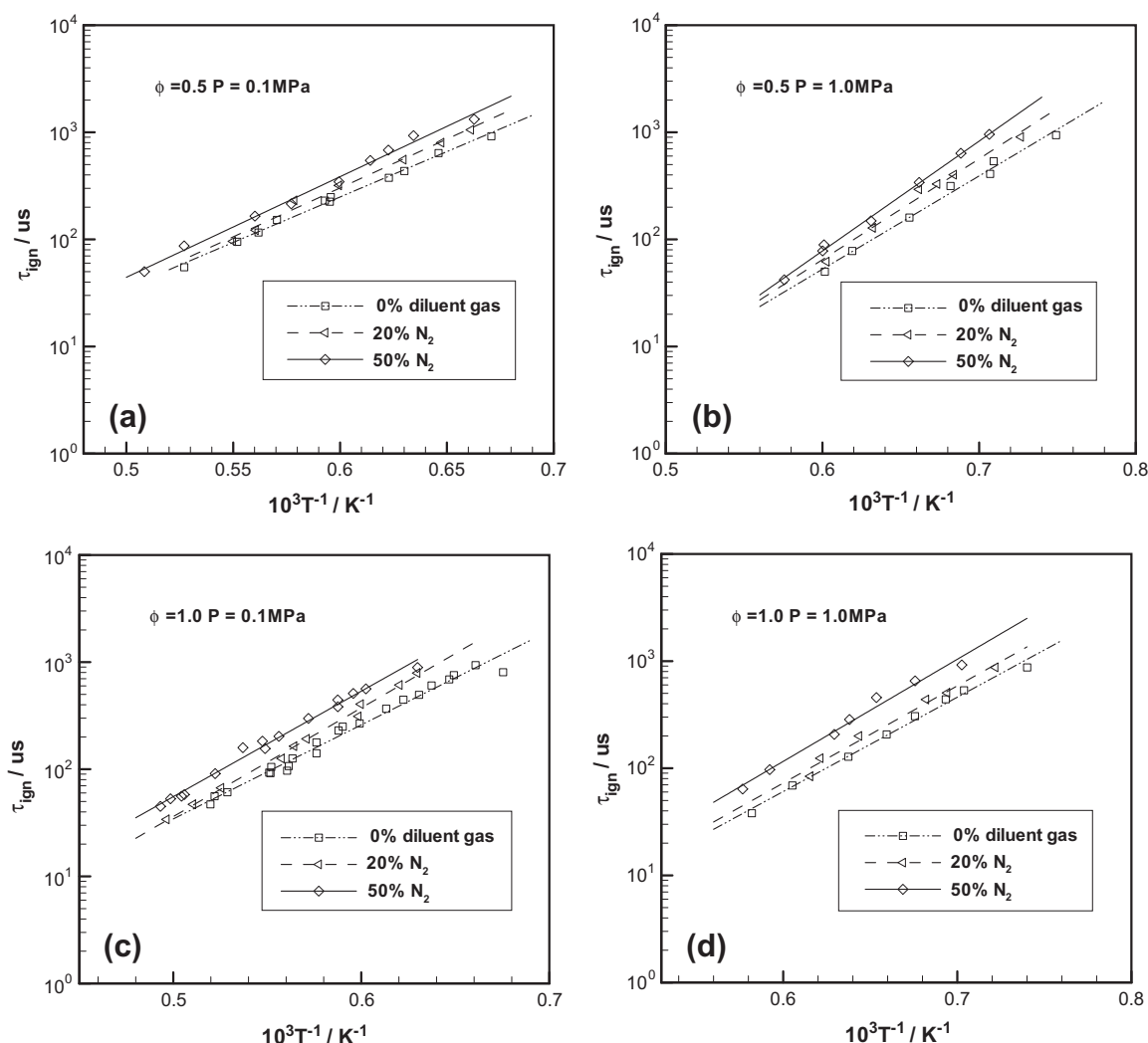


Fig. 3b Ignition delays of methane/air mixture diluted by N₂.

Table 3 Max and min ignition delay times of methane/air mixture diluted by N₂ ($\phi_r = 50\%$).

ϕ	P (atm)	T (K)	τ_{ign} (μ s)	ϕ	P (atm)	T (K)	τ_{ign} (μ s)	ϕ	P (atm)	T (K)	τ_{ign} (μ s)
1.0	1.06	2027.7	45	1.0	9.48	1423.4	922	0.5	9.95	1737.2	42
1.0	0.95	1587.5	892	0.5	1.01	1966.8	50	0.5	9.48	1415.5	957
1.0	4.85	1784.0	63	0.5	0.98	1508.9	1324	2.0	0.98	2087.8	43
1.0	4.72	1495.5	748	0.5	4.8	1798.1	41	2.0	0.94	1646.5	810
1.0	9.54	1734.0	64	0.5	4.95	1469.7	801				

Eqs. (3)–(5) show that τ_{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 167.95×10^3 , 169.69×10^3 and 171.02×10^3 (J/mol) at $\phi = 0.5$, 1.0 and 2.0, respectively, indicating that increasing ϕ has little effect on the global activation energy of this mixture.

Ignition delays of methane/air mixture diluted by N₂

The typical pressure and CH* chemiluminescence signals in the ignition process of methane/air mixture diluted by N₂ ($\phi_r = 20\%$ 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.

Fig. 3b illustrates the measured ignition delays of methane/air mixture diluted by N₂ with ϕ_r is 20% and 50%, respectively. A linear relationship also exists between the reciprocal of temperature and the logarithm of the ignition delay times of methane/air mixture diluted by N₂. An increase in the dilution coefficient of N₂ from 0% to 20%, then to 50%, results in increasing of the ignition delays of methane/air mixture.

Correlation formulas for the ignition delay time with p and ϕ at $\phi_r = 0\%$, 20% and 50% are obtained by linear regression analysis and the results are shown as follows:

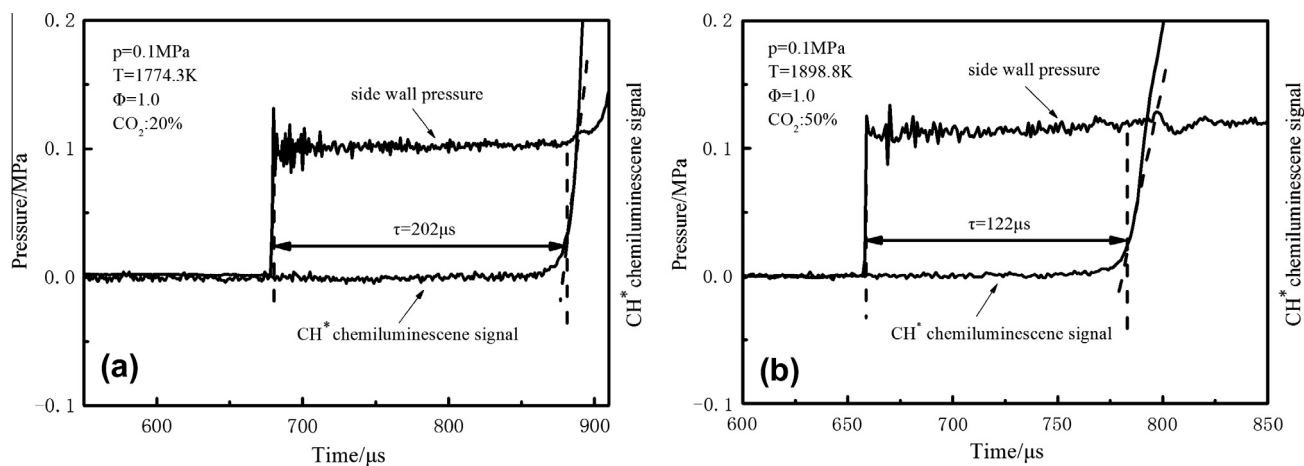


Fig. 4a Pressure and CH^* chemiluminescence signals in ignition process of methane/air mixture diluted by CO_2 .

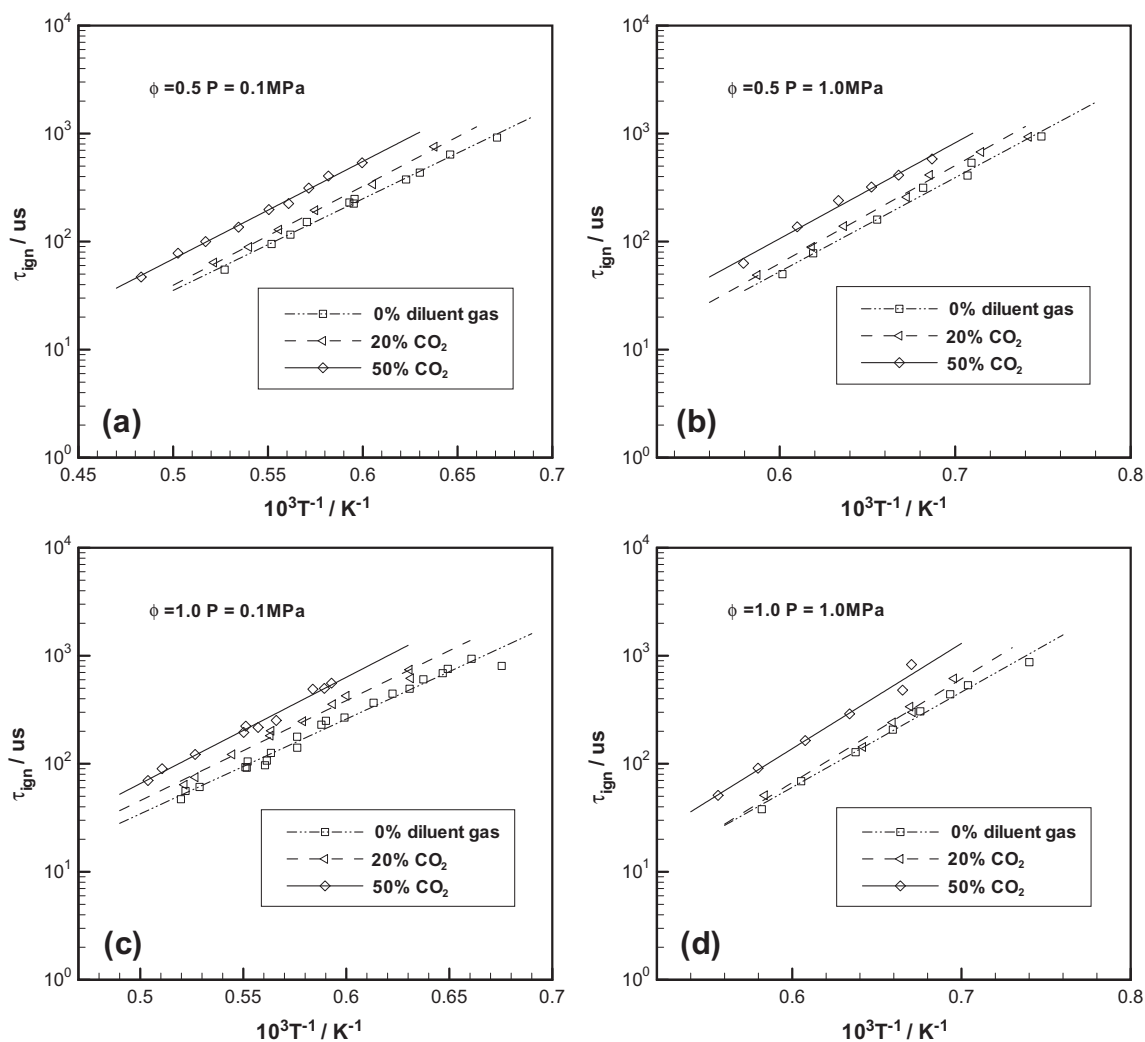


Fig. 4b Ignition delays of methane/air mixture diluted by CO_2 .

Table 4 Max and min ignition delay times of methane/air mixture diluted by CO₂ ($\phi_r = 50\%$).

ϕ	P (atm)	T (K)	τ_{ign} (μ s)	ϕ	P (atm)	T (K)	τ_{ign} (μ s)	ϕ	P (atm)	T (K)	τ_{ign} (μ 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				

$$\phi_r = 0\% : \tau_{ign} = 1.36 \times 10^{-3} \times p^{-0.68} \times \phi^{0.01} \times e^{(168,028/(RT))} \quad (6)$$

$$\phi_r = 20\% : \tau_{ign} = 0.91 \times 10^{-3} \times p^{-0.71} \times \phi^{0.32} \times e^{(178,499/(RT))} \quad (7)$$

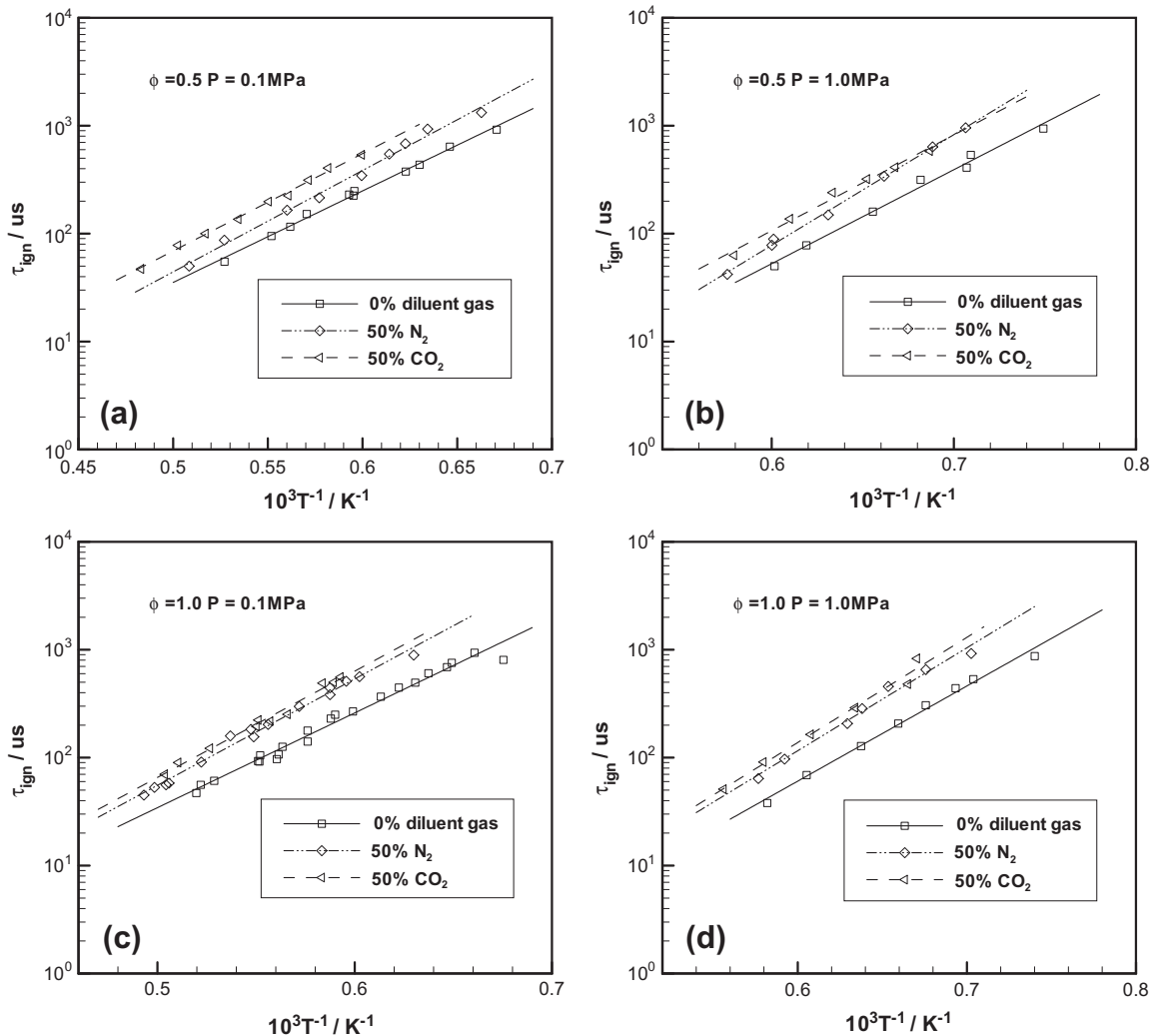
$$\phi_r = 50\% : \tau_{ign} = 0.72 \times 10^{-3} \times p^{-0.69} \times \phi^{0.43} \times e^{(186,560/(RT))} \quad (8)$$

Eq. (6) shows that the exponents of ϕ is 0.01, which indicates τ_{ign} has little dependence on equivalence ratio at $\phi_r = 0\%$. With ϕ_r increasing from 0% to 50%, the exponent of ϕ is increasing, indicating that the dependence of the ignition delays on ϕ

becomes stronger with ϕ_r increasing. Meanwhile, the global activation energy of the mixture is 168.03×10^3 , 178.5×10^3 and 186.56×10^3 (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.

Ignition delays of methane/air mixture diluted by CO₂

The typical pressure and CH* chemiluminescence signals in the ignition process of methane/air mixture diluted by CO₂ ($\phi_r = 20\%$ 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.

**Fig. 5** Comparisons of the effect of N₂ and CO₂ on ignition delays of methane/air mixture ($\phi_r = 50\%$).

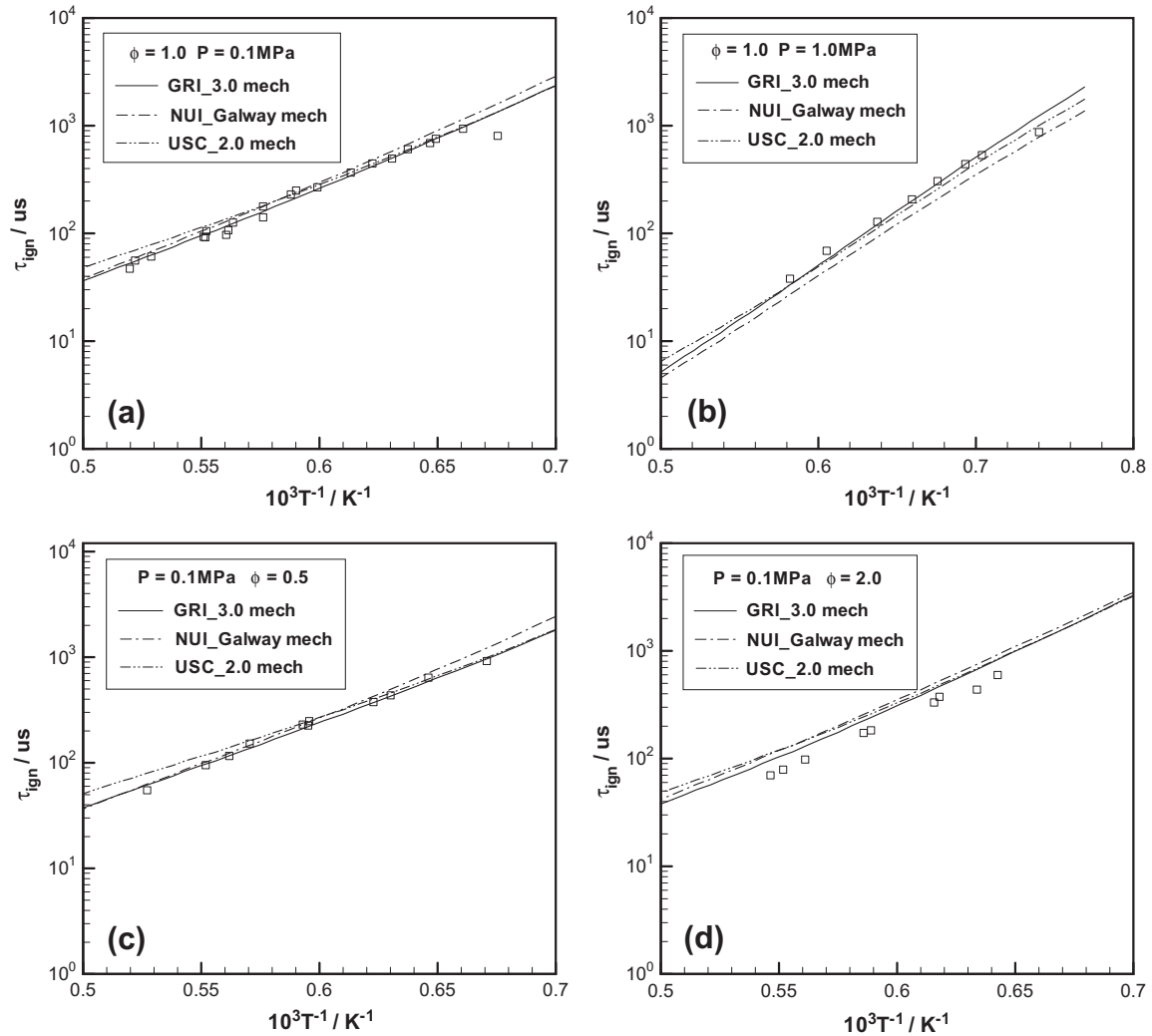


Fig. 6 Measured and calculated ignition delays for methane/air mixture using different kinetic models.

Fig. 4b illustrates the measured ignition delays of methane/air mixture diluted by CO₂ with ϕ_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 CO₂. Meanwhile, an increase in the dilution coefficient of CO₂ from 0% to 20%, then to 50%, also results in an increase in the ignition delays of methane/air mixture.

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

$$\phi_r = 20\%: \tau_{ign} = 1.71 \times 10^{-3} \times p^{-0.74} \times \phi^{0.26} \times e^{(171,851/(RT))} \quad (9)$$

$$\phi_r = 50\%: \tau_{ign} = 1.84 \times 10^{-3} \times p^{-0.71} \times \phi^{0.29} \times e^{(177,003/(RT))} \quad (10)$$

Comparisons of the effects of N₂ and CO₂ on ignition delays of methane/air mixture

Fig. 5 illustrates comparisons of the effects of N₂ and CO₂ on ignition delays of methane/air mixture with the dilution

coefficients of N₂ and CO₂ are 50%. From Fig. 5 we can see that ignition delays of methane/air mixture diluted by CO₂ are longer than that of N₂ 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 N₂ and CO₂ on ignition delays of methane/air mixture becomes smaller. Furthermore, it is noteworthy that the lines for methane/air mixture diluted by N₂ and CO₂ ($\phi_r = 50\%$) at $\phi = 0.5$ will be crossed at low ignition temperatures, which suggests that the discrepancy of the effects of N₂ and CO₂ 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.

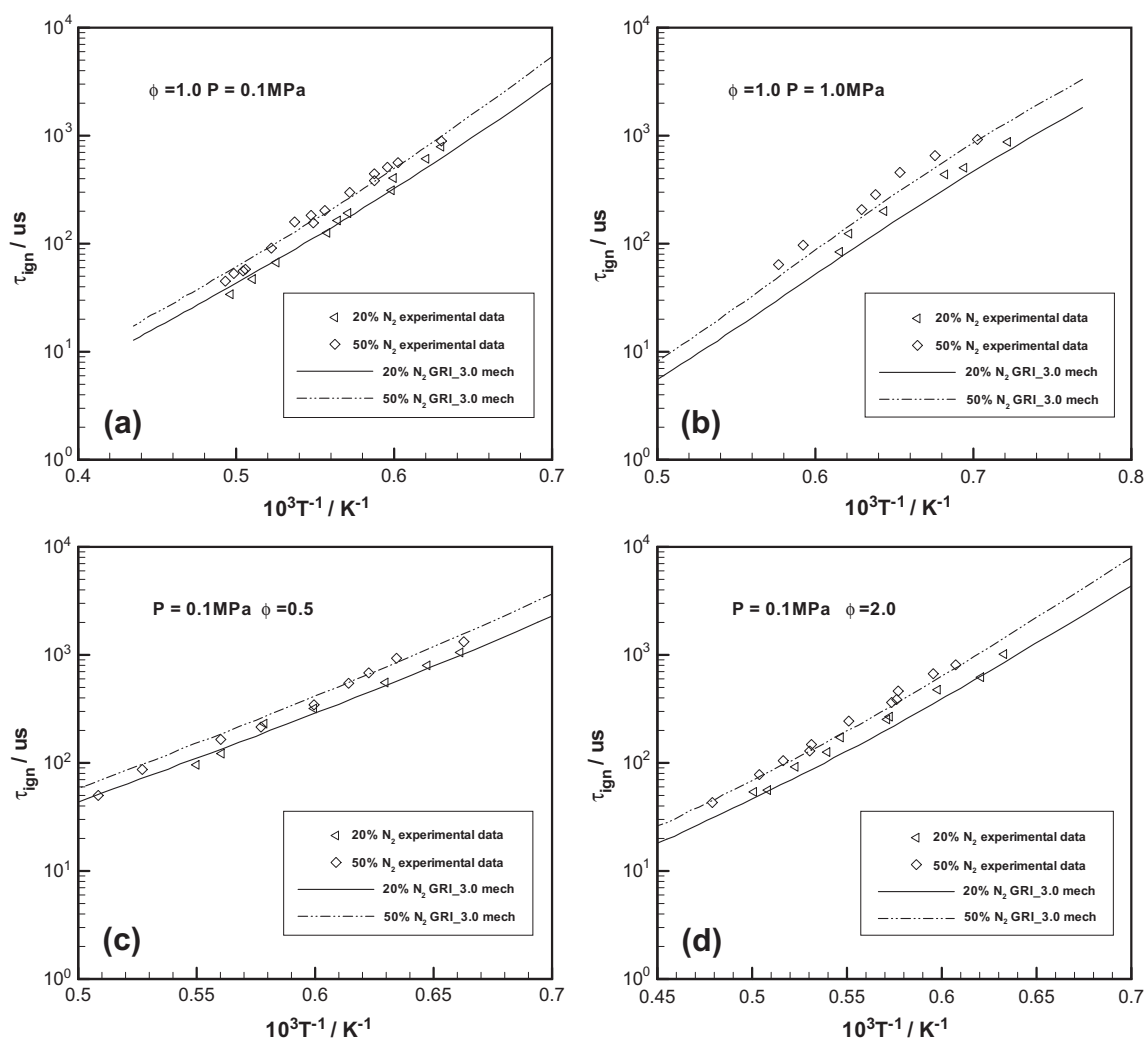


Fig. 7a Measured and calculated ignition delays for methane/air mixture diluted by N₂.

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 $T = 1000\text{--}2500\text{ K}$, $p = 0.1\text{--}1.0\text{ MPa}$ and $\phi = 0.1\text{--}5.0$. USC_2.0 mechanism was developed from GRI_3.0 mechanism, and extra includes H₂/CO optimal model [30], C-2 reaction model [31], C-3 reaction model based on oxidation and pyrolysis of C₃H₆ [32], and C-4 reaction model based on oxidation and pyrolysis of 1-3-C₄H₆. 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 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 mixtures diluted by N₂ and CO₂.

Comparisons of calculated ignition delays of methane/air mixture diluted by N₂ and CO₂ 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 N₂ and CO₂ with $\phi_r = 50\%$ agree well with experimental data. When the dilution coefficients of N₂ and CO₂ are 20%, discrepancies exist between the calculated ignition delays and experimental data at some conditions. However, this discrepancy is within the experimental uncertainty limits ($\pm 10\%$).

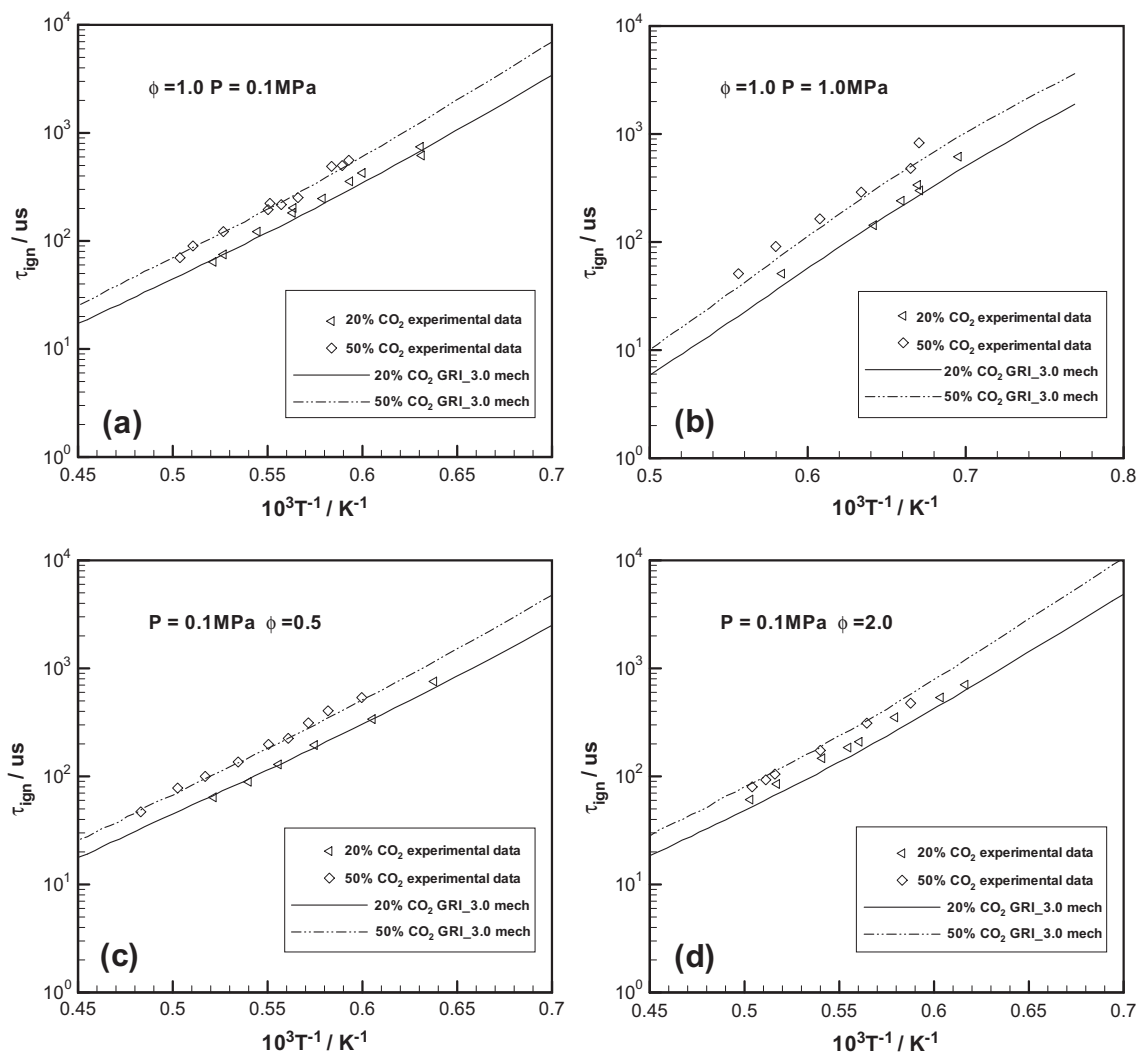


Fig. 7b Measured and calculated ignition delays for methane/air mixture diluted by CO₂.

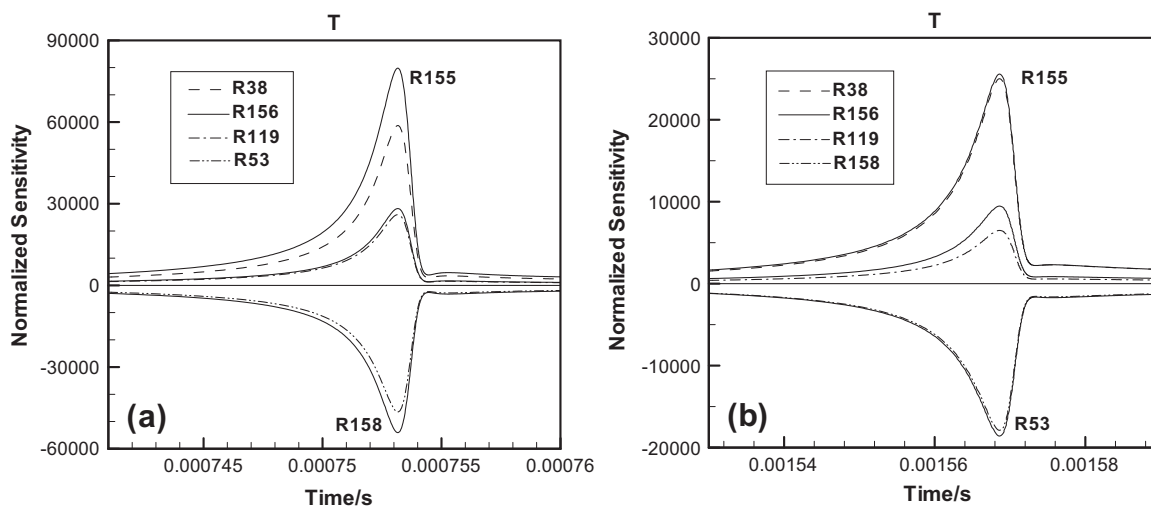


Fig. 8a Effects of N₂ on the sensitivity coefficients of the key reactions (a: $\phi_r = 0\%$, b: $\phi_r = 50\%$).

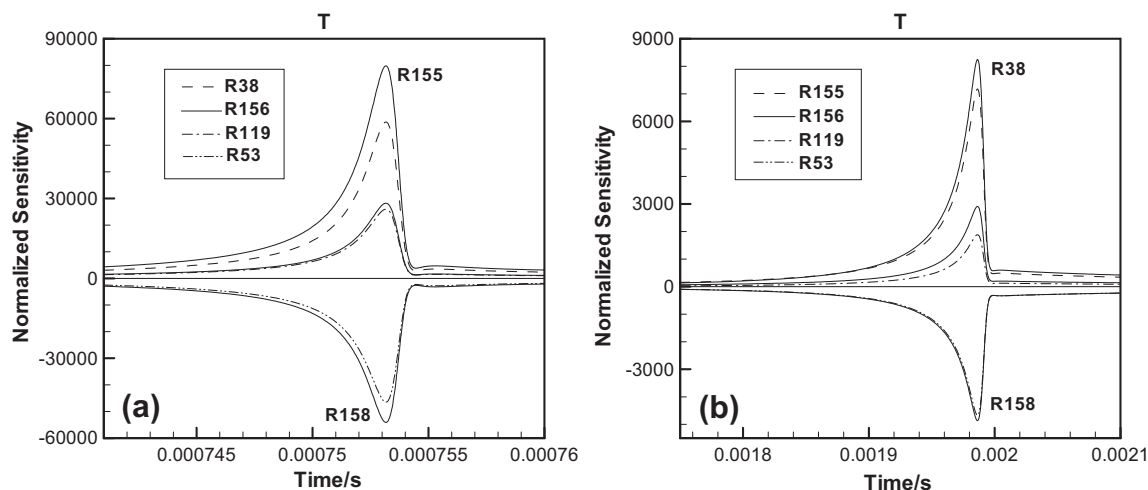


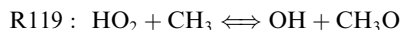
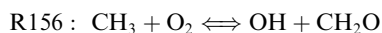
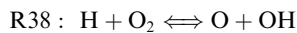
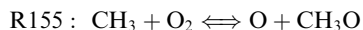
Fig. 8b Effects of CO₂ on the sensitivity coefficients of the key reactions (a: $\phi_r = 0\%$, b: $\phi_r = 50\%$).

Sensitivity analysis

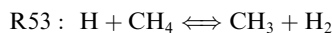
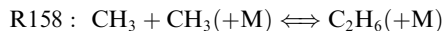
Sensitivity analysis is always used to illustrate the key reactions in the reaction mechanism which will promote or inhibit the combustible mixture ignition, and it also helps to further understand the chemical kinetic characteristics in the process of ignition. The detailed descriptions of sensitivity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

The sensitivity analysis is conducted for methane/air mixture diluted by N₂ and CO₂ 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:



The dominant reactions inhibiting methane/air mixture ignition are:



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 inhibition reactions are the chain termination reaction R158 and the consumption reactions of methane R53.

Figs. 8a and 8b shows the effects of N₂ and CO₂ 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 N₂ and CO₂, leading to the weakening on accelerated ignition tendency. Furthermore, with methane/air mixture diluted by CO₂, the sensitivity coefficients of these key ignition promotion reactions decrease greater than that of the mixture diluted by N₂. That is to say, comprised with N₂, the inhibition effect of CO₂ on methane/air mixture ignition is greater and this is consistent to the experimental results in Fig. 5. N₂ and CO₂ 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 N₂ and CO₂ 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 ϕ (compared the results in Figs. 3a and 3b of this paper with the results in Fig. 3 of Zhang et al. [24]). N₂ has been constantly treated as non reactive bulk gas which does not participate in ignition and combustion. However, CO₂ is a major product of combustion while it is chemically passive as well. Adding CO₂ into fuel/air system may possibly influence the chemical kinetics and thus the ignition delay. CO₂ modifies the ignition kinetics in two main ways. First, the reverse of the reaction, $\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$, decreases the H atom concentration and weakens the ignition. Second, dilution with CO₂ results in an overall stronger third-body efficiency of the mixture than dilution with N₂.

Fig. 8c gives the effects of N₂ and CO₂ 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

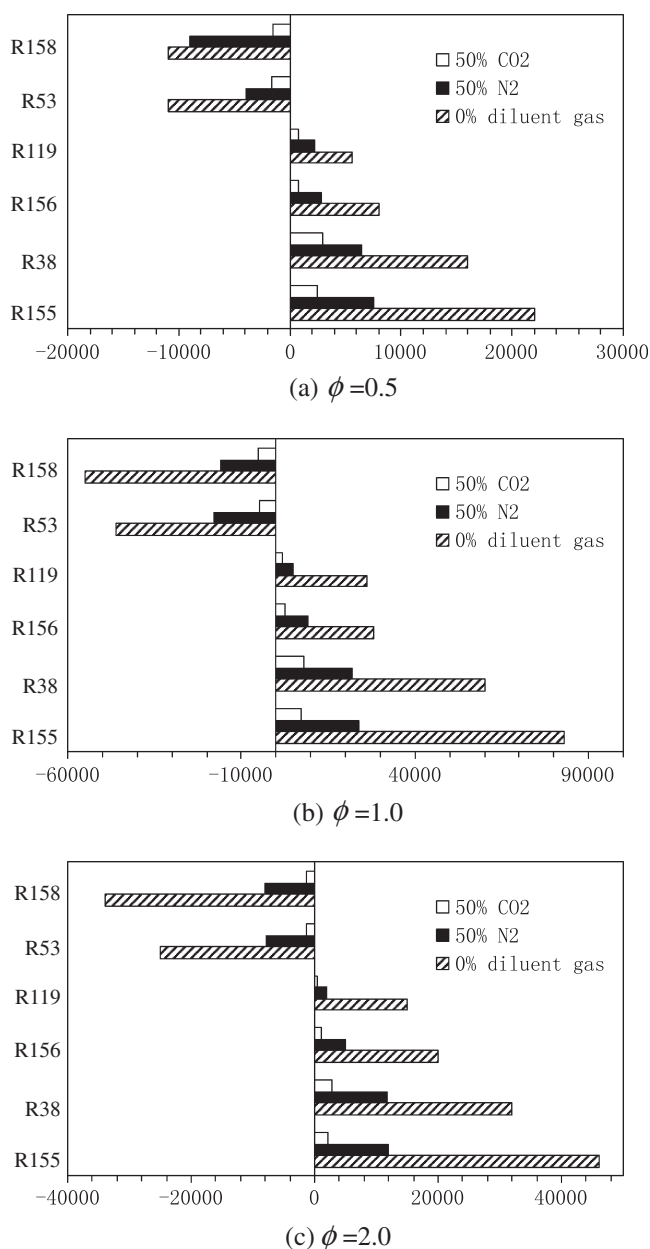


Fig. 8c Comparisons of the effects of N₂ and CO₂ on sensitivity coefficients of the key reactions.

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 NUI_Galway 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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References

- [1] Troiani G. Effect of velocity inflow conditions on the stability of a CH₄/air jet-flame. *Combust Flame* 2009;156:539–42.
- [2] Razus DM, Krause U. Comparison of empirical and semi-empirical calculation methods for venting of gas explosions. *Fire Safety J* 2001;36:1–23.
- [3] Hirano T. Gas explosions caused by gasification of condensed phase combustibles. *J Loss Prevent Proc* 2006;19:245–9.
- [4] Hirano T. Methodology for case studies of an accidental gas explosions. *J Loss Prevent Proc* 2001;14:553–7.
- [5] Maremonti M, Russo G, Salzano E, Tufano V. Numerical simulation of gas explosions in linked vessels. *J Loss Prevent Proc* 1999;12:189–94.
- [6] Chen ZY, Zhang YJ, Chou CL, Li Y, Wang ZH, Ge YT, Zheng CG. Trace element emissions from spontaneous combustion of

- gob piles in coal Mines, Shanxi, China. *Int J Coal Geol* 2008;73:52–62.
- [7] Shearer MJ, Vincent HYT, Corr B. Analysis of results from large scale hydrocarbon gas explosions. *J Loss Prevent Proc* 2000;13:167–73.
- [8] Ferrara G, Benedetto AD, Salzano E, Russo G. CFD analysis of gas explosions vented through relief pipes. *J Hazard Mater* 2006;137:654–65.
- [9] Oh KH, Kim H, Kim JB, Lee SE. A study on the obstacle-induced variation of the gas explosion characteristics. *J Loss Prevent Proc* 2001;14:597–602.
- [10] Shebeko YN, Tsarichenko SG, Korolchenko AY. Burning velocities and flammability limits gaseous mixture at elevated temperatures and pressure. *Combust Flame* 1995;102:427–37.
- [11] Bielert U, Sichel M. Numerical simulation of premixed combustion processes in closed tubes. *Combust Flame* 1998;114:397–419.
- [12] Chen ZY, Tang CL, Fu J, Jiang X, Li QQ, Wei LJ, Huang ZH. Experimental and numerical investigation on diluted DME flames: thermal and chemical kinetic effects on laminar flame speeds. *Fuel* 2012;102:567–73.
- [13] Chen ZY, Wei LJ, Huang ZH, Miao HY, Wang XB, Jiang DM. Measurement of laminar burning velocities of dimethyl ether-air premixed mixtures with N₂ and CO₂ dilution. *Energy Fuels* 2009;23(2):735–9.
- [14] Li QQ, Fu J, Wu XS, Tang CC, Huang ZH. Laminar flame speeds of DMF-iso-octane-air-N₂/CO₂ mixtures. *Energy Fuels* 2012;26(2):917–25.
- [15] Hu EJ, Jiang X, Huang ZH, Iida N. Numerical study on the effects of diluents on the laminar burning velocity of methane/air mixtures. *Energy Fuels* 2012;26(2):917–25.
- [16] Stone R, Clarke A, Beckwith P. Correlations for the laminar-burning velocity of methane/diluent/Air mixtures obtained in free-fall experiments. *Combust Flame* 1998;114:546–55.
- [17] Konnov AA, Dyakov IV. Measurement of propagation speeds in adiabatic cellular premixed flames of CH₄ + O₂ + CO₂. *Exp Therm Fluid Sci* 2005;29:901–7.
- [18] Liang YT, Zeng W, Hu EJ. Experimental study of the effect of nitrogen addition on gas explosion. *J Loss Prevent Proc* 2013;26:1–9.
- [19] Kumar K, Sung CJ. An experimental study of the auto-ignition characteristics of conventional jet fuel/oxidizer mixtures: Jet-A and JP-8. *Combust Flame* 2010;157:676–85.
- [20] Kumar K, Sung CJ. A comparative experimental study of the auto-ignition characteristics of alternative and conventional jet fuel/oxidizer mixtures. *Fuel* 2010;89:2853–63.
- [21] Lifshitz A, Scheller K, Burcat A, Skinner GB. Shock tube investigation of ignition in methane/oxygen/argon mixtures. *Combust Flame* 1971;16:311–21.
- [22] Huang J, Hill PG, Bushe WK, Munshi SR. Shock-tube study of methane ignition under engine-relevant conditions: experiments and modeling. *Combust Flame* 2004;136:25–42.
- [23] Zhang YJ, Jiang X, Wei LJ, Zhang JX, Tang CL, Huang ZH. Experimental and modeling study on auto-ignition characteristics of methane/hydrogen blends under engine relevant pressure. *Int J Hydrogen Energy* 2012;37:19168–76.
- [24] Zhang YJ, Huang ZH, Wei LJ, Zhang JX, Law CK. Experimental and modeling study on ignition delays of lean mixtures of methane, hydrogen, oxygen, and argon at elevated pressures. *Combust Flame* 2012;159:918–31.
- [25] Zhang YJ, Huang ZH, Wei LJ, Niu S. Experimental and kinetic study on ignition delay times of ethane/hydrogen/oxygen/nitrogen mixtures by shock tube. *Chin Sci Bull* 2011;56:2853–61.
- [26] Petersen EL, Hall JM, Smith SD. Ignition of lean methane-based fuel blends at gas turbine pressures. *J Eng Gas Turb Power* 2007;129(4):937–44.
- [27] Smith GP, Golden DM, Frenklach M, Moriarty NW, Eiteneer B, Goldenberg M. GRI-Mech 3.0; 2000. <http://www.me.berkeley.edu/gri_mech/>.
- [28] Wang H, You X, Joshi AV, Davis SG, Laskin A, Egolfopoulos F. USC 2.0 Mech; 2007. <http://ignis.usc.edu/USC_Mech_II.htm/>.
- [29] Petersen EL, Kalitan DM, Simmons S, Bourque G, Curran HJ, Simmie JM. Methane/propane oxidation at high pressures: experimental and detailed chemical kinetic modeling. *Proc Combust Inst* 2007;31:447–54.
- [30] Davis SG, Joshi AV, Wang H. An optimized kinetic model of H₂/CO combustion. *Proc Combust Inst* 2005;30(1):1283–92.
- [31] Wang H, Laskin A. A comprehensive kinetic model of ethylene and acetylene oxidation at high temperatures. Delaware: University of Delaware; 1998.
- [32] Davis SG, Law CK, Wang H. Propene pyrolysis and oxidation kinetics in a flow reactor and laminar flames. *Combust Flame* 1999;119(4):375–99.
- [33] Dryer FL, Chaos M. Ignition of syngas/air and hydrogen/air mixtures at low temperatures and high pressures: experimental data interpretation and kinetic modeling implications. *Combust Flame* 2008;152:293–9.
- [34] Vlachos DG. Reduction of detailed kinetic mechanisms for ignition and extinction of premixed hydrogen/air flames. *Chem Eng Sci* 1996;51:3979–93.