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Shock tube study on ignition delay of multi-component syngas mixtures – Effect of equivalence ratio

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ABSTRACT

Ignition delays were measured in a shock tube for syngas mixtures with argon as diluent at equivalence ratios of 0.3, 1.0 and 1.5, pressures of 0.2, 1.0 and 2.0 MPa and temperatures from 870 to 1350 K. Results show that the influences of equivalence ratio on the ignition of syngas mixtures exhibit different tendency at different temperatures and pressures. At low pressure, the ignition delay increases with an increase in equivalence ratio at tested temperature. At high pressures, however, an opposite behavior is presented, that is, increasing equivalence ratio inhibits the ignition at high temperature and vice versa at intermediate temperature. The affecting degree of equivalence ratio on ignition delay is different for each mixture at given condition, especially for the syngas with high CO concentration. Sensitivity analyses demonstrate that reaction $H + O_2 = O + OH$ (R1) dominates the syngas oxidation under all conditions. With the increase of CO mole fraction, reactions $CO + OH = CO_2 + H$ (R27) and $CO + HO_2 = CO_2 + OH$ (R29) become more important in the syngas ignition kinetics. With the increase of pressure, the reactions related to HO_2 and H_2O_2 play the dominate role. The opposite influence of equivalence ratio on ignition delay at high- and intermediate-temperatures is chemically interpreted through kinetic analyses.

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Introduction

Energy with high efficiency and low emissions can be produced from syngas by using the advanced combustion technology – Integrated Gasification Combined Cycle (IGCC). Syngas is expected to play an important role in future energy. The fuel flexibility of gas turbines has been acknowledged because composition of gas turbine fuels

can be varied from one gas to another. To ensure the consistency, reliability and efficiency of the gas turbine if syngas is considered as a real source, it is necessary to design a combustor with the adaptability and reliability, based on the ignition characteristics of syngas systems. Variations in the H_2/CO ratio along with various concentrations of N_2 , H_2O , CO_2 , CH_4 , and impurities have considerable influence on the performance and operability of combustion device [1,2].

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The H_2/CO system was previously studied over wide range of conditions in some facilities. Shock tube was used to investigate the kinetics of H_2/CO oxidation under high temperature and low pressure conditions [3–5]. Kalitan et al. [6] reported the ignition delay of lean syngas/air mixtures with various CO/H_2 blending ratios at temperatures from 890 to 1300 K and pressures of 0.1, 0.25 and 1.5 MPa. They indicated that current kinetic models were in good agreement with the experimental data at high temperature and low pressure, but some differences between the predictions and experiments presented at lower temperature and higher pressure. Ignition delays of lean $H_2/CO/O_2/Ar$ mixtures were also measured by Herzler and Naumann [7] at temperatures from 1020 to 1260 K and pressure of 1.6 MPa. They found that none of the mechanisms can well reproduce the experiments, and believed that hydrogen chemistry dominated the kinetic system of H_2/CO fuel blend when hydrogen fraction less than 50%. Moreover, the ignition delays of CO/H_2 /air mixtures were studied by Petersen et al. [8] under practical conditions (940–1148 K, 1.7–3.3 MPa). Although the equivalence ratios varied from 0.33 to 0.6, limited experimental data are really not enough to examine the effect of equivalence ratios on the ignition delay. Sivaramakrishnan et al. [9] studied the oxidation of H_2/CO mixtures in a high pressure shock tube at pressures of 2.1–50 MPa. Their experiment showed that CO oxidation is inhibited as pressure is increased. Recently, Mathieu et al. [10] studied the effects of NH_3 impurity on the ignition of a real syngas produced from biomass at temperatures from 990 to 2000 K and pressures of 0.16, 1.25 and 3.2 MPa. They indicated that the syngas composition could significantly affect the ignition delay, but NH_3 had only negligible effect. Mittal et al. [11] studied the ignition delay of $H_2/CO/O_2$ mixtures with CO fractions from 0% to 80%, temperatures from 950 to 1100 K, pressures from 1.5 to 5.0 MPa, and equivalence ratios from 0.36 to 1.6 in a rapid compression machine. They suggested that the reaction involving chemical properties of HO_2 and H_2O_2 were important to H_2/CO oxidation at moderate temperature and high pressure. Fotache et al. [12] reported a non-premixed ignition in counter-flow CO/H_2 vs. heated air

jets. They found that the temperature range of the glow regime and the glow intensity decreased with the increase of hydrogen fraction, and the glow could not be detected when hydrogen fraction over than 73%. Yetter et al. [13–15] and Roesler et al. [16] studied the moist CO oxidation in an atmospheric pressure flow reactor, and the mixture was also studied in a variable pressure flow reactor by Kim et al. [17] at temperatures of 850–1200 K and pressures of 0.96 MPa. They developed a detail kinetic mechanism of syngas. Walton et al. [18] studied the simulated ignition of syngas mixtures ($H_2/CO/O_2/N_2/CO_2$) with H_2/CO ratios from 0.25 to 4.0 under the conditions relevant to gas turbine utilization. They provided a simplified Arrhenius correlation to calculate ignition delays of syngas for designing combustor. More recently, the author conducted the study on ignition delay of multi-composition syngas using shock tube [19]. Behind the reflected shock conditions covered the temperatures of 870–1350 K, pressures of 0.2–2.0 MPa at equivalence ratio of 1.0. Six kinetic models were carefully evaluated by measured ignition delay data and found that none of them could well predict the experimental observation.

Although ignition delays of syngas have been extensively studied, the effect of equivalence ratio on the ignition did not reported and chemically interpreted. The objective of this study is to provide new ignition delay data of syngas mixtures over wide range of conditions by a shock tube, and to interpret the effect of equivalence ratios on the ignition.

Experimental setup and simulation procedure

Shock tube experiment

All experiments were performed behind the reflected shock wave in a stainless-steel shock tube facility [20]. Details on the layout is presented in Fig. 1. The facility has a 5.3-m long driven section and a 4.0-m long driver section with diameter of 11.5 cm. Double polycarbonate diaphragms separate the driver and driven sections before the experiment, and a shock

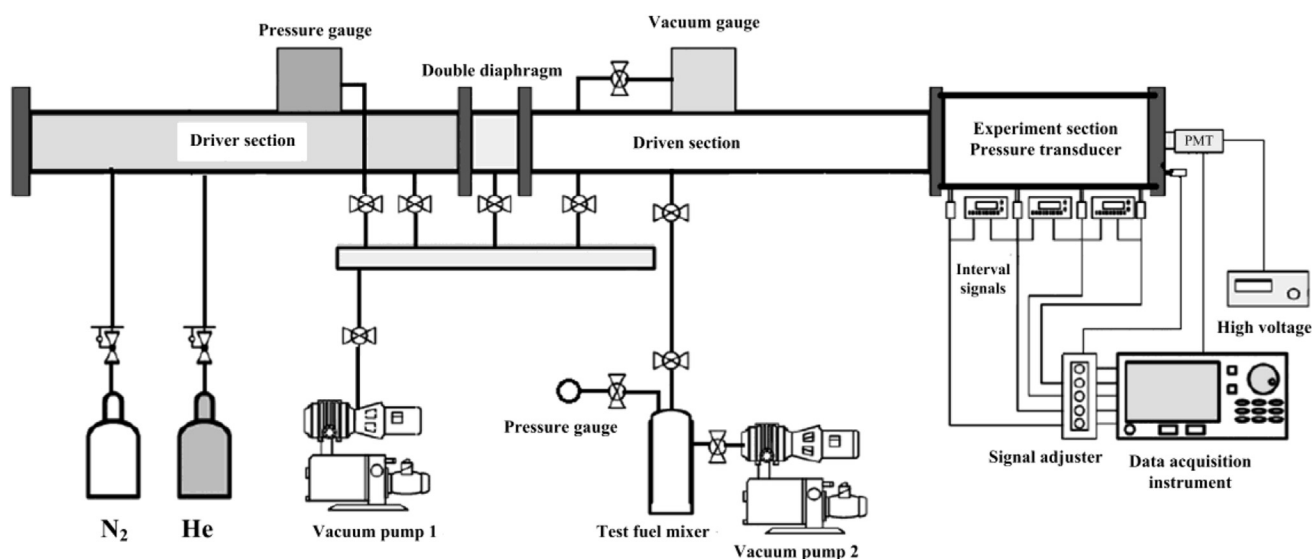


Fig. 1 – Schematic diagram of shock tube.

wave is generated by bursting the diaphragms. Tailored gas mixtures of nitrogen and helium were used as the driver gas to achieve reflected shock long test times.

The reactant mixtures were prepared separately in a 128 L stainless-steel tank according to the partial pressure of each gas component, and the mixtures were kept 12 h to obtain a perfect mixing. Purities of H₂, CO, CO₂, N₂, O₂ and argon are 99.999%, 99.99%, 99.99%, 99.999%, 99.99% and 99.995% respectively. Table 1 and Table 2 give the compositions and content of the tested syngas mixtures. Before each experiment, the shock tube was evacuated to the pressure below 10⁻⁶ bar by a Nanguang vacuum system. Reliability of the facility has been validated in the previous works for various fuel mixtures and under different conditions [20,21].

Four fast-response pressure transducers are mounted at fixed intervals of 30 cm along the end part of driven section. Three time counters are used to record the time intervals when the incident shock wave passes each pressure transducer. The incident shock velocity at the end-wall is determined by linear extrapolating the shock velocity profile to the end-wall. Typical attenuation rates of the incident shock are found to be approximately 1%. On the end-wall, another pressure transducer is installed to measure the pressure behind the reflected shock wave. Also, OH* emission (wavelength of 307 nm) at the same position was captured by a photomultiplier through a narrow band pass filter. The temperature behind the reflected shock wave is calculated by the chemical equilibrium software GASEQ [22] using assumption of frozen chemistry. The typical uncertainty of the temperature is about ±16 K.

Ignition delay is defined as the time interval between the arrival of the reflected shock wave at the end-wall and the onset of ignition, which is determined by the extrapolation of the steepest rise in the OH* chemiluminescence to the zero baseline, as shown in Fig. 2. Note that a pressure rise ($dp/dt = 4.22\%/ms$) before ignition was observed due to the non-ideal gas-dynamic effect, and this was taken into account in the simulation for ignition delay.

Computational kinetic mechanism and simulation method

In this study, the latest updated kinetic mechanism, NUIG-H₂/CO Mech [23] developed by Combustion Chemistry Center of National University of Ireland (NUI), was chosen to calculate the ignition delay and conduct the kinetic analysis. The kinetic model includes 15 species and 41 elementary reactions. The detailed chemical kinetic mechanism is based on the hierarchical nature of combustion mechanisms of H₂/O₂ mixtures [24] which has been validated by the hydrogen experiments of Mittal et al. [11]. In NUIG-H₂/CO Mech, several key reaction rates were re-evaluated and modified using the

Table 2 – Composition of the reactant mixtures investigated.

Mixtures	ϕ	% H ₂	% CO	% CO ₂	% N ₂	% O ₂	% Ar
SH70	0.3	1.58	0.67	0	0	3.75	
	1.0	2.81	1.19	0	0	2	94
	1.5	3.16	1.34	0	0	1.5	94
SH33	0.3	0.75	1.50	0	0	3.75	94
	1.0	1.33	2.67	0	0	2	94
	1.5	1.5	3	0	0	1.5	94
SH50C30	0.3	0.96	0.98	0.83	0	3.23	94
	1.0	1.54	1.57	1.34	0	1.55	94
	1.5	1.68	1.72	1.46	0	1.13	94
SH26N58	0.3	0.4	1.09	0	2.02	2.49	94
	1.0	0.56	1.54	0	2.85	1.05	94
	1.5	0.6	1.63	0	3.02	0.74	94

recently published rate constants. For example, the reaction rate of chain branching reaction $H + O_2 = O + OH$ was replaced by the value measured of Hong et al. [25], and those of pressure-dependent reactions $H + O_2 (+M) = HO_2 (+M)$ and $H_2O_2 (+M) = OH + OH (+M)$ were replaced by the values of Fernandes et al. [26] and Bates et al. [27]. In addition, elementary reactions related to OH* emission were added into this mechanism.

Ignition delays of the syngas mixtures were simulated using the CHEMKIN II package [28] with SENKIN code [29]. Here the pressure rise effect (dp/dt) was taken into account in the simulation for ignition delay. Chaos et al. [30] proposed a SENKIN/VTIM approach to improve predictions in ignition delays and yield very similar values to those computed using the CHEMSHOCK model proposed by Li et al. [31] for the low concentration mixtures at moderate-low temperature. In this study, the SENKIN/VTIM proposed was used to calculate the ignition delays.

To further confirm the reasonability of SENKIN/VTIM approach, the measured ignition delays were compared with the predictions using both SENKIN/VTIM approach and conventional constant U, V assumption with NUIG-H₂/CO mechanism [23] for the SH70 mixture at pressure of 1.0 MPa,

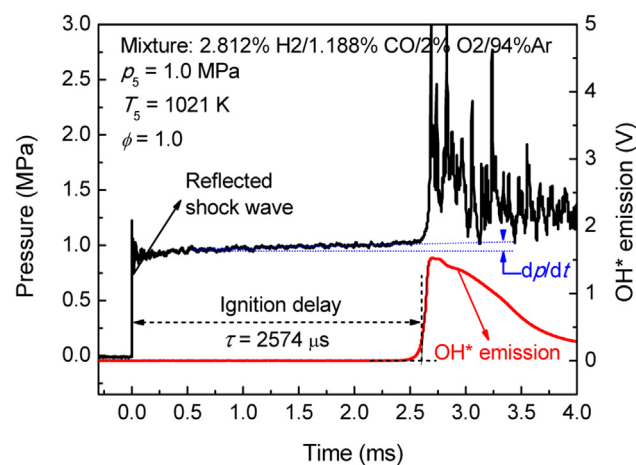


Fig. 2 – Ignition delay measurement from endwall pressure and OH* emission. Experiment was performed with stoichiometric mixture of syngas SH70 at 1.0 MPa and 1021 K.

Table 1 – Composition of syngas studied.

Mixtures	% H ₂	% CO	% CO ₂	% N ₂	% H ₂ /(H ₂ + CO)
SH70	70	30	0	0	70
SH33	33	67	0	0	33
SH50C30	35	35	30	0	50
SH26N58	11	31	0	58	26

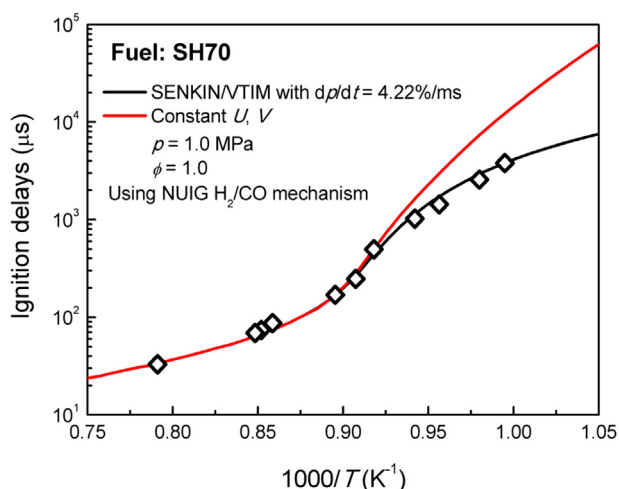


Fig. 3 – Comparison between the calculations performed using SENKIN/VTIM with $dp/dt = 4.22\%/ms$ and constant U, V assumption. Measured ignition delays of syngas SH70 are also plotted.

as shown in Fig. 3. Result shows that the ignition delays predicted by the two methods are in good agreement with measurements at temperature above 1100 K. At temperature below 1100 K, however, the measured ignition delays are only consistent with those predicted by the SENKIN/VTIM,

and are shorter than those predicted by the constant U, V assumption.

Results and discussion

All experiments were covered four syngas mixtures (SH70, SH33, SH50C30 and SH26N58) in the ranges of temperatures from 870 K to 1350 K, pressures of 0.2, 1.0 and 2.0 MPa, and equivalence ratios of 0.3, 1.0 and 1.5. Experimental data and conditions are provided in the [Supplementary Materials](#). In the following section, the effects of equivalence ratio on the ignition delays of multi-component syngas will be examined at pressures of 0.2, 1.0 and 2.0 MPa, respectively.

Ignition delays at low pressure

Fig. 4 gives the simulated and measured ignition delays of four syngas at the pressure of 0.2 MPa. The predictions are generally in good agreement with the measurements. Under the fuel-rich condition, the NUIG- H_2/CO mechanism gives slight over-prediction for all tested syngas mixtures. A negligible effect of equivalence ratio is exhibited at the relatively low temperature ($T < 920$ K). However, with an increase of temperature, the inhibiting effect on the ignition becomes significant with an increase in the equivalence ratios. In other words, fuel-lean mixture has high reactivity due to the sufficient oxygen molecule in the fuel oxidation, whereas low

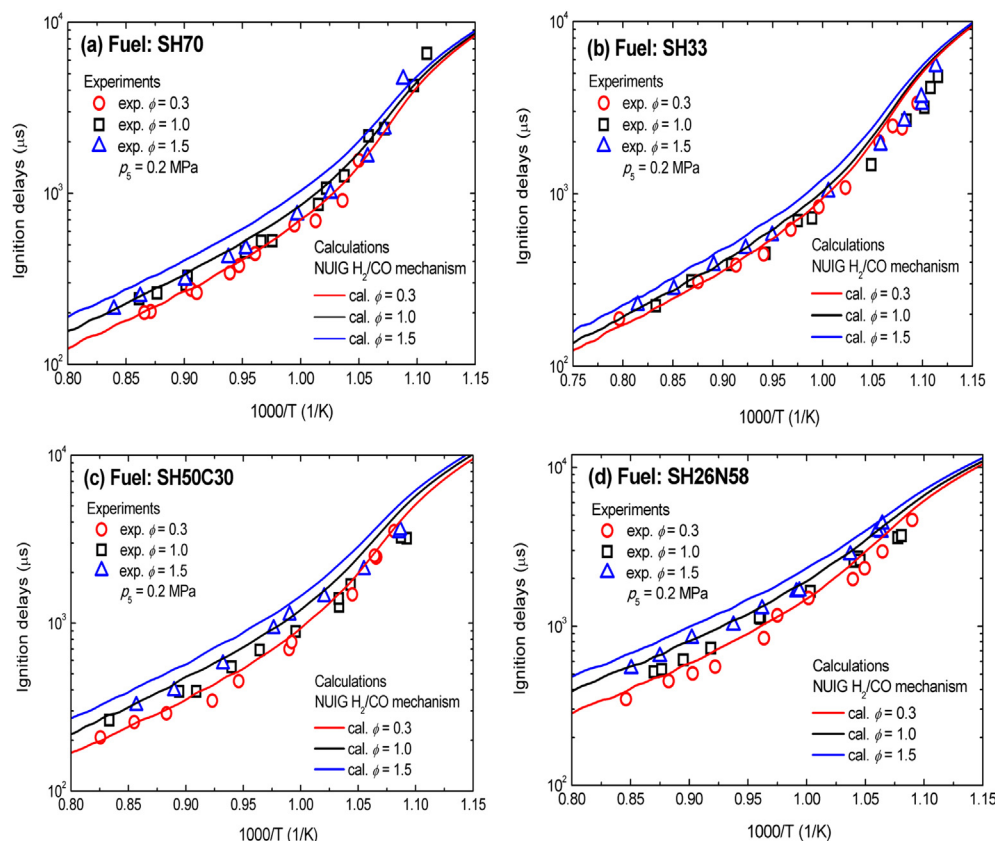


Fig. 4 – Ignition delays of syngas mixtures at different equivalence ratios and $p = 0.2$ MPa. (a) Syngas SH70; (b) Syngas SH33; (c) Syngas SH50C30; (d) Syngas SH26N58.

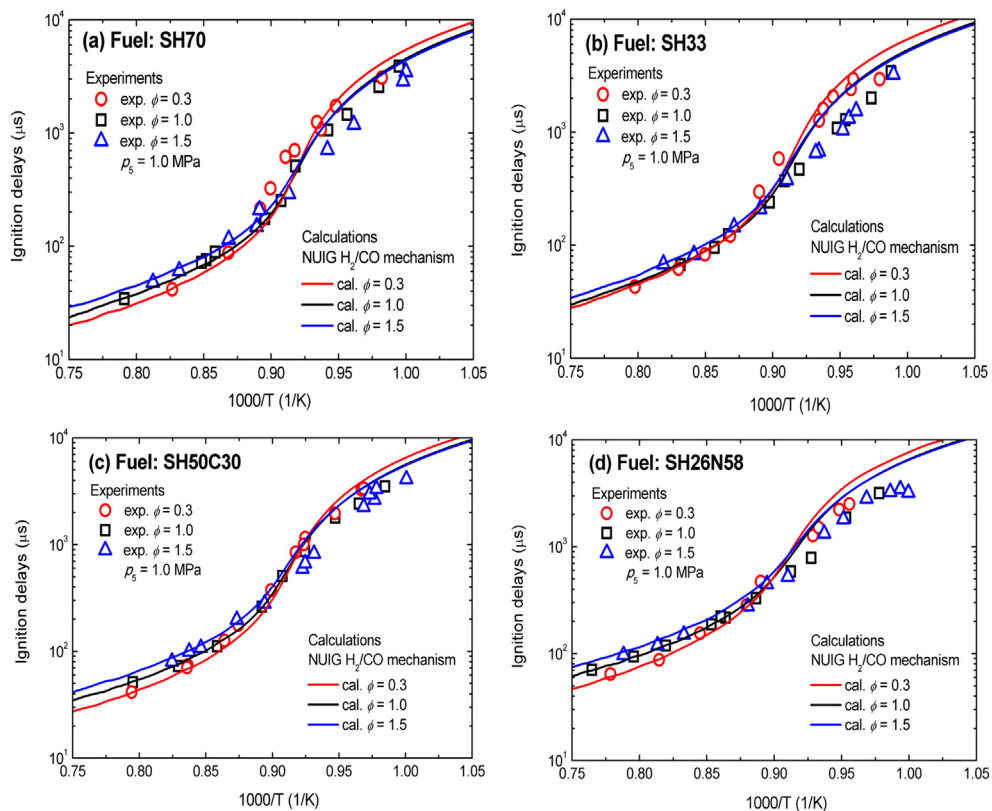


Fig. 5 – Ignition delays of syngas mixtures at various equivalence ratios and $p = 1.0$ MPa. (a) Syngas SH70; (b) Syngas SH33; (c) Syngas SH50C30; (d) Syngas SH26N58.

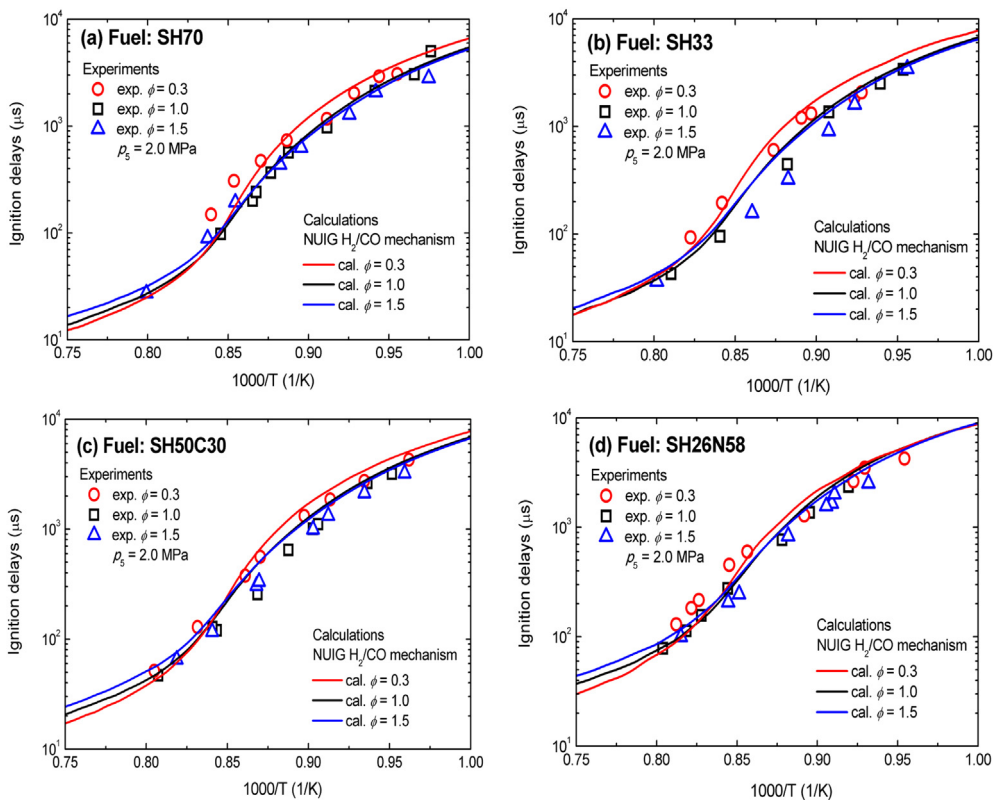


Fig. 6 – Ignition delays of syngas mixtures at various equivalence ratios and $p = 2.0$ MPa. (a) Syngas SH70; (b) Syngas SH33; (c) Syngas SH50C30; (d) Syngas SH26N58.

reactivity of fuel-rich mixture is due to the insufficiency oxygen molecule. It can be explained that the concentrations of free radicals, OH, O and H are really considerably high at high temperature and low pressure due to the slow reaction rate of pressure-dependent reaction and the active cycle of chain branching. With increasing the mole fraction of oxygen molecular in the test mixture, the free radicals will be significantly increased, leading to accelerating the auto-ignition. Similar phenomenon was reported by Zhang et al. [29] in the study on the ignition of methane and hydrogen mixtures. It is noted that the convergence only appears at the temperature around 900 K and low pressure condition. For higher pressure (1.0 and 2.0 MPa), however, this phenomenon will occur at the temperature below 900 K [32], and it will be evidenced in following section of this study.

The effects of equivalence ratio on the ignition delay show a similar trend for the four syngas mixtures. Among them, syngas containing higher concentration of inert gas, SH26N58, shows the most sensitive dependency, while syngas with the highest CO concentration, SH33, shows the most insensitive dependency on equivalence ratio. The cause for the equivalence ratio dependency is attributed to the discrepancy of syngas composition. Kéromnès et al. [23] and Mittal et al. [11] suggested that CO addition had an inhibiting effect on the H_2 chemistry, and this effect became significantly for the mixtures with CO concentration of 50% or higher. In this study, syngas SH33 has the highest CO concentration while CO concentrations in other three syngas mixtures are relatively

similar. It is noted that because the presence of incombustible component in the syngas SH26N58 causes the most significant mole fraction change of oxygen molecular when varying the equivalence ratios, leading to the large difference of global reaction rate at different equivalence ratios.

Ignition delays at moderate pressure

Fig. 5 gives the comparison between the measured and predicted ignition delays of the syngas mixtures at pressure of 1.0 MPa. Results show that NUIG- H_2/CO model can well capture the experimental data at temperatures over 1100 K, and shows a slight over-prediction at temperatures below 1100 K, especially for the fuel-stoichiometric and fuel-rich mixtures. Furthermore, an obvious influence of equivalence ratio on the ignition of syngas mixtures is presented under fuel-lean condition, but negligible influence under fuel-rich condition. A similar influence of equivalence ratio on the ignition delay with that at low pressure is presented at high temperature ($T > 1100$ K). Rich mixture exhibits the longest ignition delays while lean mixture presents the shortest ignition delays. The influence of equivalence ratio on the ignition delay is not distinct for the syngas SH33 due to higher CO concentration. At temperatures below 1100 K, the influence of equivalence ratio on ignition delay demonstrates an opposite trend to that at high temperature. Ignition delays increase with the decrease of equivalence ratio. The different effects of equivalence ratios on the ignition of syngas mixtures under higher

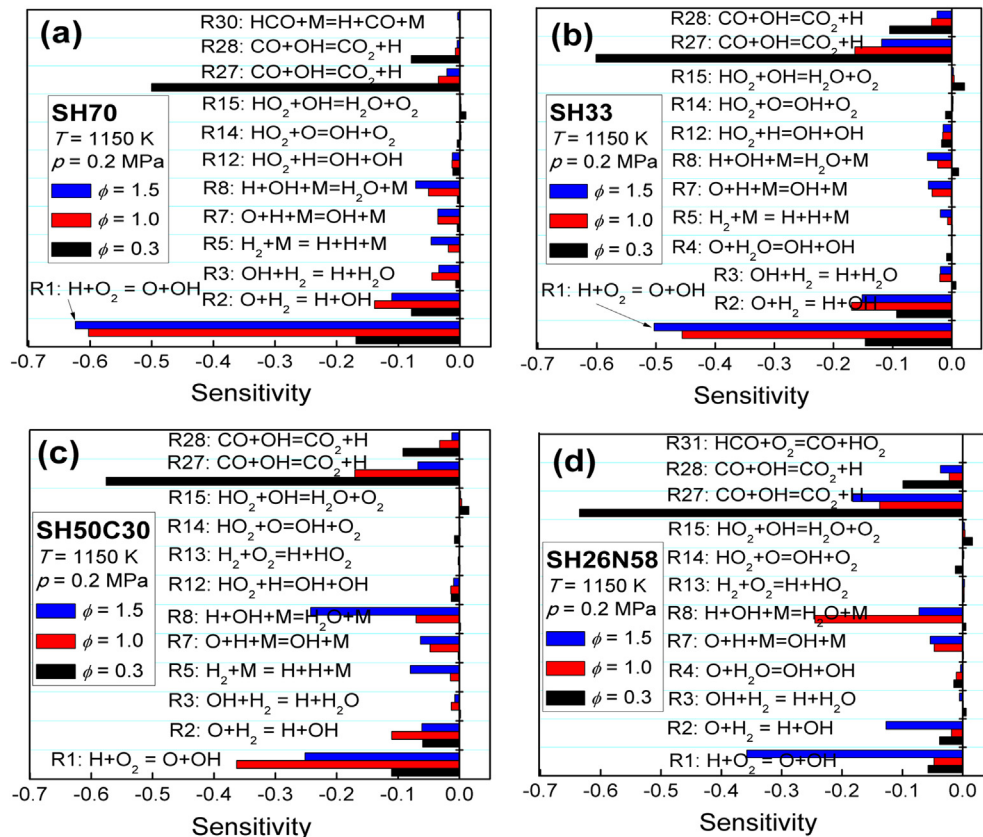


Fig. 7 – Sensitivity analysis of syngas mixtures at $p = 0.2$ MPa and $T = 1150$ K. (a) Syngas SH70; (b) Syngas SH33; (c) Syngas SH50C30; (d) Syngas SH26N58.

and lower temperatures can be explained through the competition between the chain branching reaction $H + O_2 = OH + H$ and chain termination reaction $H + O_2 (+M) = HO_2 (+M)$. The former dominates the ignition chemistry at high temperature while the latter dominates at intermediate to low temperatures. Furthermore, the experimental results show that the influence of equivalence ratio on the ignition delay of syngas mixtures is obvious under fuel-lean condition, but negligible under fuel-rich condition. This opposite influence of equivalence ratio on ignition delay at low- and high-temperatures certainly brings a cross point of both predicted and measured ignition delays. It is noted that the cross point shifts to the higher temperature at higher pressure.

Ignition delays at high pressure

Fig. 6 gives the measured and simulated ignition delays of the syngas mixtures at pressure of 2.0 MPa. In general, NUIG-H₂/CO model gives a better prediction on the ignition delays for the syngas mixtures. However, this mechanism over-predicts the ignition delays of fuel-rich SH33 mixture at intermediate temperature ($T < 1150$ K) and under-predicts those of fuel-lean SH70 and SH26N58 mixtures at high temperature ($T > 1160$ K). Compared with low and moderate pressures, the effect of equivalence ratio on the ignition

delay is insensitive, and the cross point shifts to a higher temperature (about 1190 K). Although weak effect of equivalence ratio on ignition delays is presented at high pressure, the model predictions still well captures the ignition dependency of equivalence ratio. For the syngas SH26N58, the ignition delay has little dependency at the entire temperature range.

Sensitivity analysis

To identify the dominant elementary reactions in the ignition process of syngas mixtures and interpret the chemical kinetic effect of equivalence ratio on ignition chemistry, the brute-force sensitivity analysis was made using the NUIG-H₂/CO mechanism. Rate constant of *i*th reaction k_i is individually multiplied and divided by a factor of 2, and the ignition delays $\tau(2.0k_i)$ and $\tau(0.5k_i)$ are calculated with the reaction rates of $0.5k_i$ and $2.0k_i$, respectively. Normalized sensitivity coefficient of the *i*th reaction defined as,

$$S = \frac{\tau(2.0k_i) - \tau(0.5k_i)}{1.5\tau(k_i)} \quad (1)$$

Where, k_i is rate constant of *i*th reaction, τ is ignition delay. A negative value of sensitivity coefficient indicates a promoting effect on ignition, and vice versa.

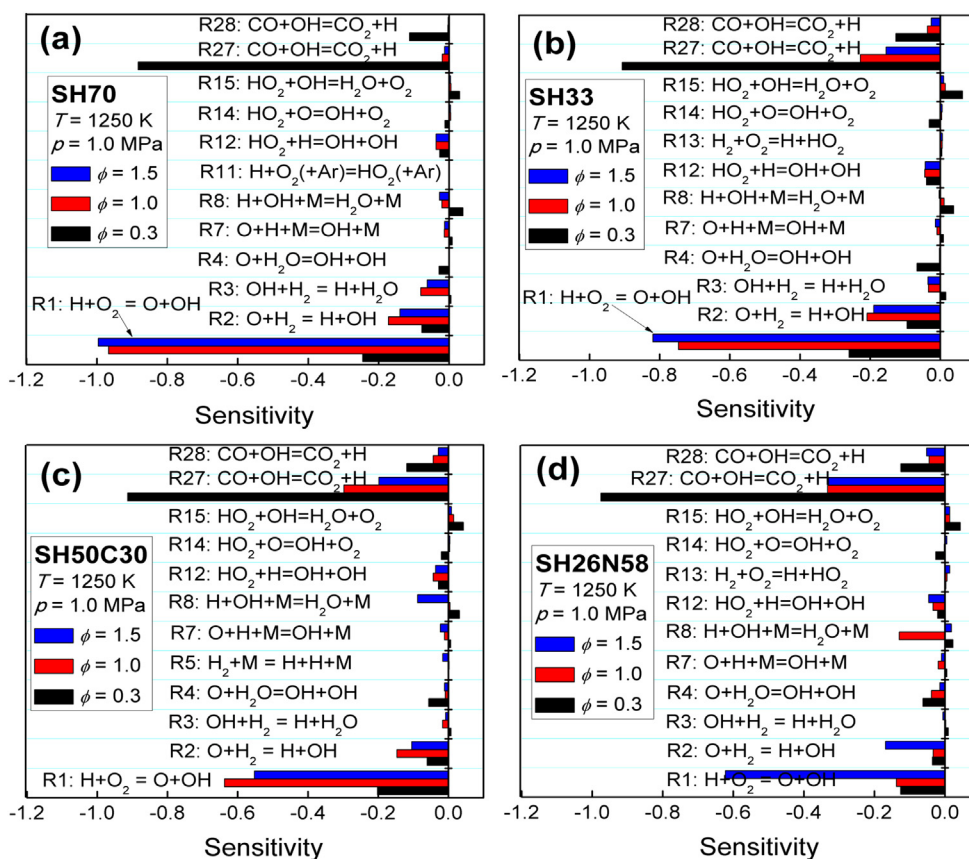


Fig. 8 – Sensitivity analysis of syngas mixtures at $p = 1.0$ MPa and $T = 1250$ K. (a) Syngas SH70; (b) Syngas SH33; (c) Syngas SH50C30; (d) Syngas SH26N58.

Sensitivity at low pressure

Fig. 7 shows the reactions with top sensitivity coefficients for syngas mixtures at various equivalence ratios, pressure of 0.2 MPa and temperature of 1150 K. It was found that the chain branching reactions $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ (R1) and $\text{O} + \text{H}_2 = \text{H} + \text{OH}$ (R2) play a dominant role in the ignition chemistry of syngas mixtures. Besides the reactions R1 and R2, ignition delay has a remarkable sensitivity to the CO related oxidation reaction $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ (R27) during the induction period [11], especially under fuel-lean condition. This comes from the production of more reactive H radicals and heat release via reactions R27, leading to the promotion of the global reaction rate. For syngas SH50C30 and SH26N58 mixtures, three-body reactions $\text{O} + \text{H} + \text{M} = \text{OH} + \text{M}$ (R7) and $\text{H}_2\text{O} + \text{M} = \text{H} + \text{OH} + \text{M}$ (R-8) become important due to more available CO_2 and/or N_2 in the syngas mixtures.

Strong influence of equivalence ratio on ignition delay was observed through the sensitivity analysis. This is more obvious for reactions R1, R2 and R27. Ignition delay is most sensitive to reaction R27 under fuel-lean condition. For syngas SH33, SH50C30 and SH26N58, the sensitivity coefficients of reaction R27 are larger than that of syngas SH70, but the effect is rapidly decayed as reactant mixture changes from fuel-lean to fuel-rich. For syngas SH70, ignition delay shows a negligible sensitivity to reaction R27 compared to reaction R1 under stoichiometric and fuel-rich conditions. Increasing the concentration of inert gas such as syngas SH50C30 (Fig. 7(c)) and syngas SH26N58 (Fig. 7(d)),

reaction R8 becomes important under stoichiometric and fuel-rich conditions. This is due to the insufficient OH radical under fuel-rich condition, leading to the promotion of water decomposition via reaction R-8.

Sensitivity analysis at high pressure

As shown in Fig. 5, the effect of equivalence ratio on ignition delay exhibits an opposite trend under high- and intermediate-temperatures. Figs. 8 and 9 give the sensitivity analysis at temperatures of 1250 K and 1025 K and to interpret this behavior.

At high temperature range, the effect of equivalence ratio on ignition delay is quite similar to that at low pressure. Reaction R1 is still the most important promoting reaction in the syngas ignition processes. The promoting role of reaction R27 in fuel-lean mixture is higher than those in fuel-rich and stoichiometric mixtures, leading to the faster ignition of fuel-lean mixtures. With an increase of equivalence ratio, the promoting role of R27 becomes non-dominant in the ignition kinetic compared to that of reaction R1, resulting in increased ignition delay of fuel-rich mixture. Compared to other three syngas mixtures, chain termination reaction $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$ (R15) of syngas SH33 gives the highest sensitivity coefficient, especially under fuel-lean condition. Furthermore, the sensitivity coefficient of syngas SH33 is increased for reaction R1 and decreased for reaction R27 with the increase of equivalence ratio. This opposite influence balances the effect of equivalence ratios on global reaction.

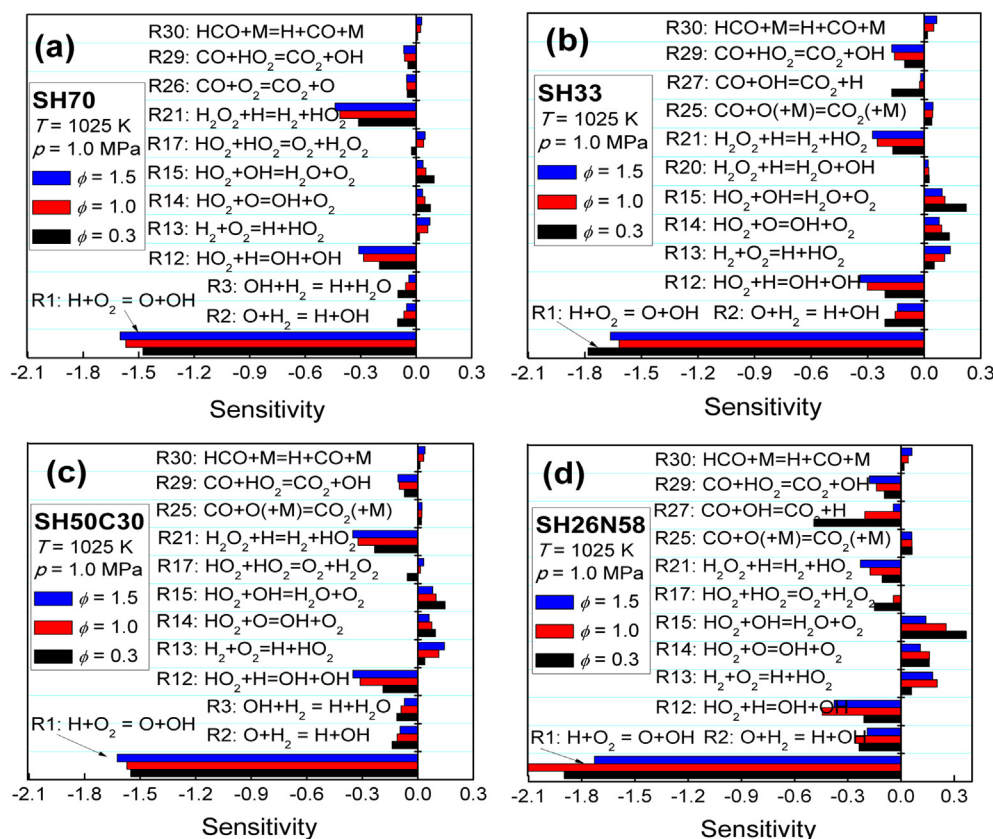


Fig. 9 – Sensitivity analysis of syngas mixtures at $p = 1.0$ MPa and $T = 1025$ K. (a) Syngas SH70; (b) Syngas SH33; (c) Syngas SH50C30; (d) Syngas SH26N58.

And this can explain the insensitivity of ignition delay on equivalence ratio for syngas SH33 compared to those of other three syngas mixtures.

At intermediate temperature range, ignition is still sensitive to reaction R1. In addition, the reactions involving formation and decomposition of HO₂ and H₂O₂ become more important to the ignition kinetic, such as reaction R12: HO₂ + H = OH + OH, reaction R21: H₂O₂ + H = H₂ + HO₂, and reaction R29: CO + HO₂ = CO₂ + OH.

At high-temperature, for the direct oxidation of CO, reaction R29 related to HO₂ radical replaces R27 to become the dominant reaction. Similar observation was also reported by Mittal et al. [11].

Actually, no substantial difference in the most dominant reactions as equivalence ratio varies from fuel-lean to fuel-rich is presented except the syngas SH26N58. In syngas SH26N58 ignition, reaction R27 still remains the remarkable promoting effect. There come from the complex dependency of chain branching cycle via R1–R3 on equivalence ratio. Stoichiometric mixture exhibits the highest sensitivity coefficient.

Conclusion

Ignition delays of four syngas mixtures were measured in shock tube at equivalence ratios of 0.3, 1.0 and 1.5, pressures of 0.2, 1.0 and 2.0 MPa and temperatures from 870 to 1350 K.

- (1) Results show that syngas with different components presents different dependency at different equivalence ratios. At low pressure (0.2 MPa), ignition delay increases with an increase in equivalence ratio. At elevated pressures (1.0 and 2.0 MPa), increasing equivalence ratio inhibits the ignition of syngas at high temperature and promotes the ignition at intermediate temperature.
- (2) Sensitivity analyses reveal that the ignition processes of the syngas mixtures are mainly controlled by chain branching reaction R1 and CO oxidation reactions R27 at high temperature while they are dominated by reaction R29 at intermediate temperature. For the syngas containing inert gas, water decomposition reaction R-8 becomes remarkably important at low pressure, especially under fuel-lean condition. The opposite effect of equivalence ratio on ignition delay at low and high temperatures under elevated pressures is attributed to the opposite trend of sensitivity coefficient for reactions R1 and R27 when equivalence ratio is increased. Furthermore, the reactions related to HO₂ and H₂O₂ play the considerable role in the ignition kinetic of syngas mixtures at elevated pressure, they are, reactions R12, R15, R21 and R29.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2014.01.170>

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