Fuel 158 (2015) 1–10

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Laminar flame speeds and ignition delay times of methane–air mixtures at elevated temperatures and pressures

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HIGHLIGHTS

- The measured laminar flame speeds from the constant volume bomb and the counter flow flame are compared.
- GRI Mech 3.0, USC Mech II, and Aramco Mech 1.3 mechanisms are validated at elevated pressures.
- Overall reaction order are analyzed at initial pressures up to 6.0 MPa.
- Correlations for laminar burning velocities and ignition delay time of methane–air mixtures are provided.

ARTICLE INFO

Article history:
Received 30 November 2014
Received in revised form 3 May 2015
Accepted 4 May 2015
Available online 12 May 2015

Keywords:
Laminar flame speed
Ignition delay time
Reaction order
Sensitivity analysis
Elevated pressures and temperatures
Correlation

ABSTRACT

Measurements on laminar flame speeds and ignition delay times of methane/air mixtures at elevated pressures and temperatures were carried out in a constant volume bomb and shock tube. The performances of GRI Mech 3.0, USC Mech II, and Aramco Mech 1.3 mechanisms were also evaluated from the data obtained. Results showed that the measured laminar flame speeds from the constant volume bomb by the linear method are slightly higher than those from the counter flow flame at rich mixtures and lower at lean mixtures. At rich mixtures, the laminar flame speeds with linear method are higher than that with non-linear method. The available mechanisms give slight overprediction to the constant volume bomb data at lean mixtures, and large underprediction at rich mixtures at elevated temperatures and pressures. Overall reaction order decreases and then increases with the rising of pressure from 0.1 to 10.0 MPa because of the chain reaction mechanism. For the ignition delay times, the three mechanisms are in good accordance with the experimental data of lean and stoichiometric mixtures at atmospheric pressure, while the discrepancy between calculation and measurement is increased at elevated pressures. These mechanisms seem to lack good sensitivity to the rich mixtures, especially at elevated pressures. Correlations for laminar burning velocities and ignition delay time of methane–air mixtures are provided.

1. Introduction

Since fossil fuel is depleting and automotive emission regulation is strengthening, researches are paying increasing attention on the study of alternative and clean fuels. One of the prospective alternative fuels is natural gas. Methane is the major constituent of natural gas as well as the smallest hydrocarbon fuel. Therefore, methane is a key fuel candidate of research. Methane has been in use on specific combustion devices like internal combustion engines and industrial gas turbines operated at high pressure and temperature.

Laminar flame speeds is a fundamental property of fuels, resulting from the combined influences of diffusivity, exothermicity, and reactivity. Besides, it is a key parameter in descripting complex combustion phenomena such as flame stabilization, extinction, turbulent flame structure and velocity [1–3]. Previously, extensive experiments have been conducted to measure the laminar burning velocities covering a wide range of conditions. The correlation of laminar flame speed as a function of temperature and pressure is necessary for the CFD simulation [4]. A plenty of research focused on the high dependence of methane–air mixture laminar flame speed on pressures and temperatures. Recently, Goswami [5] and Ranzi [6] summarized the experimental laminar burning velocities of methane–air mixtures at different pressures and temperatures for the latest sixty years, finding that large uncertainty still exists in the data. Furthermore, prediction of laminar flame speed with

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http://dx.doi.org/10.1016/j.fuel.2015.05.010
0016-2361/

the GRI Mech 3.0 mechanism shows poor performance at high pressures and temperatures [7].

The methodologies for fundamental flame speed determination involve flames that are either stationary, or propagating with respect to a quiescent unburned mixture. The former includes conical, flat, and counter-flow flames and the latter refers to the spherically expanding flames. Recently, spherically expanding flame has been widely applied to measure the laminar burning velocities for a number of fuels. The stretch rate of spherically expanding flame is well defined and this method is the best choice for the measurement at higher pressures and temperatures. In this work, the spherical expanding flame was used to measure the laminar flame speeds at elevated pressures and temperatures.

Ignition delay time is also a key parameter of fuel chemistry, which can serve as the validation parameter in the development of chemical kinetics [8]. Shock tube is a standard facility to measure the ignition delay time at high temperatures. It is zero-dimensional and homogeneous inside, so the ignition of fuel oxidizer mixtures is controlled by chemical kinetic. Additionally, shock tube can measure the ignition delay time at the specified pressure and temperature. Although much research has been reported on the ignition delay time of methane/oxygen, most of the experiments were conducted under high argon dilution conditions [9–14], and only a few work reports the auto-ignition of methane–air mixtures [15,16]. Thus, measurement on ignition delay times of methane–air mixtures is still rare and worthwhile.

The objectives of this study are to measure the laminar burning velocities at various initial pressures and high temperatures (up to 443 K), to measure the ignition delay times of methane–air mixtures under various conditions, to evaluate the kinetic models on the basis of the measured data, to discuss the pressure effect on the chain reaction mechanism, and to provide the correlations for the laminar burning velocity and the ignition delay time of the methane–air mixtures.

2. Experimental and numerical methods

Recently, Egolfopoulos [17] reviewed different experimental approaches on determination of the laminar flame speed, and recommended the spherically expanding flame method when the pressure is greater than 0.5 MPa. Details of the experimentations in this study can be found in previous literatures [18,19], and here only a brief introduction is given. The spherically propagating flames are generated in a cylindrical combustion chamber (5.5 L) bearing pressure up to 10 MPa and initial temperature of 500 K by central ignition. The propagation of flame is then imaged with Schlieren photography and recorded by a high-speed digital camera (Phantom V611) operating at 10,000 frames per second, at 720 × 720 pixels, and magnification ratio of 0.11 mm/pixel.

Mixture preparation and the resulted uncertainty in equivalence ratio are described in the following. In the spherical vessel, all pipes, valves and vessel parts sensitive to fuel condensation are heated. Partial pressure is used to accurately measure and control the filling process. Partial pressure is measured with a high-accuracy pressure transmitter (Rosemount 3051). The absolute uncertainty in equivalence ratio is less than 0.0093. In addition, mixture preparation and the resulted uncertainty in the equivalence ratio of the experiments by other research groups [7] are provided in Table 1. It can be seen that the uncertainties in mixture preparation in this study is equivalent to those of others in the laminar flame speed measurement.

Table 1
Uncertainties in mixture preparation of other groups.

Setup	Research group	Equivalence ratio uncertainty
Counter flow	USC	Less than 0.5%
Heat flux	TUE	Max ± 0.02 (absolute)
Spherical vessel	CORIA	Less than 0.01 (absolute)
	ICARE	Less than 0.0004 (absolute)
	PRISME	Max ± 0.76%
	RWTH	Less than 0.8%

Post processing of the spherical flame data is obtained from the information of the expanding flame radius over time. When the flame maintains its stability, the flame propagation speed (S_n) can be extracted according to $S_n = dR/dt$, where R is the recorded flame radius history. The existence of stretch in the front of the flame is due to its spherical shape. The flame stretch rate can be obtained from the equation $\alpha = 2S_n/R$. In this study, the linear and non-linear extrapolation methods are used to determinate the laminar flame speed. The linear method is that the flame propagation speed is linear to the stretch rate within a certain range in which the ignition effect and pressure rise are negligible; that is, $S_l - S_n = L_b \cdot \alpha$, where S_l is the unstretched propagation speed and L_b is the burned gas Markstein length. From mass conservation across the flame front, the unstretched laminar burning velocity (S_u) can be calculated by the formula $S_u = \rho_b/\rho_u \cdot S_l$, where ρ_u and ρ_b are respectively the unburned and burned gas densities. The non-linear extrapolation method is proposed by Kelly and Law [20]. By taking into account of the effect of ignition energy and pressure rise in the combustion chamber, flame photos in the range of 5 mm–25 mm are used in the analysis. In addition, we know that the flame front presented cellular instabilities at elevated pressures, so the data range were also restricted by the occurrence of cellular structure. The flame surface is smooth, free from any flame front diffusional-thermal and hydrodynamic instabilities.

A shock tube with an inner equivalent diameter of 11.5 cm was used to measure ignition delays. The detailed experimental setup has been presented and its validation has been conducted in reference [21]. The shock tube consists of a driver section and a driven section divided by double diaphragms, which are 4.0 m long and 4.8 m long respectively. Fuel mixtures entered into the driver section after the 12 hours' mixing in a cylindrical tank to ensure full homogeneity. Purities of methane, oxygen and argon are 99.9%, 99.999% and 99.999%, respectively. The measured ignition delay time (τ) in this study is defined as the time interval between the time when an incident shock wave arrived at the endwall of the shock tube and the intercept of the maximum slope of CH^* emission profile with the baseline.

Laminar flame speed was simulated with Premix code [22], which applies a hybrid time-integrating/Newton iteration method to solve the steady-state mass, species and energy conservation equations and can simulate the propagating burning process. TWOPNT, a boundary value problem solver in the Chemkin package [23], are used to solve equations. A transport property processor and a gas-phase interpreter which carry the species transport properties and process the chemical reaction mechanism are also built in the Chemkin package. Mixture-averaged transport properties are employed in this calculation. Multi-component transport option is preferred by certain modeling workgroups, such as Resources Research Institute and University of Leeds; while we choose the mixture-averaged transport properties like Lawrence Livermore National Laboratory and other groups. Ten continuation options are used in all calculations and the values of adaptive grid parameters (GRAD and CURV) varies from 0.99 to 0.01 for each case in order to obtain the grid-independent solutions. The final solutions (GRAD = 0.01, CURV = 0.01) were usually obtained with about 1300 mesh points. Convergence level for most cases is typically 2 cm s^{-1} of final grid for calculating laminar flame speeds, which is accurate enough for our results.

Calculations on the ignition delay time were made using the Senkin code [24] and the Chemkin package. The Constant volume adiabatic model is selected for the calculation. In this study, the computed ignition delay time is defined as the time interval between zero and the maximum rate of temperature rise (max dT/dt).

The chemical kinetic models utilized in the study include GRI Mech 3.0 [25], USC Mech II [26], and Aramco Mech 1.3 model [27]. There are 325 elementary chemical reactions and associated rate coefficient expressions and thermochemical parameters for the 53 species in GRI Mech 3.0. The ranges of its application are 1000–2500 K in temperature, 10 torr–10 atm in pressure and 0.1–5.0 in equivalence ratio. It includes the detailed combustion reaction mechanism for hydrogen. USC Mech II is a H_2/CO/C1–C4 kinetic model (including 111 species and 784 elementary reactions) established by the University of Southern California in 2007. It is capable to simulate the oxidation of hydrogen, carbon monoxide, and C1–C4 hydrocarbons at elevated temperature. Aramco Mech 1.3 model, including 253 species and 1542 elementary reactions, was developed by National University of Ireland in 2013 and contains the oxidation mechanism of C1–C4 hydrocarbons and a DME sub-model. In addition, the Ranzi model [6] and San Diego model [28] were also validated as shown in Supporting Materials.

3. Results and discussion

3.1. Measurements and model validations on laminar flame speed

Fig. 1a gives laminar flame speeds of methane–air mixtures at different pressures. When the pressure is increased from 0.1 to 1.0 MPa, the measured results of Park [29], Gu [30] and Rozenchan [31] keep consistency. For the fuel lean mixtures, prediction by GRI Mech 3.0 model gives slightly lower values than those from the USC Mech II model. For the fuel rich mixtures, taking into account of measurement errors and rate constant errors of kinetic model, the two kinetic models give reasonable predictions of the experimental results. Because of the difficulty at even higher pressure experimentation, only Rozenchan measured the laminar flame speeds at the pressure of 2.0 MPa and USC Mech II gives better predictions than those of GRI Mech 3.0 model in the fuel rich sides. Fig. 1b plots the laminar flame speeds for different temperatures. The star symbol represents the measurements of this study at normal pressure and temperature. Experimental values of Halter [32], Rozenchan [31] and Hassan [33] from constant volume bomb are in good agreement with current study. The data by Park using counter flow flame measurement are slightly larger than those of these measurements on the fuel lean side, but gives lower values at ϕ = 1.3. This phenomenon will be further validated under

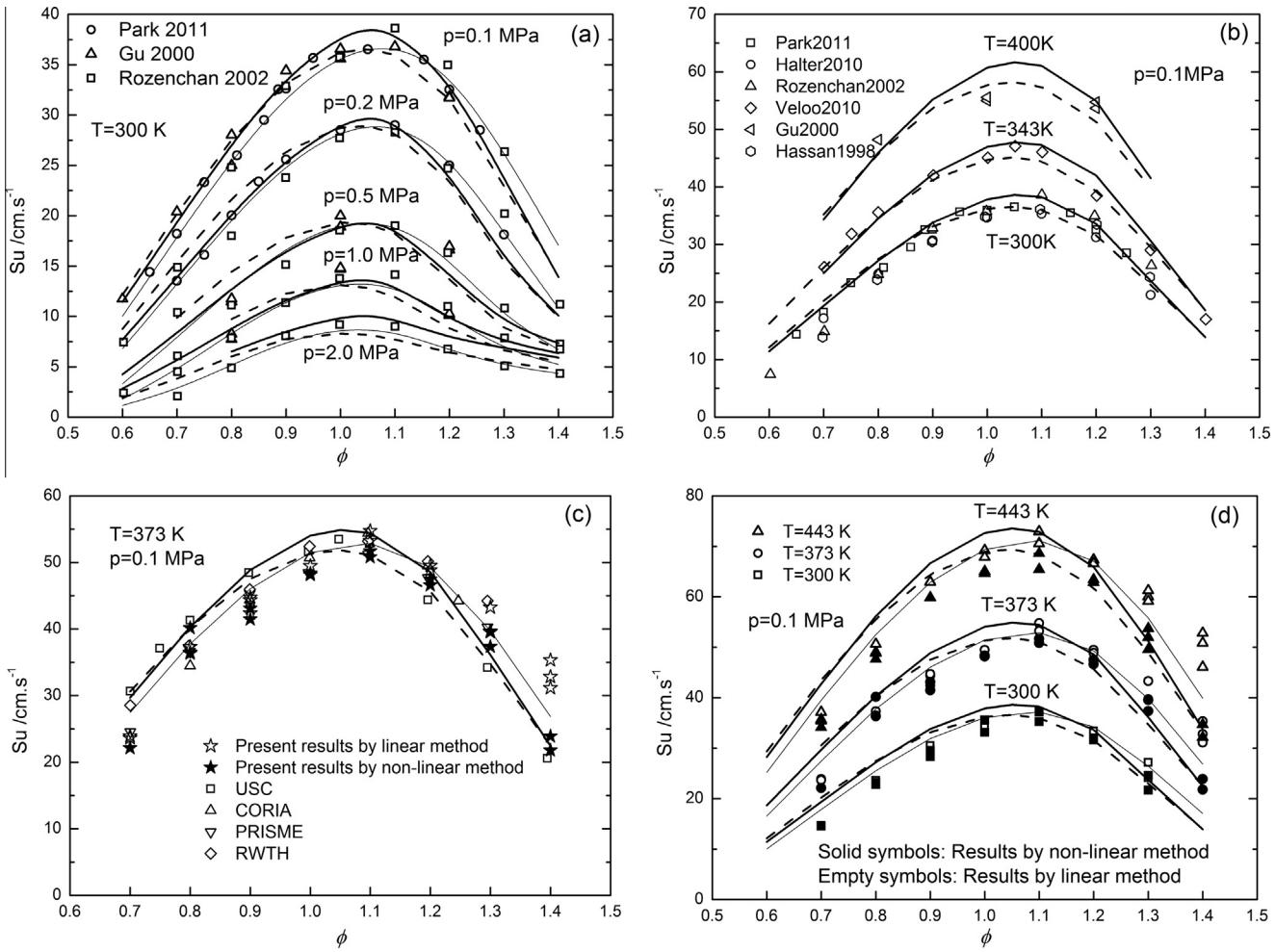

Fig. 1. Laminar flame speeds at different pressures and temperatures. Symbols: Measurements; Thick lines: Calculations with GRI Mech 3.0; Dash lines: Calculations with USC Mech II; Thin lines: Calculations with Aramco Mech 1.3.

other conditions. The data from the counter flow flame measurement at the temperature of 343 K is from Veloo [34], and only three points at $T = 400$ K were provided by Gu [30]. It is noted that both GRI Mech 3.0 and USC Mech II can well predict the laminar flame speeds at different temperatures and normal pressure (0.1 MPa).

To further validate the experimental data and evaluate the kinetic model at high temperatures, the laminar flame speeds at $T = 373$ K and $p = 0.1$ MPa are given in Fig. 1c. Data from different research groups using the constant volume bomb (CORIA, PRISME and RWTH) [7] show good agreement for the mixtures around stoichiometry, whereas larger scatter is presented for the mixtures of fuel lean ($\phi = 0.7$) conditions. USC data from counter flow flame measurement are larger than the present measurements on the fuel lean side. Simulations by USC Mech II (Dash lines) are in perfectly good agreement with USC data among all mixtures. GRI Mech 3.0 predictions show better agreement compared to those of USC prediction except for the equivalence ratios of 1.1 and 1.2. The comparison shows that the laminar flame speeds from the constant volume bomb measurement by the linear extrapolation method are slightly lower than that from the counter flow flame measurement for the fuel rich mixtures and higher for the fuel rich mixtures. Calculations with USC Mech II, GRI 3.0 Mech and Aramco Mech 1.3 are well agreement with the measurements with the non-linear method. Therefore, non-linear method is more reasonable than linear method especially for rich mixtures of methane. Fig. 1d plots the measured laminar flame speeds at different temperatures. Simulations with the three models agree well with the experimental measurements.

Fig. 2a shows the measured laminar flame speeds and their comparison with model predictions at different pressures. The data from RWTH and PRISME [7] show good agreement, and simulations fit the experimental data well for the fuel lean mixtures, but gives large underprediction for the fuel rich mixtures. This suggests these mechanisms seem to lack good sensitivity to rich mixtures at the pressures up to 0.5 MPa. Fig. 2b and c plot the measured laminar flame speeds at different pressures and two temperatures for further validation. At $p = 0.1$ MPa and 0.5 MPa, the measured data are in good agreement with those of RWTH and PRISME. At $p = 0.1$ MPa and 0.2 MPa, the simulations are slightly larger than the experimental data for the fuel lean, rich and stoichiometric mixtures. At $p = 0.5$ MPa, the simulations are in good agreement with experimental data for the fuel lean and stoichiometric mixtures, but show the underprediction for the fuel rich mixture ($\phi > 1.0$). All these comparisons indicate that these mechanisms seem to lack good sensitivity to pressure variations for the fuel rich mixtures when the pressure is greater than 0.5 MPa.

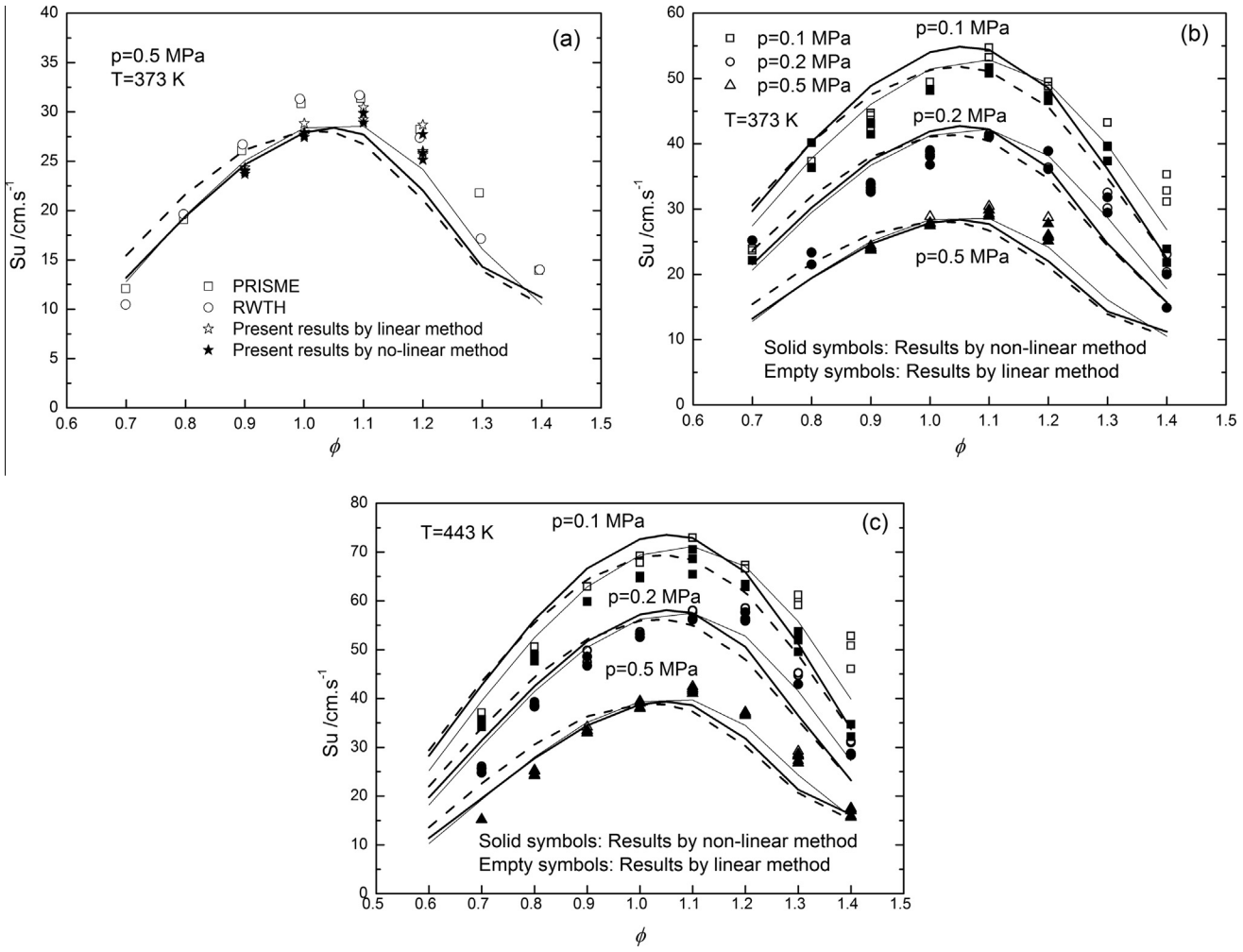

Fig. 2. Laminar flame speeds at different pressures. Symbols: Measurements; Thick lines: Calculations with GRI Mech 3.0; Dash lines: Calculations with USC Mech II; Thin lines: Calculations with Aramco Mech 1.3.

3.2. Overall reaction order

A numerical analysis was conducted in order to get insightful knowledge on the effect of initial pressure on laminar flame speed. Therefore, the stoichiometric methane–air flames at different initial pressures were investigated and the chemical effect on laminar flame speed was analyzed. Given that the predictions of USC Mech II mechanism on the measured laminar flame speed are better than those of GRI Mech 3.0 as discussed in the last section, USC Mech II model was used for the following analysis. The initial pressure is extended up to 6.0 MPa from model calculation.

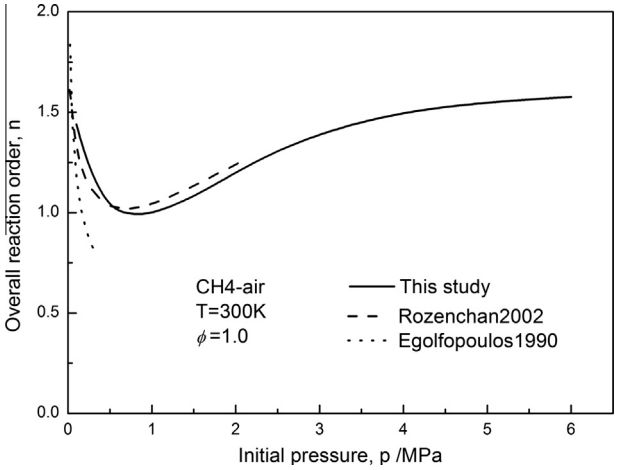

Fig. 3. Overall reaction orders at different initial pressures.

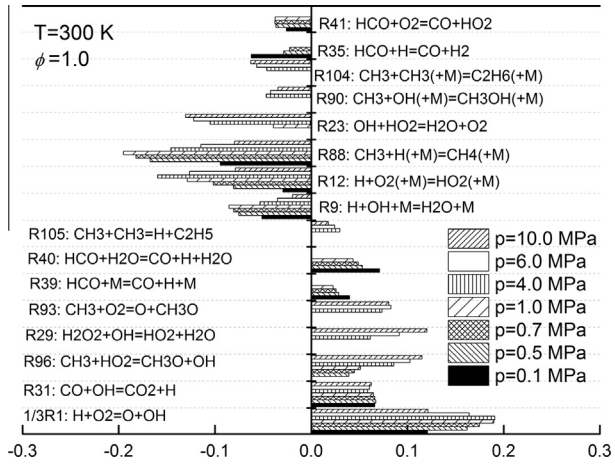

Fig. 4. Sensitivity factors at different pressures.

The effect of pressure on the chain mechanism can be identified and quantified through the overall reaction order n, which can be locally defined according to the relation $m^0 \sim p^{n/2}$, assuming negligible dependence of the thermodynamic and transport properties of m^0 on p, such as [35,36] $n = 2\left\{\frac{\partial[\ln(m^0)]}{\partial[\ln(p)]}\right\}_{Tad}$, here m^0 is mass flux (kg/m^2 s) ($m^0 = \rho_u S_u$). The slope of $\ln(m^0)$ versus $\ln(p)$ is equal to $n/2$.

Egolfopoulos and Law [35] gave the values of overall reaction order (n) for the methane–air mixtures for the pressures up to 0.3 MPa. The observed that n decreased when the pressure increased for a given equivalent ratio and explained it by the growing importance of termination reactions over branching reactions. The range of pressures is raised to 6.0 MPa in this study and n is observed to decrease at first and then increase with the increase of pressure, as shown in Fig. 3. This nonmonotonic change of the reaction order n over the pressure also supports the previous research [31,35,37]. Andrews and Bradley [37] showed that for the methane–air mixtures, n is the unity at $p > 5$ atm. Egolfopoulos and Law [35] investigated the stoichiometric methane–air mixture, and n was decreased from 1.7 to 0.9 in the case of Pu from 0.25 to 3.0 atm. Rozenchan and Law [31] demonstrated that for the stoichiometric methane–air mixture, when pressure is less than 0.7 MPa, n was decreased from 1.3 to 1.0, but when the pressure is larger than 1.0 MPa, n was increased again. This study gives a reasonable agreement with the above studies, and the behavior can be validated in the following chain mechanism analysis.

3.3. Sensitivity analysis

Sensitivity analysis can be used to find out which elementary reactions play an important role in the burning rate at elevated pressures and to identify the chain mechanism on pressure variations. The sensitivity coefficients are calculated by $S_i = \frac{k_i}{m^0}\frac{\partial m^0}{\partial k_i}$, where k_i is the reaction rate for the ith elementary reaction.

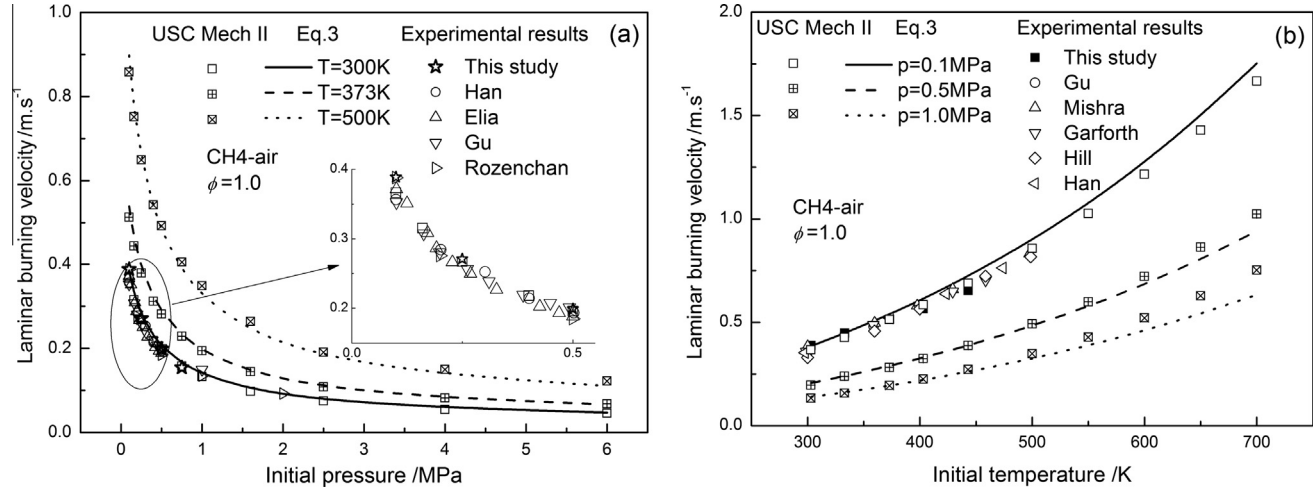

Fig. 5. Laminar flame speeds at different pressures and temperatures.

Augmentation of chain branching reaction causes the increases the concentrations of hydrogen and hydroxyl radicals and other highly reactive radical species, which promotes the laminar flame speed. In contrast, augmentation of chain termination reaction will have a negative effect to laminar flame speed because of its consumption of radical species.

Fig. 4 gives the top 16 sensitive reactions for the stoichiometric methane–air flames at different pressures, including five chain branching/propagation reactions and five chain termination reactions. R1 is the dominant chain branching reaction, which produces a great amount of O and OH radicals in the burning process. R9, R12 and R88 consume active H radicals in the burning and

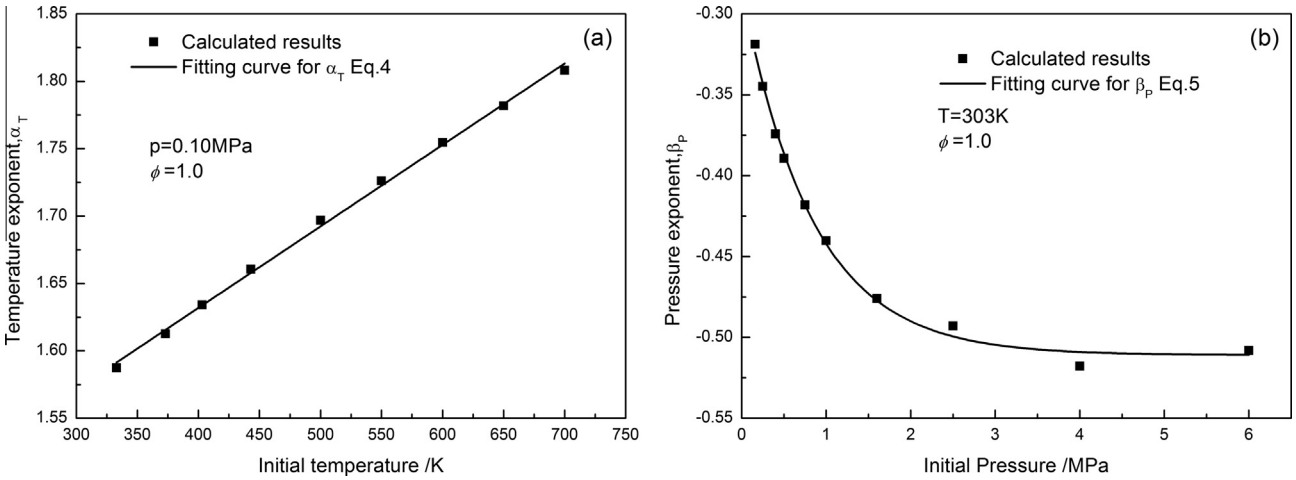

Fig. 6. Temperature exponent α_T and pressure exponent β_P for stoichiometric methane–air flames.

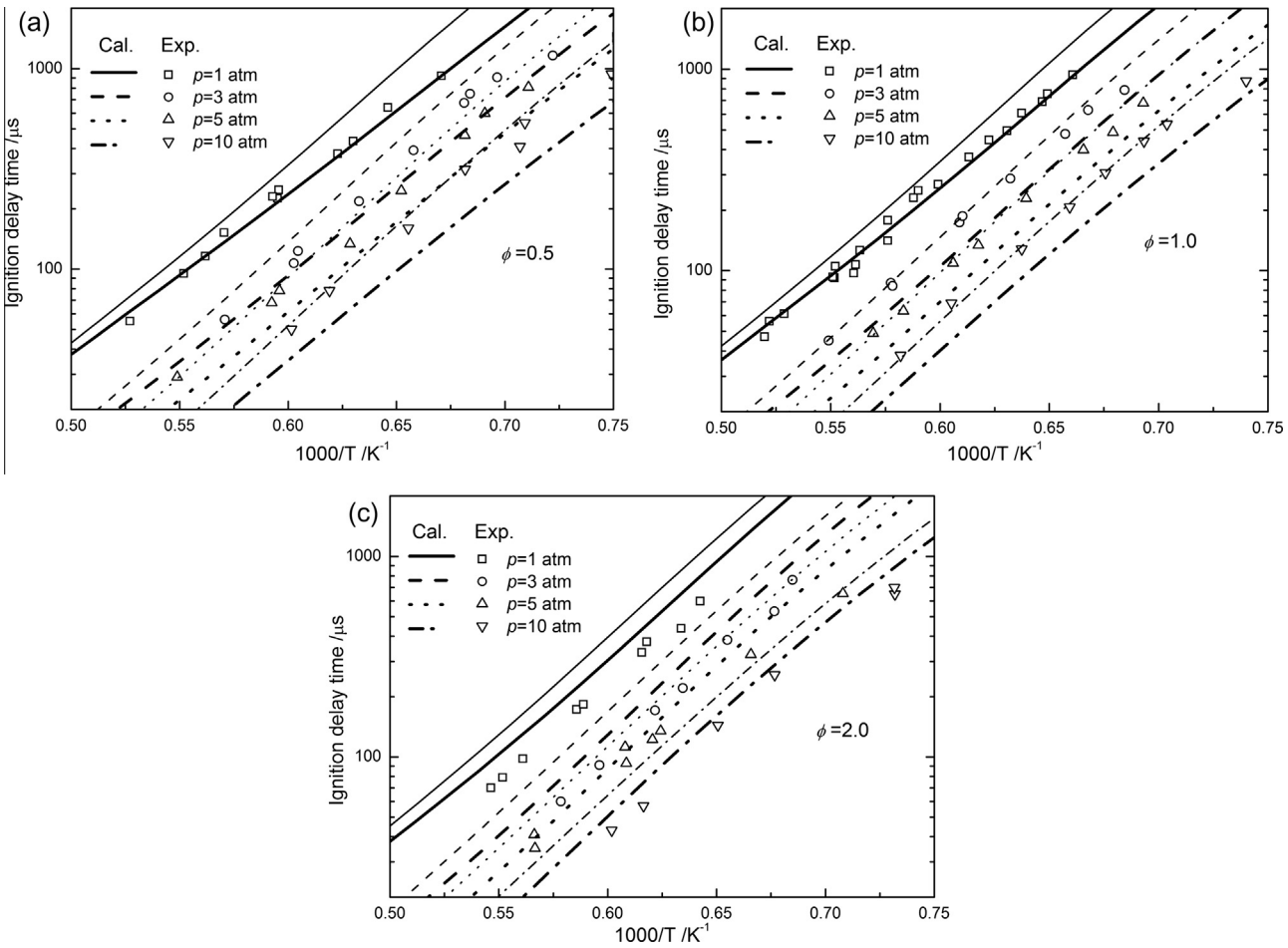

Fig. 7. Experimental and calculated ignition delay times of methane–air mixtures. Symbols: Measurements; Thick lines: Calculations with GRI Mech 3.0; Thin lines: Calculations with Aramco Mech 1.3.

therefore are the main chain termination reactions. For these four important elementary reactions, the sensitivity shows a non-monotonic behavior when pressure varies from 0.1 to 10 MPa.

The sensitivity factors of termination reactions (R9, R12 and R88) show a greater increase compared to those of main branching reaction R1, leading to the initial decrease of n when pressure is less than 1.0 MPa as shown in Fig. 3. When the pressure is further increased, the following chain branching reactions are presented and their sensitive factors become larger

$$CH_3 + O_2 = CH_3O + O \quad (R93)$$

$$CH_3 + HO_2 = CH_3O + OH \quad (R96)$$

Reaction (R93) is an endothermic reaction with relatively large activation energy (about 120 kJ/mol [38,39]); thus it is rather slow for a chain step especially at low pressures. CH_3O radicals that are produced by R93 decomposes mainly and immediately via

$$CH_3O(+M) = CH_2O + H(+M) \quad (R81)$$

As a chain branching reaction, reaction (R93) is quite slow. The very rapid decomposition reaction of methoxy, reaction (R81) follows it and produces formaldehyde and two very reactive radicals (O and H) through this two-step process. Similarly, reaction (R96) is also important and contributes a reactive OH radical. These radicals promote chain branching than the lower-pressure step. This behavior contributes to the subsequent increase in n when p is larger than 1.0 MPa.

3.4. Laminar flame speed correlations

Laminar flame speed is an important and fundamental property of combustible mixtures in many CFD combustion models [40]. Therefore, it is necessary to provide the correlation of laminar flame speed as a function of pressure and temperature. Because correlations are more easily utilized in CFD codes than the tabulated data, many researchers give their own correlations of laminar flame speeds.

Fig. 5 plots the laminar flame speeds of methane–air flames at different pressures and temperatures, combining with some literature data [30,31,41–45]. It is noted that the increase of initial pressure will decrease S_u and the increase of initial temperature will cause it to increase exponentially. From the classical theory of laminar flame speed [36,46], the variation of laminar flame speed versus pressure and temperature is in the form of $S_u \propto p^{\frac{n}{2}-1} \exp\left(-\frac{E_a}{2RT_{ad}}\right)$ (Here, n is the overall reaction order, E_a is overall reaction activation). Correlations of data on pressure and temperature are as follows,

$$S_u(p) = 0.133p^{-0.461},$$
$$R^2 = 0.9842 (T = 300\ \text{K},\ 0.1\ \text{MPa} \leqslant p \leqslant 6.0\ \text{MPa}) \quad (1)$$

$$S_u(T) = 325 \exp\left(-\frac{9439}{T + 1089}\right),$$
$$R^2 = 0.9999, (p = 0.10\ \text{MPa},\ 300\ \text{K} \leqslant T \leqslant 700\ \text{K}) \quad (2)$$

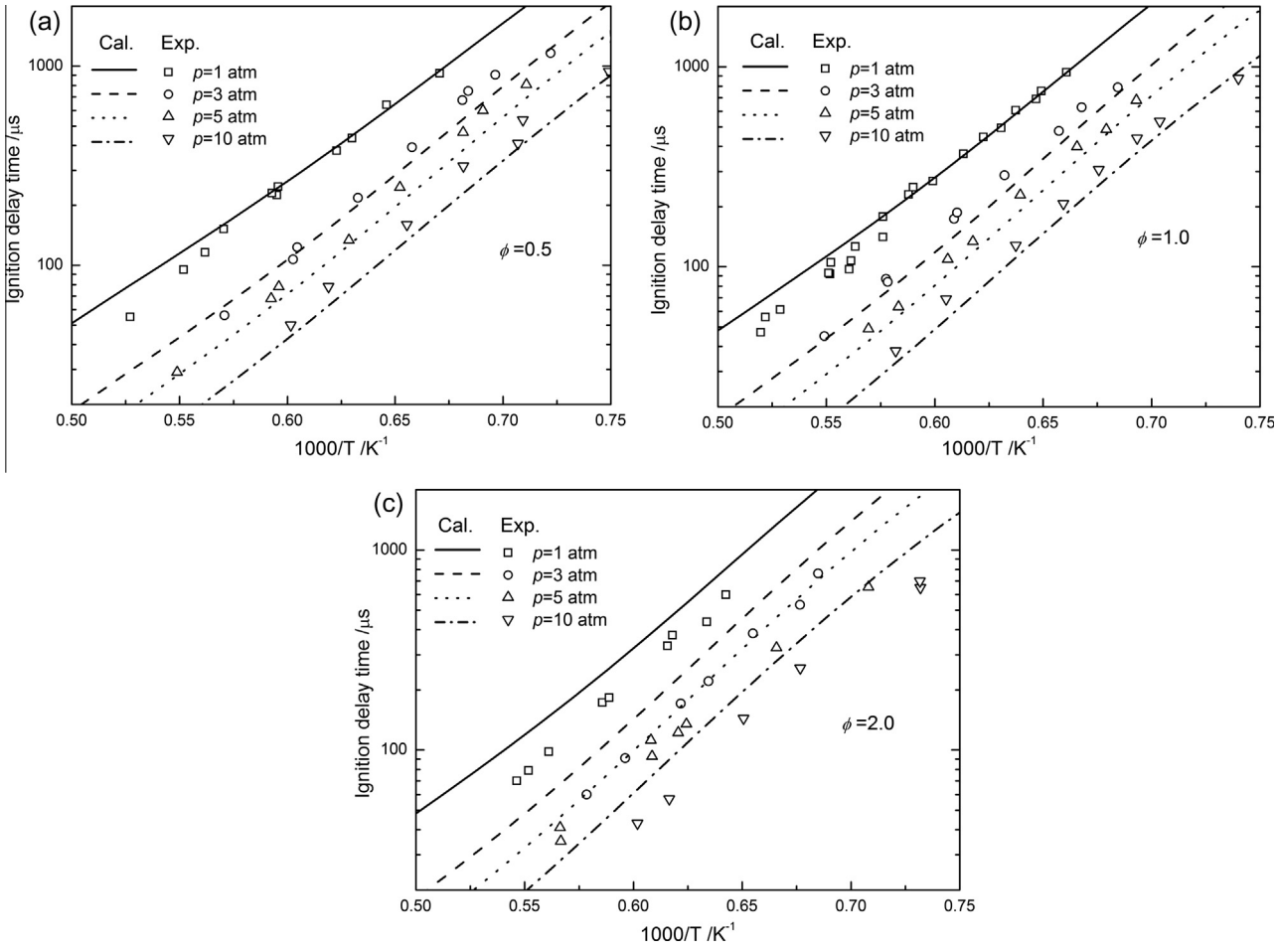

Fig. 8. Experimental and calculated ignition delay times of methane–air mixtures by USC Mech II. Symbols: Measurements; Lines: Calculations with USC Mech II.

There is a high level of agreement of the correlations and the results with USC Mech II mechanism since the coefficients are greater than 0.98. Because of the good prediction of the USC Mech II mechanism over the experimental laminar flame speed at the stoichiometric mixture, here we use the calculated results to represent the experimental data at the extended pressures and temperatures. It is also noted that the formats of Eqs. (1) and (2) are similar to their respective effect $\left(p^{\frac{n}{2}-1}\right.$ and $\left.\exp\left(-\frac{E_a}{2RT_{ad}}\right)\right)$.

From the calculation, the effects of temperature and pressure on laminar flame speed are correlated by following expression,

$$S_u = S_{u0}(T/T_0)^{\alpha_T}(p/p_0)^{\beta_P} \tag{3}$$

where the subscript 0 represents the reference condition, they are, $T_0 = 300$ K and $p_0 = 0.10$ MPa in this study. Parameters α_T and β_P depend on temperature and pressure, respectively. The, S_{u0} is the laminar burning velocity of the stoichiometric mixtures under the reference condition.

Fig. 6 gives the temperature exponent α_T and pressure exponent β_P for the stoichiometric methane–air flames. Variation of α_T, determined by $\alpha_T = \ln(S_u/S_{u0})/\ln(T/T_0)$, at an initial pressure of 0.10 MPa. α_T increases linearly with the increase of initial temperature. From the calculated values, a linear equation is fitted for the temperature exponent,

$$\alpha_T = 1.39 + 0.0006T,\ R^2 = 0.9977(300\ \text{K} \leqslant T \leqslant 700\ \text{K}) \tag{4}$$

The same method as temperature exponent is applied in the correlation of the pressure exponent at $T_u = 300$ K, determined in $\beta_P = \ln(S_u/S_{u0})/\ln(p/p_0)$. It can be observed in Fig. 6b that the pressure exponent β_P decreases with the increase of pressure. β_P as the function of initial pressure is correlated by,

$$\beta_P = 0.226\exp(-p/0.841) - 0.511,$$
$$R^2 = 0.9946(0.1\ \text{MPa} \leqslant p \leqslant 6.0\ \text{MPa}) \tag{5}$$

From the above comparisons, the calculated laminar flame speeds with USC Mech II mechanism agree reasonably with the experimental results. To validate the Eq. (3), Fig. 5 gives the comparison to the experimental results from literatures and calculated results by using Premix with USC Mech II mechanism under other initial conditions. Under higher temperature and higher pressure conditions, the calculations with Eq. (3) are in good agreement with those of USC Mech II predictions.

3.5. Measurements and model validations on ignition delay time

Figs. 7 and 8 show the measured ignition delay times of methane–air mixtures at different equivalence ratios and pressures and predictions with three kinetic models. At atmospheric pressure, GRI Mech 3.0 and USC Mech II can well predict the ignition delay time of methane–air mixtures for fuel lean and

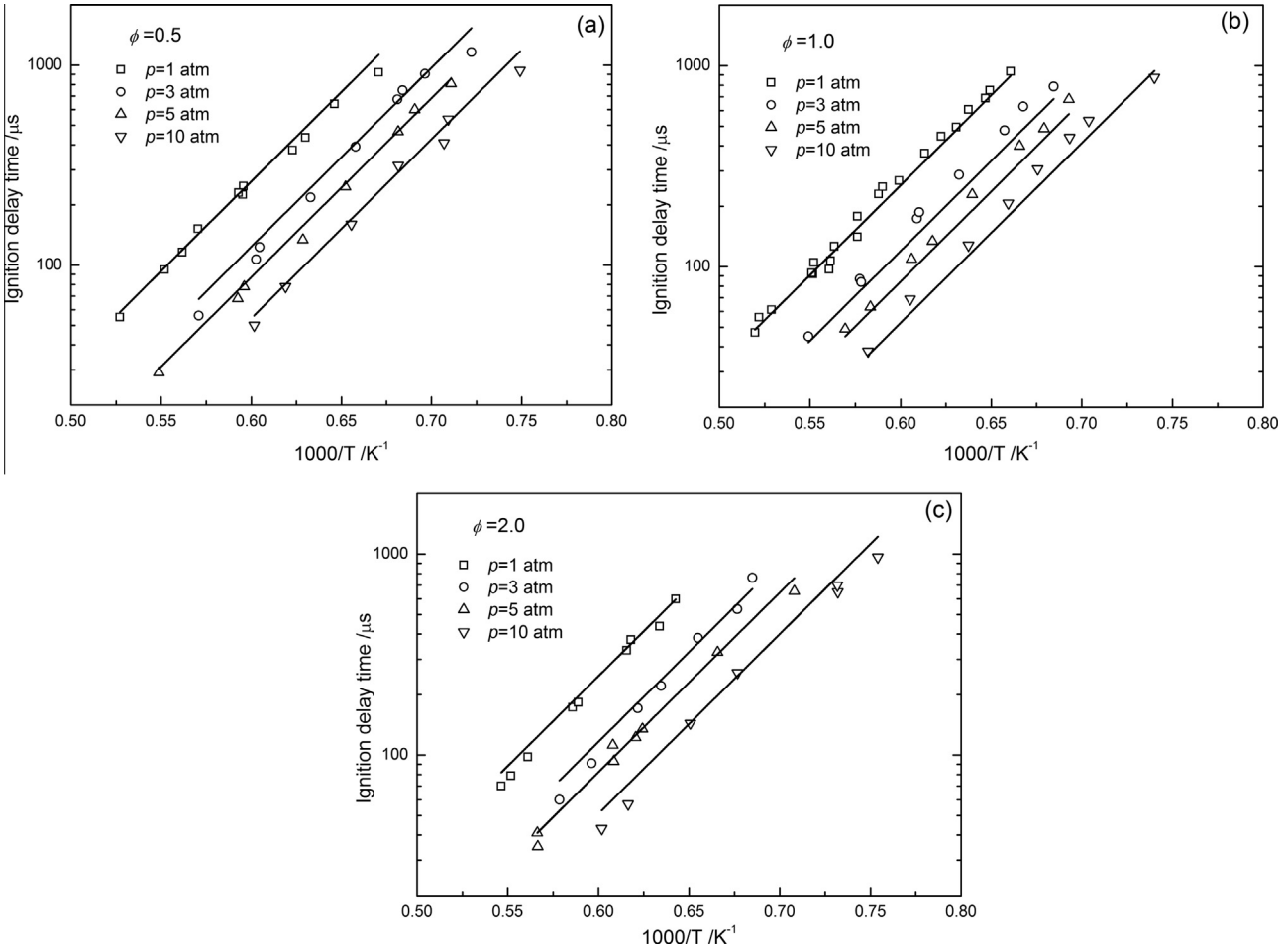

Fig. 9. Measured and fitted ignition delay times of methane–air mixtures. Symbols: Measurements; Lines: Fitted values using Eq. (6)).

stoichiometric mixtures, but Aramco Mech 1.3 overpredicts. These three kinetic models give the overpredictions for the fuel rich mixtures.

When the pressure is increased, the underpredictions with GRI Mech 3.0 are presented and the discrepancy is increased for the fuel lean and stoichiometric mixtures. For the fuel rich mixtures, GRI Mech 3.0 gives the overpredictions on the ignition delay times, but the discrepancy is smaller. Because many rate constants of USC Mech II are taken from GRI Mech 3.0, the USC Mech II calculations give only a slightly larger than those of GRI Mech 3.0, and the predictions by two kinetic models on the ignition delay time of methane–air mixtures are similar. Aramco Mech 1.3 is the latest model among the three models. It gives good predictions on ignition delay times of fuel lean and stoichiometric mixtures at high pressure, but gives overprediction for the fuel rich mixtures.

3.6. Correlation on the ignition delay time

Fig. 9 gives the measured ignition delay times of methane–air mixtures. Good linear dependence of logarithmic ignition delay times upon $1000/T$ is noted under different test conditions. Therefore, fitting correlations of ignition delay times as a function of p, ϕ and T for the methane–air mixture are correlated through regression as follows:

$$\tau = 1.09 \times 10^{-3} p^{-0.68} \phi^{-0.04} \exp\left(\frac{40.98 \pm 0.51 \text{ kcal} \cdot \text{mol}^{-1}}{RT}\right), \quad R^2 = 0.983 \tag{6}$$

where τ is ignition delay time in μs, p is pressure in atm, ϕ is equivalence ratio, $R = 1.986 \times 10^{-3}$ kcal/(mol K) is the universal gas constant, and T is temperature in K. Eq. (6) gives good regression ($R^2 > 0.98$) on the measured ignition delay times. Because of the experimental range of this study, this correlation is applicable to the temperature range of 1300–1900 K, pressure range of 1.0–10 atm, equivalence ratio range of 0.5–2.0.

4. Conclusions

Experimental and numerical study on laminar flame speeds and ignition delay times of methane–air mixtures were conducted by using the constant volume bomb, shock tube and Chemkin package. Laminar flame speed, ignition delay time, reaction order, sensitivity analysis and reaction rate analysis were performed at different initial pressures and temperatures. Correlations for laminar flame speed and ignition delay time were provided. The main results are summarized as follows:

1. Laminar flame speeds from constant volume bomb measurement from various studies are in good agreement. Data with the linear extrapolation method are slightly higher than those from the counter flow flame measurements for the fuel rich mixtures and lower for the fuel lean mixtures. At rich mixtures, the laminar flame speeds with linear method are higher than that with non-linear method. The non-linear extrapolation method is more reasonable than linear method especially for rich mixtures of methane.
2. GRI Mech 3.0 model gives slightly lower laminar flame speed than USC Mech II model for the fuel lean mixtures. The three kinetic models (GRI Mech 3.0, USC Mech II, Aramco Mech 1.3) can well predict the laminar flame speed for different pressures at high temperatures and pressures.
3. Overall reaction order decreased first and then increased with the increase of pressure because of the chain reaction mechanism.
4. At atmospheric pressure, GRI Mech 3.0 and USC Mech II well predict the ignition delay time of methane–air mixtures for fuel lean and stoichiometric mixtures, but give overpredictions for fuel rich mixtures. At elevated pressures, GRI Mech 3.0 and USC Mech II give the underpredictions and the discrepancy is increased for the fuel lean and stoichiometric mixtures. The two models give the overpredictions on for fuel rich mixtures with small discrepancy. Aramco Mech 1.3 gives good predictions on the ignition delay times of fuel lean and stoichiometric mixtures at high pressure, but gives overprediction for fuel rich mixtures.

Acknowledgments

This study is supported by the National Natural Science Foundation of China (91441118) and the State Key Laboratory of Engines at Tianjin University (SKLE201502). The support from the Fundamental Research Funds for the Central Universities is also appreciated.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2015.05.010.

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