

Experimental and numerical investigation of vitiation effects on the auto-ignition of *n*-heptane at high temperatures

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ABSTRACT

The ground test in wind-tunnel with high temperatures plays an important role in the scramjet design and refinement. To simulate supersonic flight conditions, combustion-heated approach in ground tests introduces carbon dioxide and water vapor in the test flow. Understanding of vitiation effects is crucial for extrapolating the ground test results to the actual flight conditions. The primary goal of this work is to investigate the vitiation effects of CO₂ and H₂O on auto-ignition of *n*-heptane. With 20% CO₂ or H₂O replacement of N₂ in air, ignition delay times of *n*-heptane/air were investigated behind reflected shock waves at temperatures of 1050–1400 K, pressures of 2 and 10 atm, and with equivalence ratios of 1.0 and 0.5. The addition of CO₂ shows slightly inhibiting effect, whereas H₂O shows a promoting effect on the ignition of *n*-heptane. Further numerical simulations of kinetic mechanism were performed to investigate the thermal, chemical and third-body collision effects of CO₂ and H₂O separately. Results indicated that the thermal effect of CO₂ is the dominant factor for the inhibiting effect on *n*-heptane ignition, and the third-body collision of H₂O is the major factor promoting the ignition of *n*-heptane.

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1. Introduction

Supersonic vehicles can fly at several times of sound speed. These vehicles provide the potential for fast transport around the world. Scramjet engine is a potential candidate for these propulsion systems. The ground test in wind-tunnel with high temperatures plays an important role in the scramjet design and refinement. Evaluation and interpretation of ground test data in wind tunnels are essential for the development of supersonic propulsion engines [1,2]. In ground experiment, air is heated to simulate the high-speed conditions. Hydrocarbon combustion-heated wind-tunnel is widely used for supersonic combustion studies. This combustion-heated approach introduces water vapor and carbon dioxide in the test flow, which is different from actual atmosphere case [3–12]. Therefore, understanding of vitiation effects is crucial for extrapolating the ground test results to the actual flight conditions. In comparison to pure air, CO₂ and H₂O have higher specific heat capacity. As a result, vitiation compositions can change the specific heat capacity of the fuel/air mixture, reduce the flame temperature and affect the heat transfer losses. Meanwhile, the vitiation

components may involve in chemical reactions of fuels to affect the auto-ignition and combustion characteristics of fuels [13–20].

Experimental and theoretical efforts have been made to investigate the vitiation mechanism on the ignition characteristics of fuels. Levy et al. have experimentally found that CO₂ has negligible effect on ignition delay times of methane at high temperatures in shock tube [21]. Yu et al. have studied the effect of CO₂ on the auto-ignition of natural gas in a rapid compression machine and found that no effect on the ignition delay could be discerned [22]. Guang et al. have measured the *n*-heptane ignition delay with CO₂ addition in a rapid compression machine under low temperatures, and found that CO₂ has different effects on the two stages of ignition delay of *n*-heptane [23]. Koroglu et al. have measured the methane ignition delay times in CO₂ diluted mixtures in a shock tube and the results showed the increase of ignition delay time as the amount of CO₂ dilution increase [24,25]. Tingas et al. have analyzed the effect of CO₂ dilution on the adiabatic and isochoric auto-ignition of CH₄/air mixtures with computational singular perturbation (CSP) algorithmic tools, and found that increasing CO₂ dilution causes longer ignition delays because of the large specific heat of CO₂ [26]. Sabia et al. have investigated the effect of CO₂ on propane auto-ignition delay times under mild combustion operative conditions, they found that CO₂ sensibly reduced the auto-ignition delay times with

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respect to N_2 and suggested that CO_2 drastically alter the main branching mechanisms as third molecular species in termolecular reactions and/or by decomposition reactions [27].

Das et al. have studied the auto-ignition of moist hydrogen/oxidizer mixtures in a rapid compression machine and found that H_2O addition increases the ignition delay of hydrogen at 1 MPa, but promotes auto-ignition at 3 and 7 MPa, due to the high third body efficiency of water $H + O_2(+H_2O) = HO_2(+H_2O)$ and $H_2O_2(+H_2O) = OH + OH(+H_2O)$, respectively [28]. Donohoe et al. have investigated the influence of steam dilution on the ignition of H_2 , CO and natural gas blends at elevated pressures and found that only CO was strongly influenced by H_2O addition [29]. Levy et al. have experimentally found that H_2O has negligible effect on ignition delay times of methane at high temperatures in shock tube [21]. Yu et al. have reported that there is no effect of H_2O addition on the ignition delay of natural gas [22].

From the literature, it is concluded that the effects of vitiation were related to conditions and fuels. In most of these studies, the effects of CO_2 and H_2O were analyzed. However, it is not yet clear which effect governs the ignition process. Although there are many studies of vitiation effects on combustion performance, most vitiation mechanism studies focused on the C0–C3 fuels, only limited studies focused on high carbon number hydrocarbons. *n*-Heptane is a representative normal alkane in liquid hydrocarbon fuels, and it is often chosen as a surrogate of complex practical fuels [30,31]. As ignition delay is an important parameter for the combustion process, the study of vitiation effects on the auto-ignition is important to scramjet development. To figure out how the vitiation effect on the ignition of *n*-heptane, experimental and numerical studies were conducted to investigate the vitiation effects of CO_2 and H_2O on the ignition delay time of *n*-heptane at high temperatures in this work.

2. Experimental method

Ignition delay time measurements were carried out in a stainless steel heated shock tube with an internal diameter of 10 cm. The shock tube facility contains a 2 m driver section and a 5 m driven section, which has been described in detail in previous publications [32,33]. Polycarbonate diaphragms with different thicknesses were used to provide different nominal reflected shock pressures. Pure helium was used as the driver gas for all experiments, resulting in a test time of approximately 2 ms.

Four PCB piezoelectric pressure transducers (model 113B), located over the last 1.0 m of the driven section, with rise times of less than 1.0 μs , were used to measure the shock velocity. The pressure signals were collected by a digital oscilloscope (Tektronix DPO5054). Three incident velocities were obtained and linearly extrapolated to the shock tube end-wall to determine the shock velocity at the end-wall. The attenuation rates of incident shock wave were in the range of 0.5–2.0%/m. The ignition temperature T and pressure P were calculated using one-dimension normal-shock model (shock-tube code of the CHEMKIN package [34]) with initial temperature, pressure, mixture composition in the driven section and incident shock velocity. Due to the uncertainty in the measured incident shock wave velocity, this method results in an approximate uncertainty of 0.7% and 1.2% in post-shock temperature and pressure, respectively.

The mixtures of *n*-heptane/air with CO_2 or H_2O were prepared manometrically in a 40 L heated mixing tank with a 2% uncertainty in all reactant concentrations. In order to prevent the condensation of heptane and water vapor, the mixing tank, the gas manifold to the shock tube, and the driven section were electrically heated and kept to 100 °C. Six independent current circuits were used to provide a uniform temperature distribution along the tube length with

uncertainty of less than 2 °C. In this work, a molar ratio of 1:3.76 of $O_2:N_2$ was used to prepare fuel/air mixtures. 20% CO_2 or H_2O was introduced to partially replace N_2 in the mixtures to study the vitiation effects on the auto-ignition delay time of *n*-heptane. Compositions of the mixtures are list in Table 1.

The light emission during the ignition process was exported using a quartz optical fiber located at the same cross-section as the last PCB pressure transducer. A grating monochromator coupled with a photomultiplier tube was set to 431 nm to detect the chemiluminescence from electronically excited CH^* radical at the shock tube side-wall (1.5 cm from end-wall). Reflected pressure and emission signals were recorded by a digital oscilloscope (Tektronix TDS5054B) to determine the ignition delay time (τ). Ignition delay time is defined as the time between the arrival of the reflected shock wave and the onset of CH^* emission at the side-wall. Typical pressure and CH^* emission profiles are shown in Fig. 1. The passing of the reflected shock wave was determined by the step rise in pressure. The reflected pressure kept constant within 1 ms. Just prior to ignition, the pressure increase gradually due to the energy release, and went up sharply when ignition took place. The pressure trace is in concert with simulation of NUI mechanism [35]. The uncertainty of ignition delay time mainly comes from the uncertainty of temperature, which is determined by the uncertainty in the measured incident shock wave velocity. The uncertainty analysis was conducted according to the work by Petersen et al. [36] and Zhukov et al. [37]. The overall ignition uncertainty, calculated from the root-mean-square sum of the uncertainties from reflected shock temperature and pressure, the reactant mixture composition, and the determination of the ignition delay time from pressure and CH^* emission signals, is estimated to be within 20%.

3. Results and discussion

3.1. Experimental results

Till now, there are several works related to the ignition delay time of *n*-heptane/air measured around 10 atm at high temperatures. Fig. 2 shows the comparison of current ignition delay times with measurements from others [38–41] by shock tube. The error bars represent the 20% uncertainties in the measured ignition delay times. The ignition time dependence on pressure $\tau \sim P^{-1}$ was employed to scale the ignition delay times to 10 atm for comparison. Our ignition results are in good agreement with other experimental data.

The vitiation effects of CO_2 and H_2O on *n*-heptane ignition were investigated over the temperature range of 1050–1400 K at pressures around 2 and 10 atm, and with equivalence ratios (ϕ) of 1.0 and 0.5. The ignition results are tabulated in Table 2. Since the actual pressures of the ignition delay time data are close to the investigated pressure, for one set of data on one plot, the simple power law pressure scaling of $\tau \sim P^{-1}$ was applied to scale the data. The results are plotted in Figs. 3 and 4. Ignition delay time exhibits Arrhenius temperature dependence in current high-temperature range, thus, experimental data are fitted using an Arrhenius-type

Table 1
Mixture compositions investigated in this study (mole fraction).

Mixture	ϕ	<i>n</i> -C ₇ H ₁₆ %	O ₂ %	N ₂ %	CO ₂ %	H ₂ O%
1	1.0	1.87	20.61	77.52	0	0
2	1.0	1.87	20.61	55.52	20	0
3	1.0	1.87	20.61	55.52	0	20
4	0.5	0.95	20.80	78.25	0	0
5	0.5	0.95	20.80	58.25	20	0
6	0.5	0.95	20.80	58.25	0	20

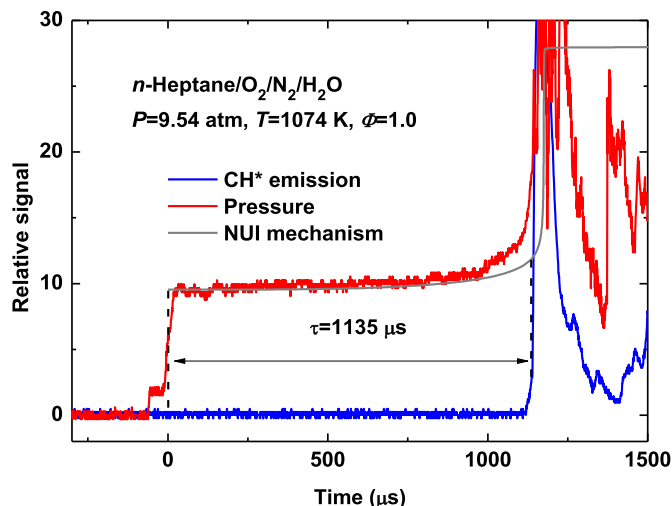


Fig. 1. Example of ignition delay time measurement.

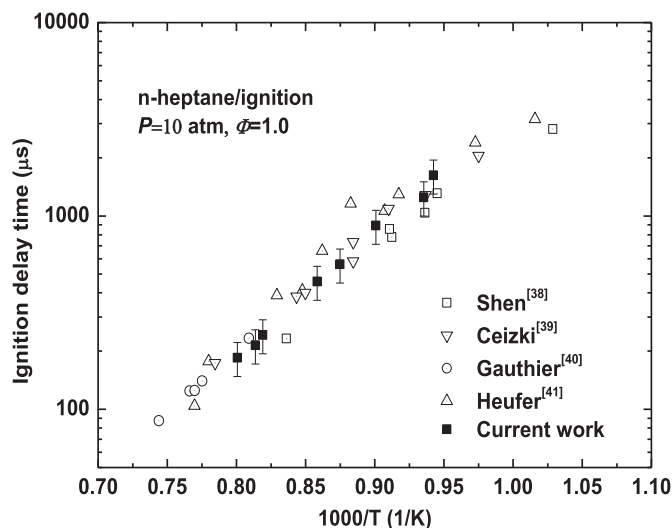


Fig. 2. Comparison of current stoichiometric *n*-heptane/air ignition delay time measurements at 10 atm with measurements of other groups at high temperatures.

expression $\tau \sim \exp(A/T)$. The slopes in these figures represent the sensitivity of ignition on temperature. In these figures, solid symbols represent shock tube ignition delay times while solid lines represent corresponding fitting results.

Fig. 3 shows the impact of CO_2 on the ignition delay time of *n*-heptane. At 10 atm, the slight elongation of ignition delay times with CO_2 addition is observed within the investigated temperature range. And the inhibiting effect of CO_2 becomes greater as the temperature turn to the low temperature range. At 1100 K, when CO_2 was added, the ignition delay time increased by 20% and 30% for stoichiometric and fuel-lean mixtures conditions, respectively. At 2 atm, the CO_2 slows the ignition of *n*-heptane at fuel lean condition, whereas it has little effect on the ignition delay time of *n*-heptane at stoichiometric condition.

Fig. 4 shows the impact of H_2O on the ignition delay time of *n*-heptane. At stoichiometric condition, The H_2O addition shows a promoting effect on the ignition of *n*-heptane at 2 and 10 atm. At 1100 K, when H_2O was added, the ignition delay time decreased by 41% and 14% for 2 and 10 atm, respectively. At equivalence ratio of 0.5 with pressure of 2 atm, the promoting effect becomes greater as the temperature decreases.

3.2. Mechanism validation

Kinetic mechanism for *n*-heptane oxidation has been extensively investigated in literatures. In this work, the CRECK mechanism [42], San Diego Mechanism [43], mechanism of Hakka et al. [44], Jertsurf 2.0 [45], LLNL mechanism [46], and NUI mechanism [35] have been used to simulate the auto-ignition delay time of *n*-heptane as a function of temperature, pressure and equivalence ratio, as well as the vitiation addition. Numerical simulation was carried out using CHEMKIN software [34] under ideal condition by employing a zero-dimensional Closed Homogeneous Batch Reactor model with a constant volume. As the ignition time is less than 2.0 ms, which is much shorter than the diffusion time, transportation including mass diffusion and heat transfer as well as boundary layer effect is ignored. Initial reactor conditions, in the form of reactant species fraction, temperature and pressure behind reflected shock, were specified as input parameters. Thermodynamics and chemical reaction dynamics of mechanisms coupled with fundamental mass and energy conservation and state equations were applied to model the ignition process. The results are shown in Fig. 5. After evaluating the performance of mechanisms in simulating the ignition delay time, the recently published mechanism from NUI [35] was chosen for further analysis as it can well predict ignition delay times of *n*-heptane at most conditions. This detailed NUI mechanism (1268 species and 5336 reactions) is developed to describe *n*-heptane oxidation which has also been widely validated for a series of experimental observations including ignition delay times, speciation profiles measured in a jet-stirred reactor and laminar flame speeds over a wide range of conditions.

Fig. 6 presents the comparison of experimental results with mechanism predictions for CO_2 vitiation effect. The mechanism can well predict the experimental ignition delay times of *n*-heptane as well as the CO_2 effect. Numerical results show a slight inhibition impact on the ignition at 2 and 10 atm, however, the inhibition effect is less pronounced than that found from experiments.

Fig. 7 illustrates the comparison of experimental results with mechanism predictions for H_2O effect. At 10 atm, mechanism simulations agree well with the measured ignition delay of *n*-heptane, and the simulation can well predict the accelerating effect of H_2O on *n*-heptane ignition. At 2 atm, the ignition delay times of *n*-heptane can be well predicted by mechanism simulation, however, the mechanism fails to predict the promotion effect of H_2O on *n*-heptane ignition. As thermodynamics parameters of vitiation are much more reliable than kinetic ones, the poor prediction of mechanism mainly comes from the unfavorable kinetics of vitiation, including the third-body collision and chemical effects.

3.3. Thermal effect

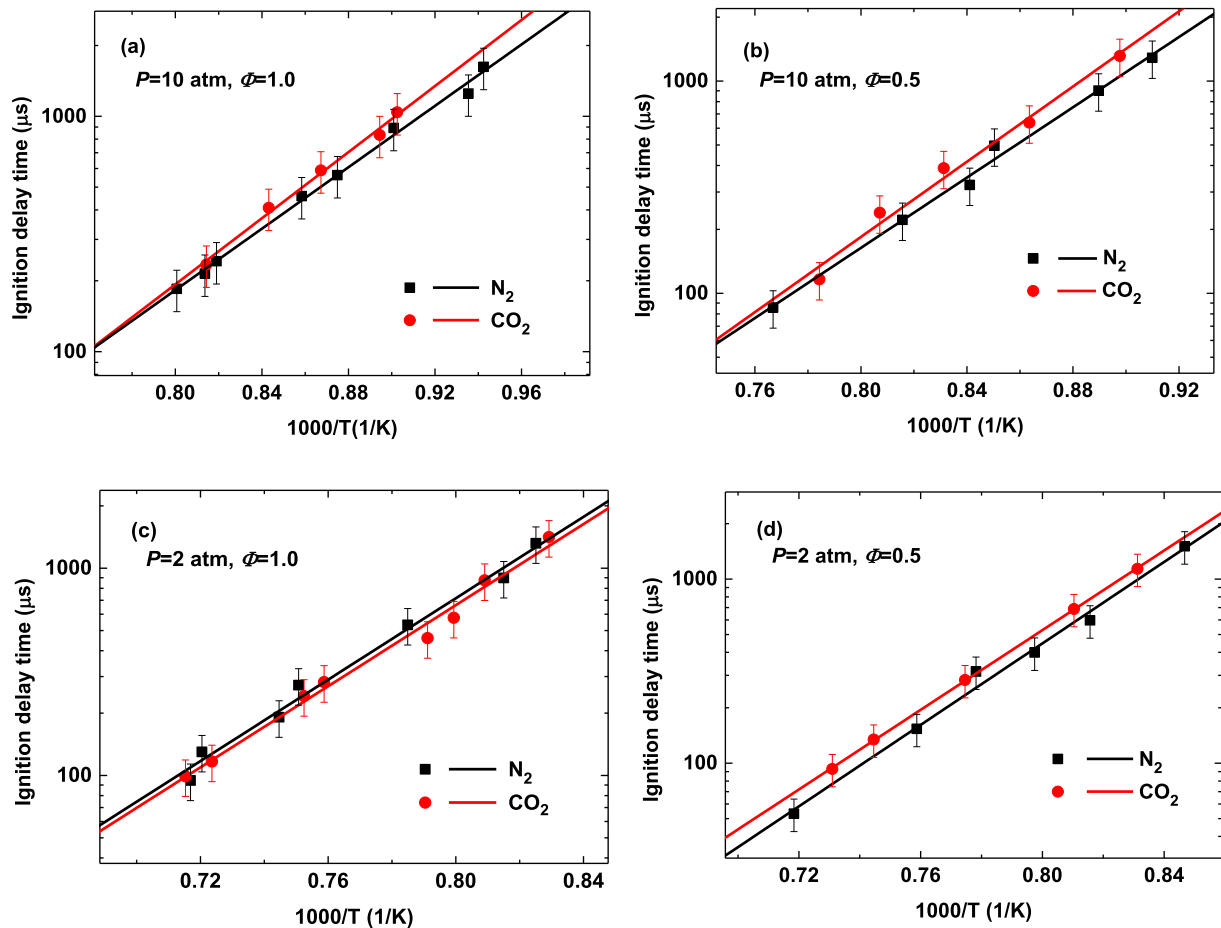
The CO_2 and H_2O vitiations have three effects on the combustion process of fuels [47]. First, Due to the higher heat capacity, the vitiation additions will reduce in flame temperature. Second, as CO_2 and H_2O have different third-body collision efficiencies in comparison to nitrogen, they can affect the ignition and combustion reaction at high pressures. Third, CO_2 and H_2O are active species that they can directly involve in the reaction of *n*-heptane to alter the kinetics by termolecular reactions and decomposition reactions. To further investigate the effects of CO_2 and H_2O on *n*-heptane ignition, numerical simulations were performed with the NUI kinetic mechanism [35] by isolating the thermal, collision and reaction effects separately.

In order to quantify the thermal effect of CO_2 and H_2O vitiation on the ignition delay times of *n*-heptane, a virtual species was introduced with the same heat capacities of CO_2 or H_2O in the detailed mechanism, but do not participate in any reactions. Thus,

Table 2

Summary of current ignition delay times.

<i>n</i> -heptane/O ₂ /N ₂				<i>n</i> -heptane/O ₂ /N ₂ /CO ₂				<i>n</i> -heptane/O ₂ /N ₂ /H ₂ O			
<i>T</i> (K)	<i>P</i> (atm)	ϕ	τ (μ s)	<i>T</i> (K)	<i>P</i> (atm)	ϕ	τ (μ s)	<i>T</i> (K)	<i>P</i> (atm)	ϕ	τ (μ s)
1395	1.97	1.0	96	1398	2.13	1.0	93	1393	2.13	1.0	79
1388	2.08	1.0	125	1382	2.03	1.0	115	1371	2.14	1.0	95
1343	1.93	1.0	198	1329	2.10	1.0	230	1329	2.06	1.0	167
1332	1.97	1.0	277	1318	1.98	1.0	285	1282	2.16	1.0	278
1274	1.98	1.0	538	1264	1.90	1.0	484	1262	2.06	1.0	376
1227	1.96	1.0	916	1251	2.04	1.0	565	1236	2.01	1.0	581
1212	1.92	1.0	1374	1236	2.09	1.0	836	1231	2.09	1.0	574
1249	10.1	1.0	183	1206	1.93	1.0	1465	1217	2.05	1.0	784
1229	9.71	1.0	221	1228	10.51	1.0	223	1319	10.54	1.0	84
1221	9.61	1.0	252	1186	10.61	1.0	385	1294	10.63	1.0	105
1165	10.83	1.0	423	1153	10.40	1.0	567	1252	10.34	1.0	177
1143	10.34	1.0	544	1118	10.54	1.0	791	1242	10.49	1.0	149
1110	10.51	1.0	849	1108	10.18	1.0	1023	1148	8.12	1.0	517
1069	10.27	1.0	1217	1368	2.09	0.5	89	1109	10.30	1.0	677
1061	9.02	1.0	1799	1343	2.10	0.5	128	1104	9.49	1.0	839
1392	2.17	0.5	49	1291	2.00	0.5	283	1097	8.65	1.0	959
1318	2.09	0.5	147	1234	2.10	0.5	655	1088	9.90	1.0	1013
1285	2.11	0.5	298	1203	2.07	0.5	1099	1074	9.54	1.0	1135
1254	1.75	0.5	456	1275	10.67	0.5	109	1053	9.94	1.0	1466
1226	2.02	0.5	591	1239	10.95	0.5	219	1307	2.19	0.5	167
1181	2.05	0.5	1470	1203	11.11	0.5	350	1246	2.06	0.5	380
1304	10.45	0.5	82	1158	11.09	0.5	574	1205	2.06	0.5	668
1226	9.77	0.5	227	1114	10.96	0.5	1198	1158	2.00	0.5	1110
1189	9.39	0.5	345								
1176	10.53	0.5	471								
1124	10.54	0.5	855								
1099	10.31	0.5	1248								

**Fig. 3.** Effect of CO₂ on ignition delay time of *n*-heptane. Points are experimental results and lines are corresponding fitting results.

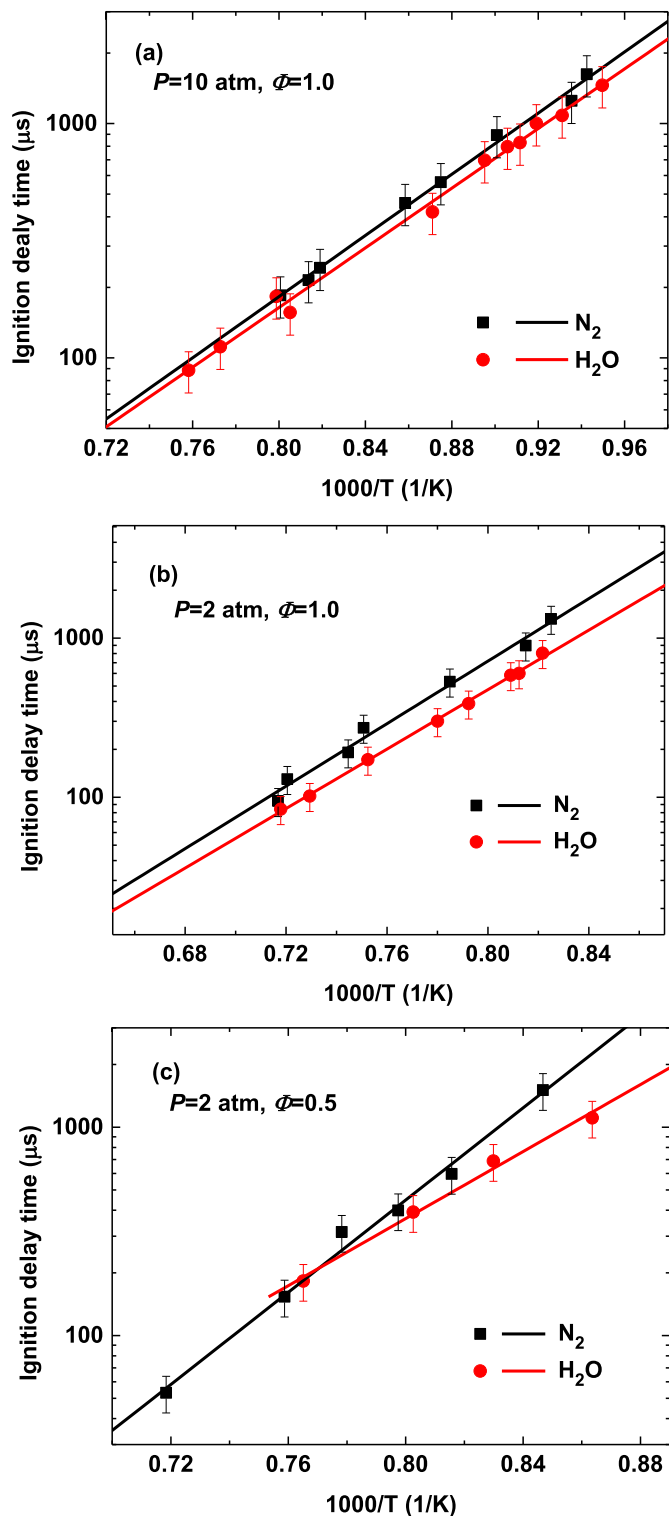


Fig. 4. Effect of H_2O on ignition delay time of n -heptane. Points are experimental results and lines are corresponding fitting results.

the variation between this case and vitiation-free one is the contribution of thermal effect.

Generally, CO_2 and H_2O have higher specific heat capacities than nitrogen, which leads to lower temperature during the ignition process. Fig. 8 shows the calculated temperature evolutions during n -heptane oxidation with and without vitiation at $P = 10$ atm,

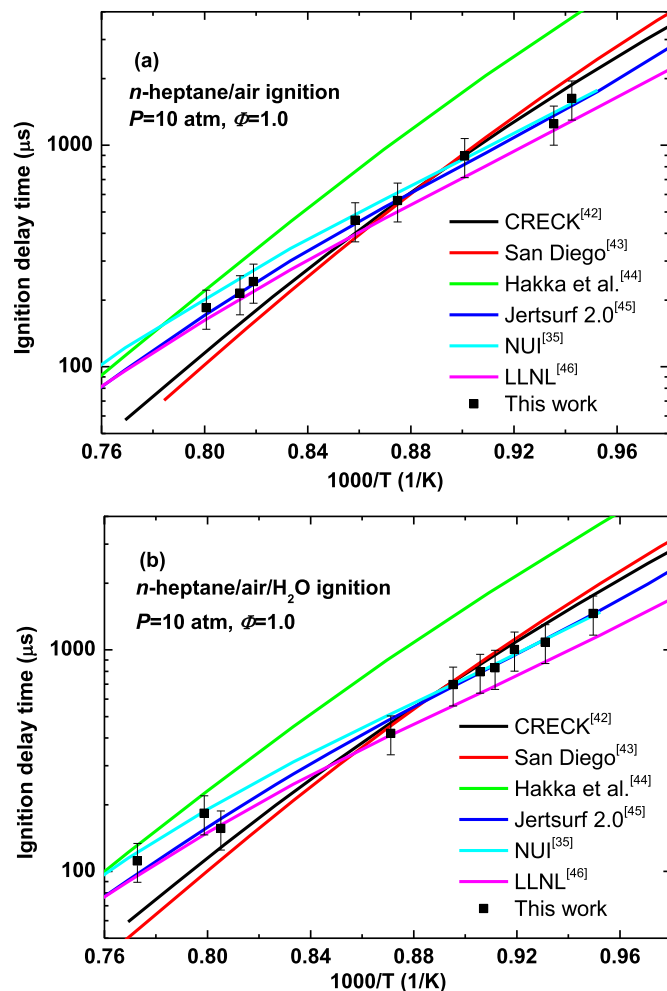


Fig. 5. Comparison of experimental results with mechanism predictions. Points are experimental results of current work and lines are mechanism results.

$T = 1100$ K and $\phi = 1.0$. It clearly shows the final adiabatic temperature decreases the most in the presence of CO_2 , and the highest in the vitiation-free case. H_2O addition results in equilibrium temperatures ranging in the middle. These observations correspond to the values of the specific heat capacities. Current simulated results are in accordance with the experimental and numerical results of Xu et al. [17] and Anderlohr et al. [19] where they found that both CO_2 and H_2O have a negative thermal impact compared to N_2 and the thermal effects of H_2O and CO_2 decrease the flame temperatures.

Fig. 9 illustrates the thermal effect of CO_2 and H_2O on the ignition of n -heptane at $P = 10$ atm, $T = 1100$ K and $\phi = 1.0$. Since the ignition delay time depends on the temperature history, both CO_2 and H_2O vitiation additions increase the ignition delay time, and CO_2 has stronger thermal effect on the ignition delay time of n -heptane, especially at low-temperature range. The conclusion agrees with Wagnon et al. and Shen's findings that species with higher specific heat capacities exhibit longer ignition delay times ($\tau_{\text{Ar}} < \tau_{\text{N}_2} < \tau_{\text{H}_2\text{O}} < \tau_{\text{CO}_2}$) [47,48].

3.4. Third-body collision effect

To isolate the effect of third-body collision on the ignition of n -heptane, mechanism simulations were conducted by removing the collision efficiencies of CO_2 and H_2O to make the vitiation addition

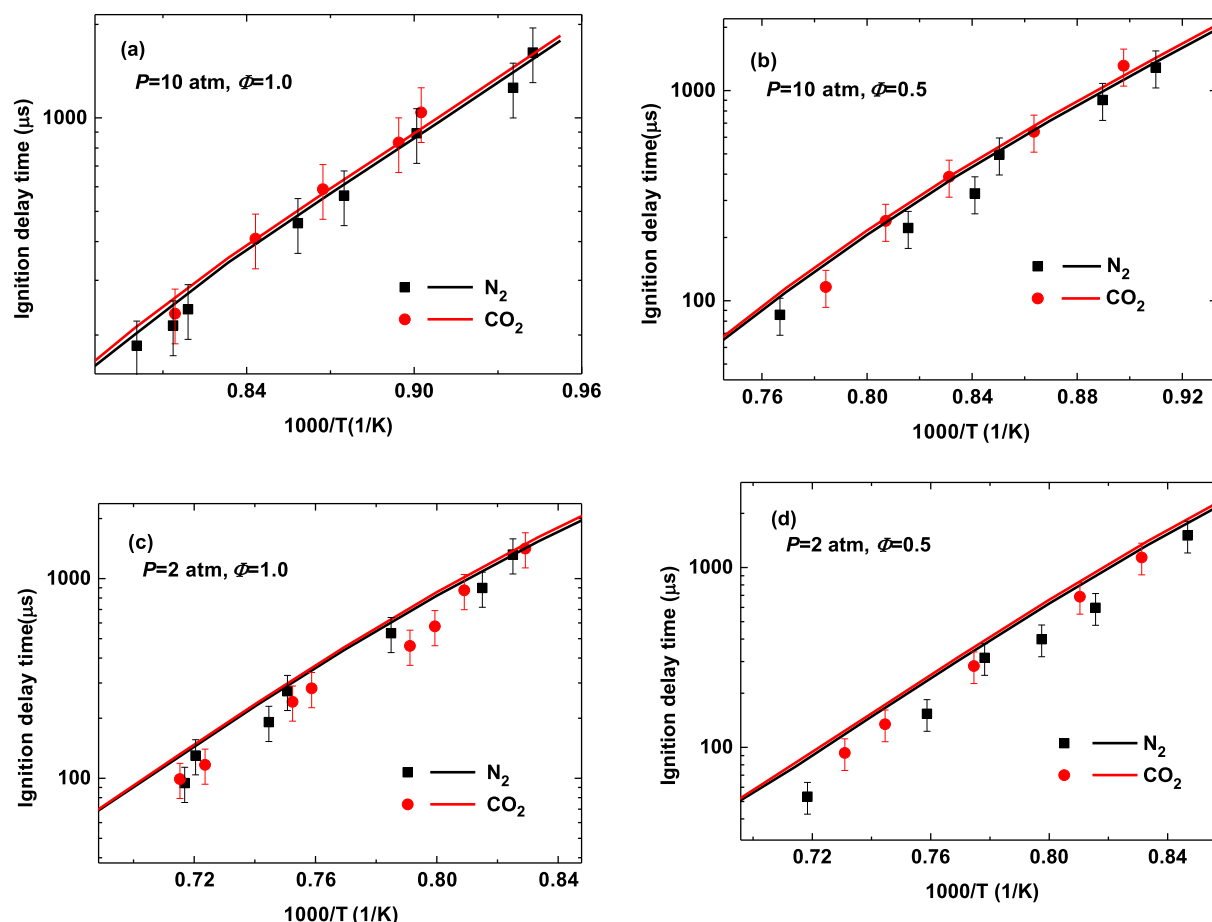


Fig. 6. Comparison of experimental results with mechanism predictions for CO₂ addition. Points are experimental results and lines are mechanism results.

having the same collision efficiency factors as N₂. By comparing the simulated ignition delay times with and without collision efficiencies, the third-body collision effect can be determined. The computed results are shown in Fig. 10. Compared to nitrogen, CO₂ and H₂O have much higher collision efficiencies. In this detailed mechanism [35], 46 collision reactions are involved, the third-body collision efficiencies of CO₂ are between 1.6 and 3.8, and these values of H₂O are between 3.65 and 12. When the collision efficiencies of CO₂ were varied, the change of ignition delay time is indiscernible, whereas an obvious change was displayed in the case of H₂O, especially at low temperatures, where the addition of H₂O as a third-body collision partner promotes the ignition of *n*-heptane. Anderlohr et al. also pointed out that H₂O has a much larger promoting effect on ignition of *n*-heptane/iso-octane/toluene mixtures than CO₂ due to its larger third-body efficiency [19]. Their results are in agreement with this work.

3.5. Chemical effect

The total effects of vitiation additions include thermal, third-body collision and chemical effects. In the detailed mechanism, by removing the collision efficiencies of CO₂ or H₂O, the third-body collision effect has been ruled out, and only thermal and chemical effects have been included. Thus, by comparing the ignition results between the case and the one with a virtual species having the same heat capacities of CO₂ or H₂O without collision efficiencies (only thermal effect), the influence of vitiation chemistry can be determined. Simulation results are shown in Fig. 11. The numerical

results show there is no chemical effect of CO₂ and H₂O on ignition delay time of *n*-heptane under the investigated conditions. At high temperatures, although CO₂ and H₂O are active species, and they will participate in the reactions of *n*-heptane via decomposition and recombination reactions, the overall chemical effect is negligible. The results agree with the conclusion of Donohoe et al. that the addition of water has no significant direct chemical effect on the ignition delay time of syngas and natural gas blends [29].

By combining the thermal, collision and chemical effects, the overall effect of vitiation additions can be summarized. The collision and chemical effects of CO₂ are negligible while the thermal effect is visible due to its higher specific heat capacity, which leads to a slightly increase of ignition delay time of *n*-heptane. The numerical results are in accordance with the experiments. Although H₂O involves in many reactions in the detailed mechanism, the chemical effect of H₂O is negligible. The thermal effect of H₂O is minor and has an inhibition impact on the ignition delay time of *n*-heptane. H₂O has significant larger collision efficiencies compared to N₂, which accelerate the ignition process of fuel. In total, the third-body collision is the dominant factor in the ignition process, the addition of H₂O promotes the ignition of *n*-heptane at high pressures, as found by experiments.

3.6. Sensitivity analysis

In order to determine the important reaction for the ignition delay time of *n*-heptane, a brute force sensitivity analysis was performed using CHEMKIN software at $T = 1100$ K and $\phi = 1.0$ with

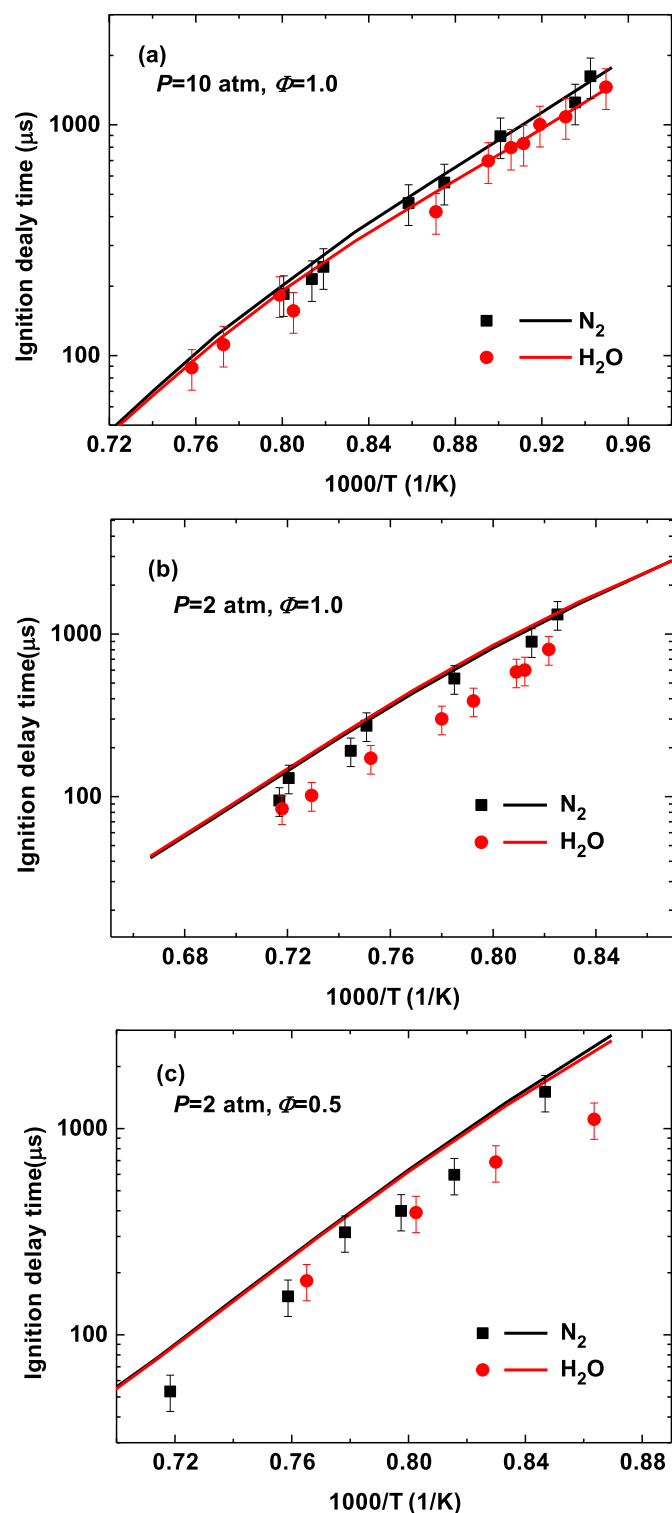


Fig. 7. Comparison of experimental results with mechanism predictions for H_2O addition. Points are experimental results and lines are mechanism results.

pressures of 2 and 10 atm. In the analysis, rate constants of each reaction were doubled to obtain the ignition delay time $\tau(2k)$. The sensitivity coefficient (S) is then defined as the change in the ignition delay, $S = [\tau(2k) - \tau(k)] / \tau(k)$. It can be concluded that a reaction with a positive sensitivity coefficient inhibits ignition while that with a negative sensitivity coefficient promotes ignition. Fig. 12

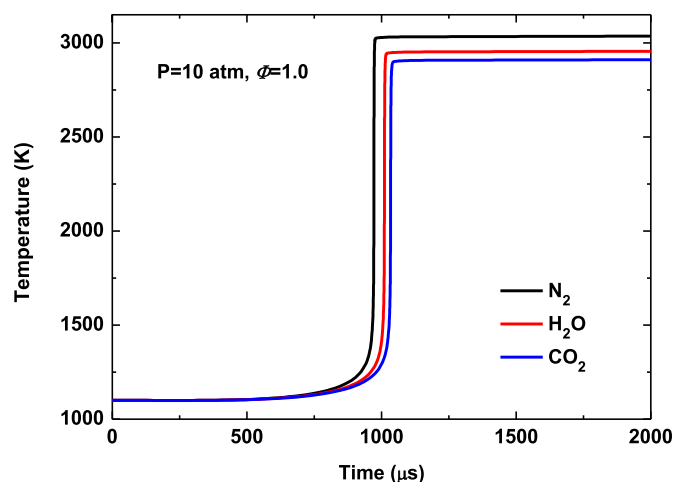


Fig. 8. Thermal effect of CO_2 and H_2O on temperature evolutions. $P = 10$ atm, $T = 1100$ K and $\phi = 1.0$.

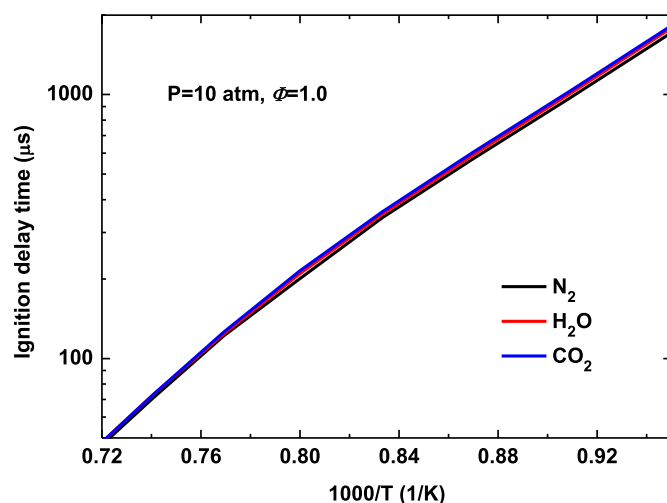


Fig. 9. Thermal effect of CO_2 and H_2O on n -heptane ignition delay time. $P = 10$ atm, $T = 1100$ K and $\phi = 1.0$.

demonstrates such a sensitivity analysis. Neither CO_2 nor H_2O involves in the important reactions in this figure, indicating that the chemical effect of CO_2 and H_2O are not significant. The sensitivity analysis agrees with the simulated results of section 3.5.

In Fig. 12, in addition to chain reactions, third-body collision decomposition reactions are important to the ignition of n -heptane. The collision decomposition reaction $\text{H}_2\text{O}_2 (+\text{M}) = 2\text{OH}$ is the dominant promoting reaction reactivity which is strongly governed by the efficiencies of its collision partners, and the promoting effect becomes stronger at higher pressure. As the collision efficiencies of H_2O is much larger than that of CO_2 or N_2 , the H_2O addition can significantly accelerate this reaction, resulting in a decrease in ignition delay time of n -heptane. On the other hand, the collision decompositions of heptane radical and butane reduce the reaction reactivity, leading to longer ignition delays.

Besides, H-atom abstraction reaction from n -heptane by HO_2 radicals has large negative sensitivity, which converts HO_2 radicals into H_2O_2 , strongly promotes reactivity. The main chain-branching reactions $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ and $\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$ have moderately high negative sensitivity coefficients. On the other hand, the chain terminating reactions of HO_2 radicals have large

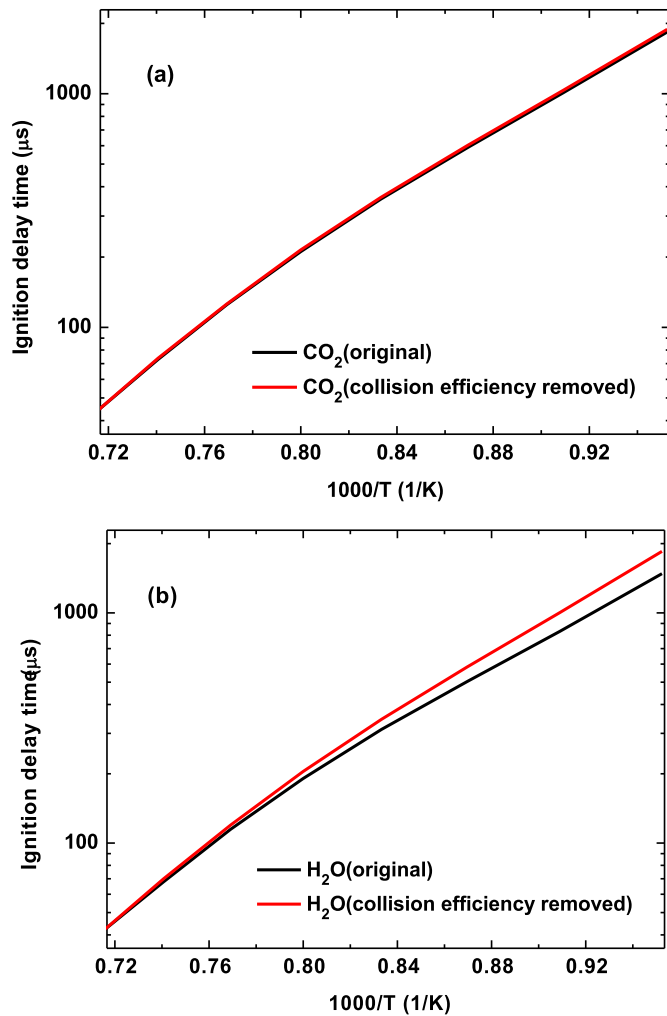


Fig. 10. Third-body collision effect of CO_2 and H_2O on n -heptane ignition delay time. $P = 10$ atm, $T = 1100$ K and $\phi = 1.0$.

positive sensitivity, which inhibiting reactivity. The chain termination reaction $\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_4 + \text{O}_2$ plays an inhibition role on the reactivity and has strong positive effect on n -heptane ignition.

The sensitivity analysis from Fig. 12 indicates that reactions involving HO_2 and OH radicals have strong effect on the ignition of n -heptane. The effects of CO_2 and H_2O addition on HO_2 and OH radicals have been simulated at 1100 K, 10 atm. As shown in Fig. 13. The simulation results show that H_2O addition promotes the peak of HO_2 and OH radicals in the induction time. On the other hand, the OH mole fraction increases when H_2O is added, leading to a decrease in ignition delay time. On the contrary, CO_2 addition slightly inhibits the peak of HO_2 and OH radicals in the induction time, and the OH mole fraction decreases as CO_2 is added. As a result, the CO_2 exhibits an inhibition effect on the ignition of n -heptane.

4. Conclusions

This paper provides new experimental data for vitiation effects on the auto-ignition of n -heptane over the temperature range of 1050–1400 K at pressures around 2 and 10 atm, and with equivalence ratios of 1.0 and 0.5. By comparing the ignition delay times of n -heptane and those of n -heptane with CO_2 or H_2O , the vitiation effects have been obtained. CO_2 addition has a slight inhibiting effect, whereas H_2O addition shows a promoting effect on the

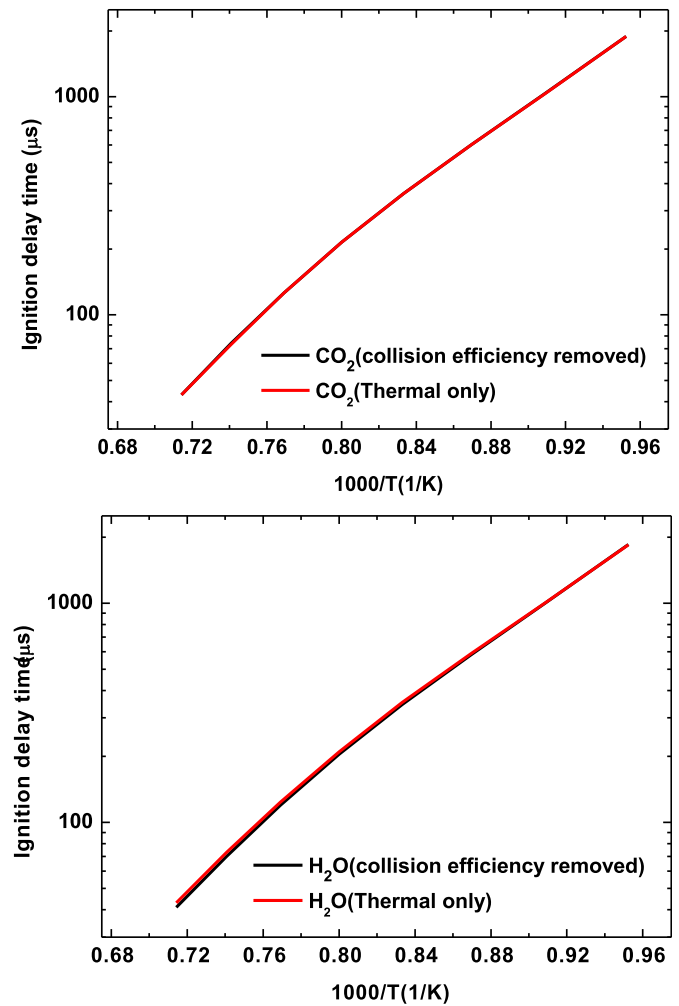


Fig. 11. Chemical effect of CO_2 and H_2O on n -heptane ignition delay time. $P = 10$ atm, $T = 1100$ K and $\phi = 1.0$.

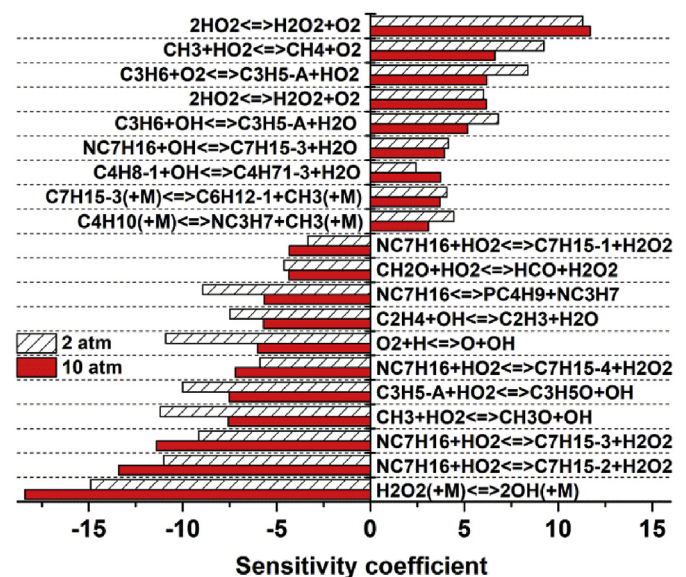


Fig. 12. Sensitivity analysis on the ignition delay time of n -heptane at $T = 1100$ K and $\phi = 1.0$.

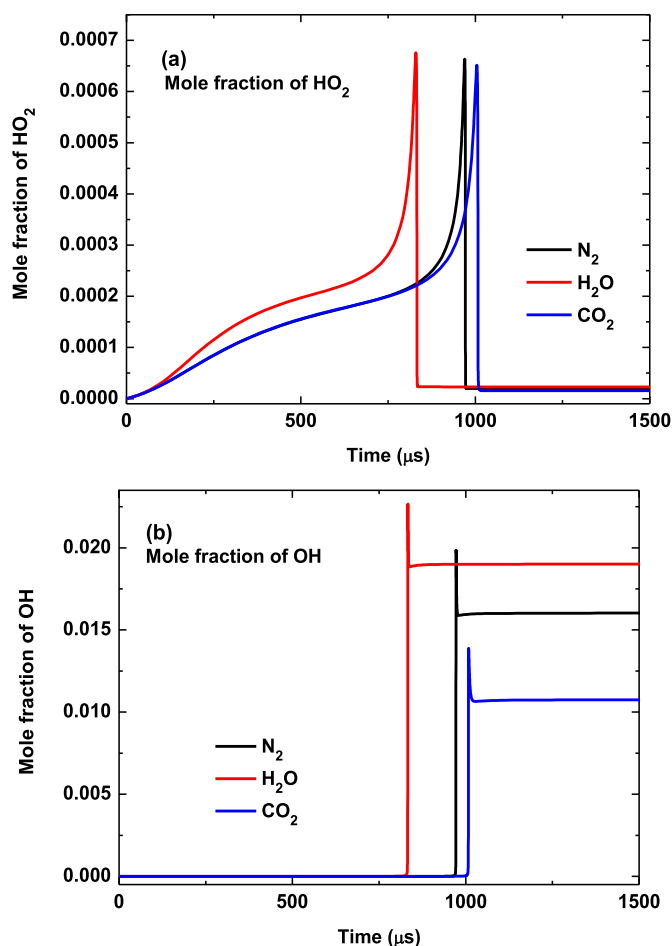


Fig. 13. Effects of CO_2 and H_2O on HO_2 and OH profiles. $P = 10$ atm, $T = 1100$ K and $\phi = 1.0$.

ignition of *n*-heptane. Current study of vitiation effects on the auto-ignition provides fundamental data to scramjet development.

Several kinetic mechanisms for *n*-heptane oxidation have been used to simulate the auto-ignition delay time of *n*-heptane as a function of temperature, pressure and equivalence ratio, as well as the vitiation addition to validate the performance of mechanism. Recently published mechanism from NUI [35] can well predict current experimental data at most conditions.

Numerical study has been performed to analysis the thermal, chemical and third-body collision effects of CO_2 and H_2O on ignition of *n*-heptane. The thermal effect is the major factor which leads to a slightly increase of ignition delay time of *n*-heptane, whereas the collision and chemical effects of CO_2 are negligible. The third-body collision of H_2O is the dominant factor in the ignition process, which promotes the ignition of *n*-heptane. The chemical and thermal effects of H_2O are negligible. Sensitivity analysis shows that the CO_2 and H_2O additions can affect the formation of HO_2 and OH radicals to impact the reactivity of *n*-heptane.

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References

- [1] Doig G. Transonic and supersonic ground effect aerodynamics. *Prog Aero Sci*

- 2014;69:1–28.
- [2] Tirres C, Bradley M, Morrison C, Edelman R. A flow quality analysis for future hypersonic vehicle testing. In: AIAA; 2002. p. 2706.
- [3] Pellett GL, Bruno C, Chinitz W. Review of air vitiation effects on scramjet ignition and flameholding combustion processes. In: AIAA; 2002. p. 3880.
- [4] Ingenito A, Moretto A, Agresta A, Andriani R, Gamma F, Roncioni P, et al. Air vitiation effects in scramjet engines. In: AIAA; 2013. p. 3701.
- [5] Rockwell RD, Goyne CP, Haw W, Krauss RH, McDaniel JC, Trefny CJ. Experimental study of test-medium vitiation effects on dual-mode scramjet performance. *J Propuls Power* 2011;27:1135–42.
- [6] Rockwell RD, Goyne CP, Haw W, McDaniel JC, Goldenstein CS, Schultz IA, et al. Measurement of water vapor levels for investigating vitiation effects on scramjet performance. *J Propuls Power* 2011;27:1315–7.
- [7] Tatman BJ, Rockwell RD, Goyne CP, McDaniel JC, Donohue JM. Experimental study of vitiation effects on flameholding in a cavity flameholder. *J Propuls Power* 2013;29:417–23.
- [8] Wang Y, Song W, Shi D, Fu Q, Wang Y. Experimental study of vitiation effects on combustion characteristics of a supersonic combustor. *Combust Sci Technol* 2017;189:1500–9.
- [9] Wang Y, Song W, Fu Q, Shi D, Wang Y. Experimental study of vitiation effects on hydrogen/kerosene fueled supersonic combustor. *Aero Sci Technol* 2017;60:108–14.
- [10] Fuller CC, Gokulakrishnan P, Klassen MS, Roby RJ, Kiel BV. Investigation of the effects of vitiated conditions on the autoignition of JP-8. In: AIAA; 2009. p. 4925.
- [11] Ingenito A. Theoretical investigation of air vitiation effects on hydrogen fuelled scramjet performance. *Int J Hydrog Energy* 2015;40:2862–70.
- [12] Li J, Song W, Luo F, Shi D. Experimental investigation of vitiation effects on supersonic combustor performance. *Acta Astronaut* 2014;96:296–302.
- [13] Renard C, Dias V, Van Tiggelen PJ, Vandooren J. Flame structure studies of rich ethylene-oxygen-argon mixtures doped with CO_2 , or with NH_3 , or with H_2O . *Proc Combust Inst* 2009;32:631–7.
- [14] Le Cong T, Bedjanian E, Dagaut P. Oxidation of ethylene and propene in the presence of CO_2 and H_2O : experimental and detailed kinetic modeling study. *Combust Sci Technol* 2010;182:333–49.
- [15] Lavadera ML, Sabia P, de Joannon M, Cavaliere A, Ragucci R. Propane oxidation in a jet stirred flow reactor. The effect of H_2O as diluent species. *Exp Therm Fluid Sci* 2018;95:35–43.
- [16] Hong D, Liu L, Huang Y, Zheng C, Guo X. Chemical effect of H_2O on CH_4 oxidation during combustion in $\text{O}_2/\text{H}_2\text{O}$ environments. *Energy Fuels* 2016;30:8491–8.
- [17] Xu H, Liu F, Sun S, Zhao Y, Meng S, Tang W. Effects of H_2O and CO_2 diluted oxidizer on the structure and shape of laminar coflow syngas diffusion flames. *Combust Flame* 2017;177:67–78.
- [18] Zhang W, Chen Z, Shen Y, Shu G, Chen G, Xu B, et al. Influence of water emulsified diesel & oxygen-enriched air on diesel engine NO-smoke emissions and combustion characteristics. *Energy* 2013;55:369–77.
- [19] Anderlohr JM, da Cruz AP, Bounaceur R, Battin-Leclerc F. Thermal and kinetic impact of CO , CO_2 , and H_2O on the postoxidation of IC-engine exhaust gases. *Combust Sci Technol* 2010;182:39–59.
- [20] Li A, Zhu L, Deng Z, Gao Z, Huang Z. A fundamental investigation into chemical effects of carbon dioxide on intermediate temperature oxidation of biodiesel surrogate with laminar flow reactor. *Energy* 2017;141:20–31.
- [21] Levy Y, Olchanski E, Sherbaum V, Erenburg V, Burcat A. Shock-tube ignition study of methane in air and recirculating gases mixtures. *J Propuls Power* 2006;22:669–76.
- [22] Yu Y, Vanhove G, Griffiths JF, De Ferrières S, Pauwels J-F. Influence of EGR and syngas components on the autoignition of natural gas in a rapid compression machine: a detailed experimental study. *Energy Fuels* 2013;27:3988–96.
- [23] Guang HY, Yang Z, Huang Z, Lu X. Experimental study of *n*-heptane ignition delay with carbon dioxide addition in a rapid compression machine under low-temperature conditions. *Chin Sci Bull* 2012;57:3953–60.
- [24] Koroglu B, Pryor OM, Lopez J, Nash L, Vasu S. Methane ignition delay times in CO_2 diluted mixtures in a shock tube. In: AIAA; 2015. p. 4088.
- [25] Koroglu B, Pryor OM, Lopez J, Nash L, Vasu SS. Shock tube ignition delay times and methane time-histories measurements during excess CO_2 diluted oxy-methane combustion. *Combust Flame* 2016;164:152–63.
- [26] Tingas EA, Im HG, Kyritsis DC, Goussis DA. The use of CO_2 as an additive for ignition delay and pollutant control in CH_4/air autoignition. *Fuel* 2018;211:898–905.
- [27] Sabia P, Lavadera ML, Giudicianni P, Sorrentino G, Ragucci R, de Joannon M. CO_2 and H_2O effect on propane auto-ignition delay times under mild combustion operative conditions. *Combust Flame* 2015;162:533–43.
- [28] Das AK, Sung C-J, Zhang Y, Mittal G. Ignition delay study of moist hydrogen/oxidizer mixtures using a rapid compression machine. *Int J Hydrog Energy* 2012;37:6901–11.
- [29] Donohoe N, Heufer KA, Aul CJ, Petersen EL, Bourque G, Gordon R, et al. Influence of steam dilution on the ignition of hydrogen, syngas and natural gas blends at elevated pressures. *Combust Flame* 2015;162:1126–35.
- [30] Westbrook CK, Mehl M, Pitz WJ, Kukkadapu G, Wagnon S, Zhang K. Multi-fuel surrogate chemical kinetic mechanisms for real world applications. *Phys Chem Chem Phys* 2018;20:10588–606.
- [31] Cai G, Abraham J. Multidimensional simulations of non-reacting and reacting diesel and biodiesel sprays. *Energy* 2017;119:1221–9.
- [32] Zhang C, Li B, Rao F, Li P, Li X. A shock tube study of the autoignition

- characteristics of RP-3 jet fuel. *Proc Combust Inst* 2015;35:3151–8.
- [33] He J, Xian L, Li P, Zhang C, Wang J, Li X. Experimental study of the soot formation of RP-3 behind reflected shock waves. *Fuel* 2017;200:47–53.
- [34] ANSYS chemkin 17.0 (15151), ANSYS Reaction Design. 2016. San Diego.
- [35] Zhang K, Banyon C, Bugler J, Curran HJ, Rodriguez A, Herbinet O, et al. An updated experimental and kinetic modeling study of *n*-heptane oxidation. *Combust Flame* 2016;172:116–35.
- [36] Petersen EL, Rickard MJA, Crofton MW, Abbey ED, Traum MJ, Kalitan DM. A facility for gas- and condensed-phase measurements behind shock waves. *Meas Sci Technol* 2005;16:1716–29.
- [37] Zhukov VP, Sechenov VA, Starikovskiy AY. Autoignition of kerosene (Jet-A)/air mixtures behind reflected shock waves. *Fuel* 2014;126:169–76.
- [38] Shen HS, Steinberg J, Vanderover J, Oehlschlaeger MA. A Shock tube study of the ignition of *n*-heptane, *n*-decane, *n*-dodecane, and *n*-tetradecane at elevated pressures. *Energy Fuels* 2009;23:2482–9.
- [39] Ciezki HK, Adomeit G. Shock-tube investigation of self-ignition of *n*-heptane-air mixtures under engine. *Combust Flame* 1993;93:421–33.
- [40] Gauthier BM, Davidson DF, Hanson RK. Shock tube determination of ignition delay times in full-blend and surrogate fuel mixtures. *Combust Flame* 2004;139:300–11.
- [41] Heufer KA, Olivier H. Determination of ignition delay times of different hydrocarbons in a new high pressure shock tube. *Shock Waves* 2010;20:307–16.
- [42] Ranzi E, Frassoldati A, Stagni A, Pelucchi M, Cuoci A, Faravelli T. Reduced kinetic schemes of complex reaction systems: fossil and biomass-derived transportation fuels. *Int J Chem Kinet* 2014;46:512–42.
- [43] Chemical-kinetic mechanisms for combustion applications. San Diego Mechanism web page, Mechanical and Aerospace Engineering (Combustion Research), University of California at San Diego; 2008. <http://combustion.ucsd.edu>.
- [44] Hakka HM, Cracknell RF, Pekalski A, Glaude P-A, Battin-Leclerc F. Experimental and modeling study of ultra-rich oxidation of *n*-heptane. *Fuel* 2015;144:358–68.
- [45] Wang H, Dames E, Sirjean B, Sheen DA, Tangko R, Violi A, et al. A high-temperature chemical kinetic model of *n*-alkane (up to *n*-dodecane), cyclohexane, and methyl-, ethyl-, *n*-propyl and *n*-butyl-cyclohexane oxidation at high temperatures. September 19, 2010. JetSurF version 2.0, <http://melchior.usc.edu/JetSurF/JetSurF2.0>.
- [46] Mehl M, Pitz WJ, Westbrook CK, Curran HJ. Kinetic modeling of gasoline surrogate components and mixtures under engine conditions. *Proc Combust Inst* 2011;33:193–200.
- [47] Wagnon SW, Wooldridge MS. Effects of buffer gas composition on auto-ignition. *Combust Flame* 2014;161:898–907.
- [48] Shen H-PS, Vanderover J, Oehlschlaeger MA. A shock tube study of iso-octane ignition at elevated pressures: the influence of diluent gases. *Combust Flame* 2008;155:739–55.