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RESEARCH PAPER

The vitiation effects of water vapor and carbon dioxide on the autoignition characteristics of kerosene

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Abstract In ground tests of hypersonic scramjet, the high-enthalpy airstream produced by burning hydrocarbon fuels often contains contaminants of water vapor and carbon dioxide. The contaminants may change the ignition characteristics of fuels between ground tests and real flights. In order to properly assess the influence of the contaminants on ignition characteristics of hydrocarbon fuels, the effect of water vapor and carbon dioxide on the ignition delay times of China RP-3 kerosene was studied behind reflected shock waves in a preheated shock tube. Experiments were conducted over a wider temperature range of 800–1 500 K, at a pressure of 0.3 MPa, equivalence ratios of 0.5 and 1, and oxygen concentration of 20%. Ignition delay times were determined from the onset of the excited radical OH emission together with the pressure profile. Ignition delay times were measured for four cases: (1) clean gas, (2) gas vitiated with 10% and 20% water vapor in mole, (3) gas vitiated with 10% carbon dioxide in mole, and (4) gas vitiated with 10% water vapor and 10% carbon dioxide, 20% water vapor and 10% carbon dioxide in mole. The results show that carbon dioxide produces an inhibiting effect at temperatures below 1 300 K when $\phi = 0.5$, whereas water vapor appears to accelerate the ignition process below a critical temperature of about 1 000 K when $\phi = 0.5$. When both water vapor and carbon dioxide exist together, a minor inhibiting effect is observed at $\phi = 0.5$, while no effect is found at $\phi = 1.0$. The results are also discussed preliminary by considering both the combustion reaction mechanism and the thermophysics properties of the fuel mixtures. The current measurements demonstrate vitiation effects of water vapor and carbon dioxide on the autoignition characteristics of China RP-3 kerosene at air-like O_2 concentration. It is important to account for such effects when data are extrapolated from ground testing to real flight conditions.

Keywords Ignition delay · Vitiation effect · Kerosene water · Carbon dioxide · Shock tube

1 Introduction

High combustion efficient engines are the key technology in the development of hypersonic air-breathing aircrafts, which attract more and more attention in recent years. Specific pulse of traditional engines, such as turbo fan and ramjet, decreases dramatically when the flight Mach rises. To resolve this problem, the concept of supersonic combustion is proposed, including the Scramjet [1] and detonation engines [2]. However, the residence time of supersonic combustion is only a few milliseconds, which has the same time scale as the ignition delay time of hydrocarbon fuels. Hence, the study of rapid spontaneous ignition and complete combustion are of great importance.

There are several kinds of fuel used in the hypersonic engines, including gaseous, solid and liquid [3–5]. In last decades, liquid hydrocarbon is studied widely due to its potential use in hypersonic flight at relatively low Mach number [6]. However, the development of propulsion systems for hypersonic flight must rely heavily on ground testing for screening and validation of engine concepts. In order to simulate hypersonic flight conditions in ground tests, the stored high-pressure air is heated significantly before expansion through a facility nozzle. Combustion air preheating

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by burning hydrocarbon fuels (e.g., H_2, CH_4, or C_3H_8) is the most widely used method for obtaining the high enthalpy airflow in ground tests of supersonic scramjets. However, the resulting high enthalpy air contains substantial amounts of contaminants, for example, water vapor as hydrogen is burned, while the major contaminants are water vapor and carbon dioxide in the case of burning hydrocarbons. So the composition of test gas heated by burning hydrocarbon fuels is different from that in the actual atmosphere case. Water vapor and carbon dioxide not only have different thermodynamic and transport properties from clean air, but also can participate directly or act as the very efficient third bodies in elementary chemical reactions. Due to differences of airflow in thermodynamic properties and chemical kinetic effects, ignition and combustion processes of fuels may be affected by contaminants in vitiated air. The successful operation of a combustion chamber requires the processes of vaporization of the liquid fuel, fuel mixing with air, autoignition, and complete combustion. It has been demonstrated that the vitiation effect on the fuel-air mixing process is negligible [7]. The ignition characteristics of fuels are more sensitive to the ignition environment such as temperature, pressure and the composition of airflow. The contaminants of H_2O and CO_2 can change the thermodynamic properties and the composition of test gas mixtures, which may obviously affect the ignition characteristics of fuels.

In hypersonic flight, the residence time of airflow in the combustion chamber is only a few milliseconds, which has the same time scale as the ignition delay time of hydrocarbon fuels. Because the contaminants may have impacts on the ignition process, the ignition characteristics of hydrocarbon fuels in ground tests may be different from that in real flights. Therefore, correct evaluation of the effects of vitiated air on ignition characteristics will be required to extrapolate from vitiated ground test data to real flight condition.

Kerosene is an important common hydrocarbon fuel preferred for hypersonic scramjets due to its stable thermodynamic properties and high energy density. The study reported herein focuses on the effects of the contaminants on ignition delay times of China RP-3 kerosene. Some studies have been reported for the vitiation effects on ignition and combustion characteristics of fuels. Experimental study and kinetic analyses of scramjet combustion by Mitani et al. [8] indicated that an easier autoignition of hydrogen with vitiated air was caused by radicals supplied from the combustion heater. Mitani [9] also found that H_2O has an inhibiting effect on ignition characteristics of hydrogen. Jacbimowski and Houghton [10] characterized the effects of H_2O and CO_2 on the ignition behaviors of hydrogen in a shock tube, and found that the ignition delay times of hydrogen was shortened by H_2O and unaffected by CO_2 at temperatures between 1 000 and 1 500 K. By simulating the ignition of hydrogen in air at static temperatures near the autoignition temperature of about 1 000 K, Hitch et al. [11] found that the ignition delay times of hydrogen increased when H_2O and CO_2 was added into the fuel mixture. Through comparative experiments between clean air and vitiated air, Le et al. [12, 13] investigated experimentally and numerically the effects of contaminants H_2O and CO_2 on the combustor performance during hydrogen and ethylene combustion. In the experiments by Le et al., clean air was heated via electric resistance and water vapor and carbon dioxide were added to simulate the vitiated air. Their results show that H_2O contaminant of inflow decrease the thrust of the combustor. Using analysis of combustion product distribution by gas chromatography, Fourier transform infrared spectroscopy, and detailed kinetic modeling, Le Cong et al. [14] investigated the effects of H_2O and CO_2 on the oxidation of ethylene. Their results showed that water vapor tends to inhibit the combustion of ethylene in fuel-rich conditions, whereas carbon dioxide has a small accelerating effect. By numerically simulating the vitiation effects in the wind tunnel, Chinitz and Erdos [15, 16] found that H_2O has an obvious inhibiting effect on the ignition of several hydrocarbon fuels at lower temperatures. All of these studies mainly focused on the fuels such as H_2, CH_4 and C_2H_4. Only limited studies have been conducted on the vitiation effects on ignition and combustion characteristics of kerosene. Hou et al. [17] studied numerically the influence of seven main species in vitiated air on the performance of the kerosene-fueled supersonic combustion, and found that the vitiated air could cause an increase in combustion efficiency and internal thrust. To compare the combustor performance under clean air and air vitiated with water vapor conditions, Xing and Xiao [18] conducted experiments on the direct-connect dual-mode kerosene-fueled scramjet engine and simulated the reacting flowfield in the combustor under the same experimental conditions, and found a significant effect of vitiated air on the combustion efficiency. By comparing the numerical results and experimental data, Li et al. [19] recently investigated the effects of H_2O and CO_2 on kerosene-fueled supersonic combustion performance, and concluded that the presence of H_2O and CO_2 contaminants results in combustor performance deterioration.

The available experimental and numerical results show that the effects of contaminants on hydrocarbon combustion are far too variable, in both magnitude and direction, for any meaningful generalization to be made. Most of the existing studies were focused on the vitiation effects on the combustion performance. Actually, ignition characteristics of fuels are more sensitive to the ignition environment, so another effective way to discuss the vitiation effects in supersonic combustion is to investigate the effects of contaminants on the ignition characteristics of fuels. Hence, it is required to investigate the vitiation effects on kerosene ignition to ensure correct interpretation of the data when they are extrapolated from vitiated ground testing to real flight. In this study, experiments were performed for the ignition of kerosene/O_2/Ar mixtures with H_2O and CO_2 contents. In order to better match the conditions to those of practical combustion devices, it is often needed to conduct igni-

tion measurements in less diluted mixtures. Thus, the aim of the present work is to study the effects of contaminants of H_2O and CO_2 on the ignition characteristics of China RP-3 kerosene in highly concentrated fuel mixtures over a wide temperature range, especially extending the low temperature bound to below 1 000 K.

2 Experimental

All ignition delay times were measured behind the reflected shock wave in a stainless steel shock tube in our laboratory. The shock tube is composed of a 3.0 m driver section and a 4.1 m driven section with both sections of 0.1 m in inner diameter. The facility has been reported elsewhere [20], but a brief description is provided here. A schematic diagram of the shock tube facility is shown in Fig. 1.

Incident shock speeds were measured over the last 1.5 m of the driven section using three piezoelectric pressure transducers (PZT) mounted on the shock tube sidewall and endwall equally spaced at 0.5 m intervals. The last transducer mounted on the endwall of the driven section was used to give the exact arrival time of the shock at the endwall, and to monitor the pressure evolution in the reflected shock region. A quartz window was installed on the sidewall close to the endwall of the driven section for monitoring emission signals from the ignition process in the reflected shock region. Emission signals focused through a lens were detected by a photomultiplier after passing through a monochromator centered at the emission line of OH* (306.5 nm). Pressure and emission signals were recorded by a transient A/D converter.

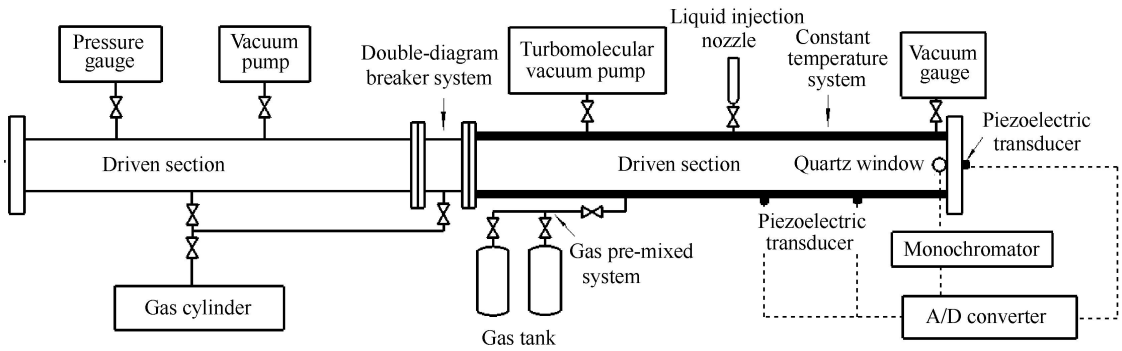

Fig. 1 Schematic diagram of the shock tube

Kerosene is a complex mixture of varieties of heavy hydrocarbons, including alkanes, cycloalkanes, aromatics, and polycyclic compounds, and the detailed composition of kerosene generally varies with sources. In this work, the test fuel is China RP-3 kerosene, including approximately 92.5% saturated hydrocarbons, 0.5% unsaturated hydrocarbons, and 7% aromatic compounds [21]. The saturated vapor pressures of kerosene are not enough for the present work at room temperature; moreover, there exists a strong adsorption of kerosene on the shock tube wall in experiments, resulting in an uncertainty in the composition determination of the test gas mixtures. An adsorption measurement by gas chromatography showed that the adsorption content of different component of kerosene is different, making the gas composition different from the liquid composition [22]. The saturated water vapor pressure is also low at room temperature; moreover, there also exists a strong adsorption of water vapor on the shock tube wall in experiments as well. To minimize the adsorption degree and to increase the test vapor pressures of kerosene and water, the driven section of the shock tube was preheated and maintained at a temperature of 135°C throughout each experiment. The experiments of measuring the adsorption degree of kerosene and water vapor on the shock tube wall were described in detail in the previous article [20]. The adsorption curves of kerosene and water vapor in Figs. 2 and 3 show that the adsorption equilibriums of kerosene and water vapor are achieved completely in 6 min and 10 min, respectively. So the pressures were measured 6 min after injecting kerosene and 10 min after injecting water as the initial experimental pressures.

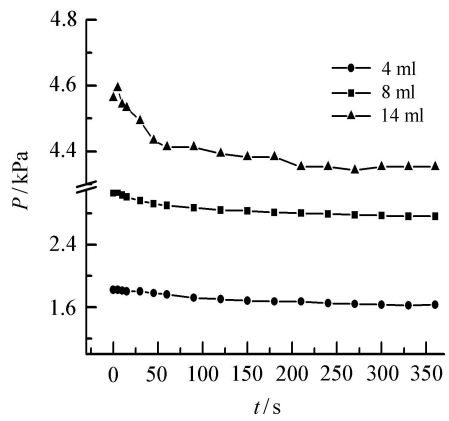

Fig. 2 Adsorption curves of China RP-3 kerosene at 135°C

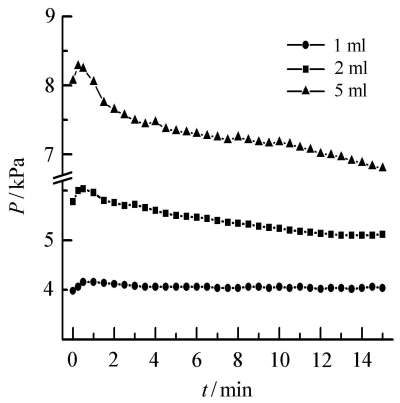

Fig. 3 Adsorption curves of water vapor at 135°C

The base experiments of measuring ignition delay times of kerosene without H_2O and CO_2 were also described in detail in the previous work [20]. In the experiments of kerosene with water vapor, water vapor was first injected into the driven section of shock tube, and the pressure was measured 10 min after it was evaporated and adsorbed using a membrane vacuum gauge (Beijing Vacuum Instrument Factory, Model ZDM-1). The following steps were the same as the base experiments. When carbon dioxide was present in test mixtures, it was added into the shock tube and its pressure was measured after kerosene was injected. Then, the prepared mixture of O_2/Ar was added into the driven section, and an additional 10 min was allowed for the gases to fully mix before bursting of the diaphragm.

Gaseq code [23] was used for computation of the reflected shock conditions by assuming frozen chemistry from measured shock velocities. Because of the complex mixture of hundreds varieties of hydrocarbons, the detailed composition of kerosene is hard to know. In the present study, a three-formula surrogate model consisting of 49% n-decane, 44% 1, 3, 5-trimethylcyclohexane, and 7% n-propyl-benzene in mole was adopted to represent China RP-3 kerosene, which gives a good discription of the thermophysical and transport properties of China RP-3 kerosene [18]. The averaged formula deduced from this surrogate model is $C_{9.49}H_{19.54}$ for calculations.

The current study mainly focused on the ignition characteristics of kerosene in engineering environments, so it is necessary to make some discussion on the choice of diluent gases. The inert diluent gas used in test mixtures does not take part in the chemical reaction. Argon and nitrogen are mainly used as diluent gas in shock tube ignition study. Davidson and Hanson [24] and Würmel et al. [25] have made a detailed discussion about the influence of diluent gas on the measured ignition delay times. It seems that nitrogen is the best choice for the diluent gas when normal combustion occurs in air. However, shock wave experiments are generally performed in argon rather than nitrogen. Since the lack of a vibrational mode in monatomic argon eliminates the possible influence of vibrational relaxation in calculating postshock conditions. Additionally, it eliminates or minimizes the shock bifurcation on sidewall in the reflected shock regime. As the main target here is to assess the influence of the contaminants on ignition characteristics of kerosene using comparative experimental method, the use of argon as diluent gas has no significant influence on the results.

The pressures and emissions of OH* at 306.5 nm behind reflected shock waves were recorded after bursting of the diaphragms. The ignition delay time could reasonably be defined as either the time of occurrence of maximum rate of change or the time when the peak value of some species or variable such as [OH], [CH], or pressure is reached, or could be based on an extrapolation of the maximum slope to the zero signal level. The deviation of ignition times using these definitions is typically less than 2% from the average [24]. In the present study, the ignition delay time is defined as the time interval between the arrival of the reflected shock wave and the onset of OH* emission at the sidewall observation location. The arrival of the reflected shock wave was determined by the step rise in pressure determined by the endwall piezoelectric pressure transducers (PZT) behind reflected shock waves. The onset of ignition was observed in the OH* emission history which was defined by linearly extrapolating the maximum slope to the baseline of the emission trace. An example of the pressure and OH* emission signal traces in the present experiments is shown in Fig. 4. In the experiment for long ignition time, the reflected shock pressure (P_5) is found to increase slowly during the ignition process. As seen in Fig. 4, the pressure rise consists of two stages. The first stage is a very slow pressure rise due to the non-ideal effects such as incident shock attenuation, boundary layer growth, and interaction of the reflected shock wave with the side-wall boundary layer. The second stage is an observable pressure rise very close to the ignition point due to the preignition. Pang et al. [26] and Chaos and Dryer [27] have discussed this phenomenon in their studies. In the current study, the first pressure rise is minor and the pressure is observed to increase at a rate of 2% per millisecond in Fig. 4a and 1% per millisecond in Fig. 4b, respectively. It can be concluded from Pang et al. [26] that the inert gases have no significant influence on the pressure rise rate due to the facility-dependent non-ideal gasdynamic effects. In their study, the pressure rise rate due to the non-ideal effects is a constant value of 2%/ms though the composition of the test gas mixture changes. As the main target of the present study is to assess the influence of the contaminants on ignition characteristics of kerosene using comparative experimental method, the non-ideal effects of the first-stage minor pressure rise can cancel out in comparative experiments. From the modeling prediction results of Pang et al. [26] and Chaos and Dryer [27], it can be seen that the preignition has a significant effect on the ignition delay time when the preignition point is far from the ignition point, but a minor effect appears when the preignition occurs near the ignition point. In the present study, the preignition point is very close to the ignition point, so the preignition effect was not considered in detail here.

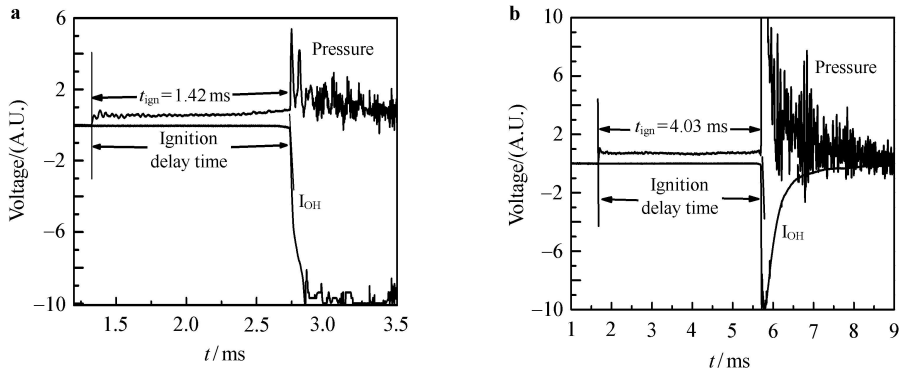

Fig. 4 Exemplary measurement of OH emission and pressure signal for reflected shock conditions. **a** 963 K, 0.28 MPa, and $\phi = 1$; **b** 812 K, 0.26 MPa, and $\phi = 1.0$

The uncertainties in shock tube experiments are mainly associated with nonideality and measurement uncertainty. Tang and Brezinsky [28] have investigated the nonideal behavior in a 5.6 m long shock tube with an inner diameter of 50.8 mm, and found that the temperature increase due to pressure variation, ΔT_5, can be up to 55 K at 2.5 MPa and 1 270 K. They concluded that for shock tube experiments with a less than 15% end wall pressure increase, the conventional treatment is suited to study chemical kinetics. A 0.5% uncertainty in shock wave velocity measurements results in about 1% and 2% experimental errors in temperature and pressure behind reflected shock waves in the present study. Usually, this can result in a 10%–15% uncertainty in ignition delay times.

3 Results and discussions

Due to the limited maximum saturation pressure of water vapor in the shock tube, the ignition pressure was determined at 0.3 MPa in this study. Considering the real concentrations of the contaminants in the combustion air preheated by burning the fuel, the concentrations of H_2O were 10% and 20%, and CO_2 were 10%. The collaborative effect of these two contaminants with different concentrations was also investigated. All of the experiments were conducted with equivalence ratios of 0.5 and 1, respectively. The initial compositions of the test mixtures are presented in Tables 1 and 2. The experimental ignition delay time data are summarized in Table 3.

Table 1 Initial composition of the test mixtures at $\phi = 0.5$ (mole fractions)

	Kerosene/%	O_2/%	H_2O/%	CO_2/%	Ar/%
Base experiment	0.6	19.88	0	0	78.52
10%H_2O	0.6	19.88	10.0	0	68.52
20%H_2O	0.6	19.88	20.0	0	58.52
10%CO_2	0.6	19.88	0	10.0	68.52
10%H_2O + 10%CO_2	0.6	19.88	10.0	10.0	58.52
20%H_2O + 10%CO_2	0.6	19.88	20.0	10.0	48.52

Table 2 Initial composition of the test mixtures at $\phi = 1.0$ (mole fractions)

	Kerosene/%	O_2/%	H_2O/%	CO_2/%	Ar/%
Base experiment	1.2	19.88	0	0	78.92
10%H_2O	1.2	19.88	10.0	0	68.92
20%H_2O	1.2	19.88	20.0	0	58.92
10%CO_2	1.2	19.88	0	10.0	68.92
10%H_2O + 10%CO_2	1.2	19.88	10.0	10.0	58.92
20%H_2O + 10%CO_2	1.2	19.88	20.0	10.0	48.92

Table 3 Summary of experimental results of ignition delay

T_5/K	P_5/MPa	t_{ign}/μs	T_5/K	P_5/MPa	t_{ign}/μs
$\phi = 0.5$, Kerosene: 0.6%, O_2: 19.88%, Ar: 79.52%					
872	0.31	4 492	1 081	0.28	1 142
917	0.29	3 192	1 163	0.32	959
967	0.35	2 213	1 226	0.28	819
1 005	0.31	1 697	1 281	0.29	589
1 038	0.28	1 448	1 386	0.26	498

Table 3 Summary of experimental results of ignition delay (continued 1)

T_5/K	P_5/MPa	t_{ign}/μs	T_5/K	P_5/MPa	t_{ign}/μs
ϕ = 1, Kerosene: 1.2%, O_2: 19.88%, Ar: 78.92%					
812	0.26	4 034	963	0.28	1 420
830	0.27	3 532	1 005	0.26	1 159
874	0.28	2 530	1 097	0.24	910
913	0.29	2 357	1 149	0.26	803
922	0.29	2 294	1 225	0.23	584
930	0.30	1 654	1 326	0.28	435
ϕ = 0.5, Kerosene: 0.6%, O_2: 19.88%, H_2O: 10.0%, Ar: 69.52%					
870	0.24	2 942	1 093	0.27	1 173
913	0.28	2 564	1 185	0.29	978
968	0.29	2 057	1 256	0.28	775
1 009	0.29	1 965	1 340	0.28	586
1 047	0.27	1 678			
ϕ = 0.5, Kerosene: 0.6%, O_2: 19.88%, H_2O: 20.0%, Ar: 59.52%					
888	0.26	1 798	1 085	0.32	1 382
930	0.28	1 710	1 086	0.32	1 258
959	0.25	1 451	1 163	0.28	1 222
982	0.29	1 730	1 204	0.26	934
1 017	0.29	1 800	1 296	0.28	738
1 039	0.29	1 641	1 404	0.29	611
ϕ = 1, Kerosene: 1.2%, O_2: 19.88%, H_2O: 10.0%, Ar: 68.92%					
846	0.32	2 815	1 073	0.25	881
858	0.31	2 285	1 119	0.27	779
889	0.28	1 829	1 178	0.28	649
930	0.27	1 450	1 221	0.27	626
995	0.27	1 179	1 296	0.26	471
1 053	0.28	889	1327	0.25	436
ϕ = 1, Kerosene: 1.2%, O_2: 19.88%, H_2O: 20.0%, Ar: 58.92%					
846	0.23	1 707	1 048	0.29	1 104
864	0.24	1 587	1 096	0.23	757
943	0.28	1 450	1 102	0.30	991
961	0.28	1 382	1 188	0.28	683
980	0.29	1 298	1 282	0.28	579
1 016	0.26	1 319	1 355	0.27	443
ϕ = 0.5, Kerosene: 0.6%, O_2: 19.88%, CO_2: 10.0%, Ar: 69.52%					
986	0.22	3 333	1 075	0.27	1 831
916	0.28	4 437	1 134	0.27	1 171
1 023	0.27	2 807	1 232	0.28	803
989	0.27	3 346	1 332	0.29	616

Table 3 Summary of experimental results of ignition delay (continued 2)

T_5/K	P_5/MPa	t_{ign}/μs	T_5/K	P_5/MPa	t_{ign}/μs
ϕ = 1, Kerosene: 1.2%, O_2: 19.88%, CO_2: 10.0%, Ar: 68.92%					
839	0.29	3 599	1 050	0.28	1 124
866	0.27	2 612	1 117	0.27	849
894	0.27	2 426	1 195	0.27	686
957	0.29	1 840	1 334	0.28	488
1 000	0.29	1 267	1 050	0.28	1 124
ϕ = 0.5, Kerosene: 0.6%, O_2: 19.88%, H_2O: 10.0%, CO_2: 10.0%, Ar: 59.52%					
885	0.26	3 981	1 166	0.28	1 249
944	0.29	3 034	1 263	0.28	863
982	0.28	2 671	1 336	0.27	715
1 025	0.27	2 357	1 451	0.28	520
1 094	0.29	1 546			
ϕ = 0.5, Kerosene: 0.6%, O_2: 19.88%, H_2O: 20.0%, CO_2: 10.0%, Ar: 49.52%					
931	0.28	2 862	1 156	0.30	1 158
977	0.30	2 309	1 260	0.29	897
990	0.27	2 247	1 352	0.28	689
1 060	0.27	1 952	1 493	0.30	576
1 108	0.29	1 366			
ϕ = 1, Kerosene: 1.2%, O_2: 19.88%, H_2O: 10.0%, CO_2: 10.0%, Ar: 58.92%					
921	0.23	2 206	1 199	0.26	727
945	0.26	1 553	870	0.27	2 761
1 038	0.30	1 193	847	0.29	3 122
1 087	0.26	1 057	1 248	0.26	620
1 147	0.27	789			
ϕ = 1, Kerosene: 1.2%, O_2: 19.88%, H_2O: 20.0%, CO_2: 10.0%, Ar: 48.92%					
841	0.27	2 878	1 004	0.27	1 397
882	0.26	2 432	1 080	0.31	1 088
919	0.28	2 139	1 148	0.27	873
944	0.31	1 963	1 236	0.27	625
953	0.23	1 656	1 293	0.26	470

3.1 The effect of water vapor on the ignition of kerosene

The effect of H_2O on the ignition delay time of kerosene at pressure of 0.3 MPa, equivalence ratios of 0.5 and 1, is shown in Figs. 5 and 6. As shown in these two figures, there exists a critical temperature for the effect of H_2O on the kerosene ignition. Above the critical temperature, H_2O has negligible effect, but a promoting effect appears below this critical temperature. It is also seen in the figures that the lower the temperature, the more dramatically the promoting effect appears. The critical temperature here was about 1 000 K at ϕ = 0.5 and about 960 K at ϕ = 1. It is also demonstrated that the ignition delay times with 20% H_2O are shorter than those with 10% H_2O at the same ignition conditions, indicating that the promoting effect was enhanced with the increase of H_2O concentration. Compared to the data without H_2O at ϕ = 0.5, the ignition delay time of kerosene with 10% H_2O decreases from 3.2 to 2.6 ms at 900 K. At the same water vapor concentration, the ignition delay time decreases from 4.1 to 3.1 ms at 870 K. When 20% H_2O was added into the fuel mixture, the ignition delay time of kerosene decreases from 3.2 to 1.9 ms at 900 K, and from 4.1 to 1.9 ms at 830 K; Compared to the data without H_2O at ϕ = 1, the ignition delay time of kerosene with 10% H_2O decreases from 2.2 to 1.8 ms at 900 K, and from 3.5 to 2.5 ms at 830 K. For addition of 20% H_2O, the ignition delay time of kerosene decreases from 2.2 to 1.5 ms at 900 K, and from 3.5 to 1.7 ms at 830 K.

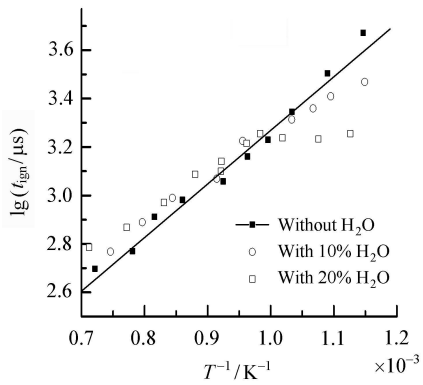

Fig. 5 Effect of water vapor on the ignition delay of kerosene at $\phi = 0.5$, $P = 0.3$ MPa

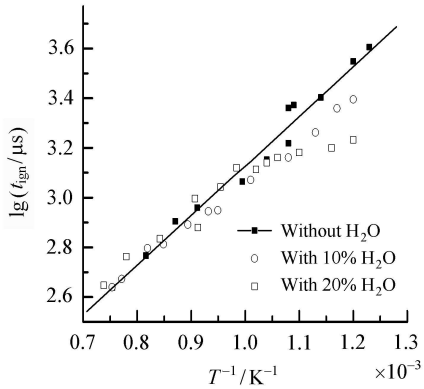

Fig. 6 Effect of water vapor on the ignition delay of kerosene at $\phi = 1$, $P = 0.3$ MPa

3.2 The effect of carbon dioxide on the ignition of kerosene

The effect of CO_2 on the ignition delay time of kerosene at pressure of 0.3 MPa, equivalence ratios of 0.5 and 1 is shown in Figs. 7 and 8. In Fig. 7, an inhibiting effect can be seen clearly below 1 300 K at $\phi = 0.5$. Compared to the data without CO_2, the ignition delay time of kerosene with 10% CO_2 increases from 1.8 to 2.9 ms at 1 000 K. From Fig. 8, it is demonstrated that the ignition delay time of kerosene does not

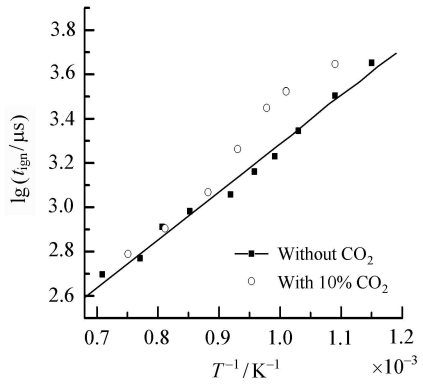

Fig. 7 Effect of carbon dioxide on the ignition delay of kerosene at $\phi = 0.5$, $P = 0.3$ MPa

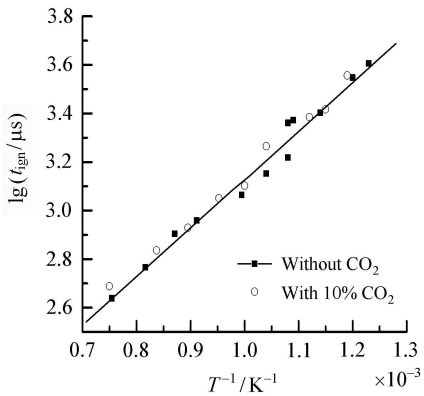

Fig. 8 Effect of carbon dioxide on the ignition delay of kerosene at $\phi = 1.0$, $P = 0.3$ MPa

change significantly throughout the experimental temperature range when 10% CO_2 was added into the fuel mixtures, indicating that carbon dioxide appears no noticeable effect on the ignition of kerosene at $\phi = 1$.

3.3 The collaborative effect of water vapor and carbon dioxide on the ignition of kerosene

In order to investigate the collaborative effect of H_2O and CO_2 on ignition characteristics of kerosene, ignition delay times of kerosene were measured over a wider temperature range of 810–1 450 K, at pressure of 0.3 MPa, and equivalence ratios of 0.5 and 1, for simultaneous addition of 10% H_2O and 10% CO_2 as well as 20% H_2O and 10% CO_2, respectively. The experiment results are shown in Figs. 9 and 10. As seen in these two figures, a minor inhibiting effect is observed at $\phi = 0.5$, while no effect is found at $\phi = 1$ when H_2O and CO_2 are added together into the test mixtures.

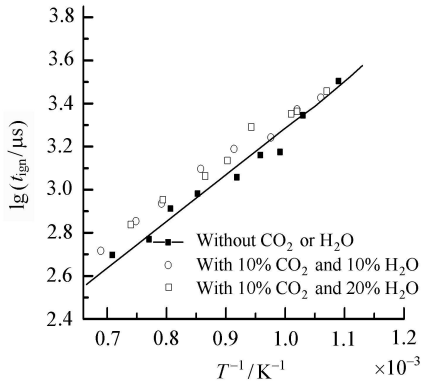

Fig. 9 Effect of water vapor and carbon dioxide on the ignition delay of kerosene at $\phi = 0.5$, $P = 0.3$ MPa

3.4 Preliminary analysis for the effect of water vapor and carbon dioxide on the ignition of kerosene

Two aspects should be considered for the effects of water vapor and carbon dioxide on the ignition of kerosene. The first

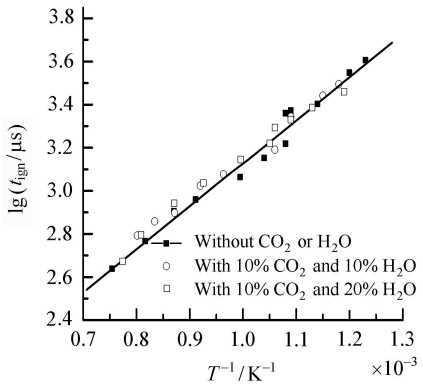

Fig. 10 Effect of water vapor and carbon dioxide on the ignition delay of kerosene at $\phi = 1.0$, $P = 0.3$ MPa

aspect is that water vapor and carbon dioxide participate in the initiation of ignition process; the other is that the addition of water vapor and carbon dioxide changes the thermophysics properties of the fuel mixtures. As we known, the ignition is highly related to the formation of free radicals and the thermophysics properties of the fuel mixtures.

The key factor in the ignition process of hydrocarbons is the rapid accumulation of free radicals such as H·, O· and OH·. Two most critical reactions in the process are

$$H\cdot + O_2 = OH + O\cdot, \tag{1}$$

$$H\cdot + HO_2\cdot = 2OH\cdot. \tag{2}$$

In the presence of water vapor, the production of hydroxyl radical is enhanced by reaction

$$H_2O + O\cdot = OH\cdot + OH\cdot. \tag{3}$$

This reaction is favorable for rapid accumulation rate of OH·. Thus, water vapor can promote the accumulation rate of OH·, leading to the ignition acceleration.

In addition, water vapor also can participate in the consumption of hydrogen atoms as a third-body in reaction

$$H\cdot + O_2 + M = HO_2\cdot + M. \tag{4}$$

Le Cong et al. [14] indicated that the chemical effect of water vapor reduced the rate of production of O· and OH· in $H\cdot + O_2 = OH + O\cdot$ through Reaction (4). The water vapor yields reduced formation of O· and OH·, and the third-body effect is more significant with the increasing temperature.

On the other hand, when the water vapor is considered as a diluent gas, the heat capacity of the fuel mixture increases when the water vapor is added. Würmel et al. [25] studied the effect of diluent gas on the ignition delay of hydrocarbon fuels by calculation. They indicated that the exothermicity of the radical growth phase causes the temperature of the mixture with high heat capacity to rise slower than that of the mixture with low heat capacity, and this leads to deceleration of the ignition. The ignition delay times of the fuel will increase because the heat capacity increases in the presence of water. Since the heat capacity increases as the temperature rises, therefore, this effect will be more significant at higher temperature.

In summary, water vapor can accelerate the ignition by participating in Reaction (3), but decelerate the ignition by the third-body and heat capacity effects. As mentioned above, the third-body and heat capacity effects are small at low temperature. At low temperatures, the major role of water vapor is its participation in Reaction (3), which promotes the ignition of the kerosene. The third-body and heat capacity effects are more significant as the temperature rises, so that these effects may cancel out with the promoting chemical reaction effect above the critical temperature. As can be seen in Figs. 5 and 6, a promoting effect appears below a critical temperature, but no effect exists above the critical temperature.

The chemical reaction between carbon dioxide and H·, O· and OH· is mainly due to the following reactions [12, 14]

$$CO_2 + H\cdot = CO + OH\cdot, \tag{5}$$

$$CO_2 + OH\cdot = CO + HO_2\cdot, \tag{6}$$

$$CO_2 + O\cdot = O_2 + CO, \tag{7}$$

$$CO_2 + H\cdot + H\cdot = CH_2\cdot + O_2. \tag{8}$$

As can be seen from these reactions, Reaction (5) is favorable for rapid accumulation rate of OH·, resulting in a promoting effect on the ignition. The other reactions have an inhibiting effect on the accumulation rate of H·, O·, and OH·, resulting in an inhibiting effect on the ignition. At the same time, the third-body and heat capacity effects also show an inhibiting effect on the ignition of kerosene. The overall effects of these factors may be described as follows: The inhibiting effect appears at low temperature (< 1 300 K) of fuel-lean ($\phi = 0.5$) conditions, but no noticeable effect appears at stoichiometric conditions or high temperature (> 1 300 K) of fuel-lean ($\phi = 0.5$) conditions.

When the two contaminants exist together, minor or no effect can be seen in the experiment because the two opposite effects of them may cancel out each other.

Although the above analysis is qualitative, it is helpful to understand the experimental results. In order to examine the contribution from a single reaction, detailed discussion based on dynamic simulation and sensitivity analysis will be made later.

4 Conclusions

Experiments were conducted on the autoignition of China RP-3 kerosene with and without water vapor or carbon dioxide addition in a shock tube over a wide temperature range of 800–1 500 K, at a pressure of 0.3 MPa, with equivalence ratios of 0.5 and 1, and oxygen concentration of 20%. Experimental results show that there exists a critical temperature for the effect of water vapor on the ignition delay time of kerosene. It appears to accelerate the ignition process below the critical temperature, but no effect above the critical temperature under the experiment conditions. Carbon diox-

ide produces an inhibiting effect on the ignition of kerosene at low temperature (< 1 300 K), but no effect at high temperature (> 1 300 K) under fuel lean ($\phi = 0.5$) conditions. The ignition of kerosene is almost not affected by the presence of CO_2 under stoichiometric conditions. A minor inhibiting effect is observed at $\phi = 0.5$, while no effect is found at stoichiometric conditions when both the water vapor and carbon dioxide exist together.

This work explores some probable reasons for the effect of water vapor and carbon dioxide on the ignition delay of China RP-3 kerosene from two aspects: H_2O and CO_2 participate in chemical reactions and change the thermophysics properties of the fuel mixtures. Water vapor can accelerate the ignition due to $H_2O + O\cdot = OH\cdot + OH\cdot$. At the same time, water vapor addition dramatically reduced the production rate of O and OH, leading to the ignition acceleration. On the other hand, the high heat capacity of the fuel mixture in the presence of water vapor will decelerate the ignition, too. Although carbon dioxide can accelerate the ignition by participating in the chemical reaction of $CO_2 + H\cdot = CO + OH\cdot$, however, the other factors such as participating in other chemical reactions Reactions (6)–(8) and changing the thermophysics properties of the fuel mixtures will decelerate the ignition.

References

1 Heiser, W.H., Pratt, D.T.: Hypersonic Airbreathing Propulsion. AIAA, Washington, D.C. (1994)

2 Teng, H.H., Jiang, Z.L.: On the transition pattern of the oblique detonation structure. J. Fluid Mech. **713**, 659–669 (2012)

3 Glassman, I., Yetter, R.A.: Combustion, (4th edn). Elsevier, Oxford (2008)

4 Ben, Y.A., Natan, B., Gany, A.: Investigation of a solid fuel scramjet combustor. J. Propuls. Power **14**, 447–455 (1998)

5 Teng, H.H., Jiang, Z.L.: Numerical simulation of one-dimensional aluminum particle–air detonation with realistic heat capacities. Combust Flame **160**, 463–472 (2013)

6 Hank, J., Murphy, J., Mutzman, R.: The X-51A Scramjet Engine Flight Demonstration Program. In: 15th AIAA International Space Planes and Hypersonic Systems and Technologies Conference. AIAA-2008-2540 (2008)

7 Pellett, G.L., Bruno, C., Chinitz, W.: Review of air vitiation effects on scramjet ignition and flam holding combustion processes. In: 38th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit. AIAA-2002-3888 (2002)

8 Mitani, T., Hiraiwa, T., Sato, S., et al.: Comparison of scramjet engine performance in Mach 6 vitiated and storage-heated air. J. Propuls. Power **13**, 635–642 (1997)

9 Mitani, T.: Ignition problems in scramjet testing. Combust Flame **101**, 347–349 (1995)

10 Jachimowski, C.J., Houghton, W.M.: Effect of carbon dioxide and water vapor on the induction period of the hydrogen-oxygen reaction. NASA TND-4685, 1968

11 Hitch. B.D., Senser, D.W.: Reduced H_2-O_2 mechanisms for use in reacting flow simulation. AIAA Paper **88**, 732–743 (1988)

12 Liu, W.X, Yang, Y., Shao, J.X., et al.: Influence of H_2O and CO_2 contamination in air on the combustion properties of ethylene. Acta Phys. Chem. Sin. **25**, 1618–1622 (2009) (in Chinese)

13 Le, J.L., Liu, W.X., Song, W.Y., et al.: Experimental and numerical investigation of air vitiation effects on scramjet test performance. In: 16th AIAA/DLR/DGLR International Space Planes and Hypersonic Systems and Technologies Conference. AIAA-2009–7344 (2009)

14 Le Cong, T., Emma, B., Dagaut, P.: Oxidation of ethylene and propane in the presence of CO_2 and H_2O: Experimental and detailed kinetic modeling study. Combust. Sci. and Techno. **182**, 333–349 (2010)

15 Chinitz, W., Erdos, J.I.: Test facility chemistry effects on hydrogen flames and detonations. In: 31st AIAA/ME/SAE/ASEE Joint Propulsion Conference and Exhibit. AIAA-1995-2467 (1995)

16 Chinitz, W., Erdos, J.I.: Test facility contaminant and atmospheric ozone effects on hydrocarbon flames and nozzle expansions. In: Proc. of 32nd AIAA/ME/SAE/ASEE Joint Propulsion Conference and Exhibit. AIAA-1996-2917 (1996)

17 Hou, L.Y., Yang, J., Ma, X.S., et al.: Influence of vitiation air from ethanol-fueled heating on kerosene-fueled supersonic combustion. J. Aero. Power **26**, 1921–1927 (2001) (in Chinese)

18 Xing, J.W., Xiao, B.G.: Numerical simulation of H_2O vitiation effects on kerosene-fueled scramjet combustor performance. J. Aero. Power **27**, 2408–2413 (2012) (in Chinese)

19 Li, J.P., Song, W.Y., Luo, F.T., et al.: Numerical investigation of H_2O and CO_2 vitiation effects on kerosene-fueled supersonic combustion. J. Propuls. Technol. **34**, 563–571 (2013) (in Chinese)

20 Liang, J.H., Wang, S., Hu, H.H., et al.: Shock tube study of kerosene ignition delay at high pressures. Science China-Physics Mechanics Astronomy **55**, 947–954 (2012)

21 Fan, X.J., Yu, G.: Analysis of thermophysical properties of Daqing RP-3 aviation kerosene. J. Propuls. Techno. **l27**, 188–192 (2006)

22 Wang, S., Fan, B.C., He, Y.Z., et al.: Shock tube study of kerosene ignition delay. Shock Waves **16**, 775–780 (2009)

23 Gaseq Chemical Equilibrium Program. Version 0.79. Computerized Educational Systems, New York (Columbia University), 2005

24 Davidson, D.F., Hanson, R.K.: Interpreting shock tube ignition data. Int. J. Chem. Kinet. **36**, 510–523 (2004)

25 Würmel, J., Silke, E.L, Curran, H.J.: The effect of diluent gases on ignition delay times in the shock tube and in the rapid compression machine. Combust. Flame **151**, 289–302 (2007)

26 Pang. G.A., Davidson, D.F., Hanson, R.K.: Experimental study and modeling of shock tube ignition delay times for hydrogen-oxygen-argon mixtures at low temperatures. P. Combust. Inst. **32**, 181–188 (2009)

27 Chaos, M., Dryer, F.L.: Chemical-kinetic modeling of ignition delay: Considerations in interpreting shock tube data. Int. J. Chem. Kinet. **42**, 143–150 (2010)

28 Tang, W.T., Brezinsky, K.: Chemical kinetic simulations behind reflected shock waves. Int. J. Chem. Kinet. **38**, 75–97 (2006)