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Shock Tube Study of JP-10 Ignition Delay Time

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JP-10 (exo-tetrahydrodicyclopentadiene, $C_{10}H_{16}$) ignition delay times were measured in a preheated shock tube. The vapor pressures of the JP-10 were measured directly by using a high-precision vacuum gauge, to remedy the difficulty in determining the gaseous concentrations of heavy hydrocarbon fuel arising from the adsorption on the wall in shock tube experiments. The whole variation of pressure and emission of the OH or CH radicals were observed in the ignition process by a pressure transducer and a photomultiplier with a monochromator. The emission of the OH or CH radicals was used to identify the time to ignition. Experiments were performed over the pressure range of 151-556 kPa, temperature range of 1000-2100 K, fuel concentrations of 0.1%-0.55% mole fraction, and stoichiometric ratios of 0.25, 0.5, 1.0 and 2.0. The experimental results show that for the lower and higher temperature ranges, there are different dependency relationships of the ignition time on the temperature and the concentrations of JP-10 and oxygen.

Key words: Ignition delay time, JP-10, Shock tube

I. INTRODUCTION

JP-10 (exo-tetrahydrodicyclopentadiene, $C_{10}H_{16}$) as a high energy density fuel is being considered for use in future scramjet and pulse detonation engines [1-3]. The ignition delay time of a fuel is usually concerned as a characteristic time to scale the duration of the gas flow passing through the combustion chamber, which is a criterion to measure the capability of the ignition and sustaining of the flame in the engine [4]. When using the computational fluid dynamics (CFD) to simulate the real process in a combustion chamber, a simplified chemical reaction model is necessary. One of the criteria of the validation of the model is that it should correctly reflect the behavior of the ignition delay time [5,6]. The ignition delay time is also a mark to indicate the effectiveness of additives to enhance the ignition process for hydrocarbon fuels [7,8].

There are three kinds of facilities for ignition time measurements. The first is the closed constant volume reaction chamber available for temperatures below 600 K with the ignition delay time of the order of 0.1 s. The second is the rapid compression apparatus available for temperatures below 900 K and the range of the ignition delay time of 10-100 ms [9]. The third is the shock tube facility available for the temperature range of 900-2500 K and even higher than that, with the measurement time range of 1 μs-10 ms [10]. At present, the shock tube is widely used in the study of the ignition delay time of hydrocarbon fuels.

Comparing the existing experimental measurement results of the JP-10 ignition delay time obtained in shock tube studies by different authors, it has been found that these measurement results are not consistent with each other and relatively dispersed. These differences may be attributed to using different methods to put the liquid fuel into the shock tube and to determine the concentration of the liquid fuel vapor in their experiments.

Davidson *et al.* have noted that the uncertainty in the concentration of the fuel vapor due to the adsorption of the fuel vapor on the shock tube wall is one of the largest sources of errors in ignition time measurements of liquid fuels [11]. To account for this effect, they put forward a technique to measure the *in situ* vapor concentration of JP-10 using laser absorption at 3.39 μm [12]. However, the adsorption effect of the fuel vapor on the optical windows should be carefully considered both in their shock tube measurements and in their separate experiment for determining the absorption coefficient of the JP-10 vapor in the absorption cell. Mikolaitis *et al.* used a flow circulation system to put the JP-10 vapor into a shock tube, in which a small evaporation chamber was connected in the circulation [13], as they injected a quantitative liquid fuel into the small chamber. Hence, how to minimize the degree of fuel vapor adsorption and enable a more accurate measurement of the JP-10 vapor concentration in gas phase may be important criteria in determining reliable ignition delay time results. Furthermore, all the existing experiments have been carried out at temperature ranges higher than 1300 K, which is not low enough for application in the case of the scramjet engine working in its lower temperature part. The current study is concerned with the ignition delay time over a wider temperature range, especially extending the lower temperature bound to 1000 K.

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II. EXPERIMENTS

The experiments were carried out in a shock tube at the Institute of Mechanics, Chinese Academy of Sciences [14]. The driver section has a length of 2.0 m and the driven section is 1.8 m in length. Both have circular cross sections with an inner diameter of 44 mm. The driven section was evacuated down to the ultimate pressure of 13 mPa by a turbomolecular pump. The outgassing rate was smaller than 6.7 mPa/min. The incident shock speeds were measured by two piezoelectric transducers mounted on the shock tube sidewall. The ± 1 μs uncertainty in shock arrival time results in a $\pm 1\%$ uncertainty in temperature. The conditions behind the reflected shock were calculated from the incident shock speed using one-dimensional shock relations. A piezoelectric transducer mounted on the endwall of the driven section was used to monitor the pressure evolution in the reflected shock region. A quartz window was installed on the sidewall very close to the endplate of the driven section to monitor the emission from the ignition process in the reflected shock region. The emission focused through a lens was detected by using a photomultiplier after passing through a monochromator centered at the emission lines of OH or CH radicals. Finally, the pressure and emission signals were recorded by a transient A/D transducer. A schematic diagram of the facility is shown in Fig.1.
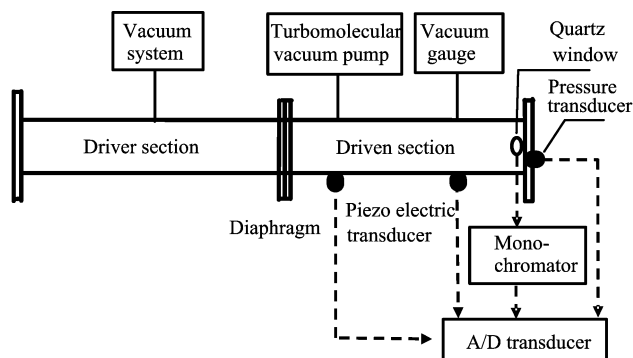

FIG. 1 Schematic diagram of shock tube facility.

A longer observation time is required as ignition times increase at the lower temperature region. For the purpose of the present effort, the shock tube was run under conditions for a tailored interface, resulting in an observation time of about 7 ms. Therefore, instead of pure He, a mixture of N_2 and He with a specific ratio was used as the driver gas to decrease the sound speed of region 3 of the shock tube and achieve conditions in which the interaction of the reflected shock with the contact surface produces no secondary reflected wave. Under conditions for a tailored interface, the lower temperature bound of experiments was extended to 1000 K in the current study.

JP-10 is a heavy hydrocarbon with 10 carbon atoms.

The vapor saturation pressure at 25 °C is about 400 Pa. There exists a severe adsorption on the wall in shock tube experiments, resulting in the uncertainty in determination of the composition of the test gas mixture. The very low vapor pressure of JP-10 also limits the experimental concentration range. To minimize the degree of adsorption and increase the test vapor pressure of JP-10, the shock tube and the mixing tank for the mixture of O_2 and Ar were preheated and maintained at 70 °C throughout the experiments. In the current study, after the shock tube was filled with JP-10, the JP-10 vapor pressures in adsorption equilibrium were measured directly by using a high-precision vacuum gauge to determine the test mixture composition. A membrane vacuum gauge (Beijing Vacuum Instrument Factory, Model ZDM-1) was selected to measure the JP-10 pressure, with a resolution of 0.1 Pa when the working pressure was under 1 kPa. The time interval from filling the shock tube with JP-10 to the diaphragm rupture was about 10 min. To estimate the adsorption extent, therefore, the adsorption curves of JP-10 in the driven section maintained at 70 °C were measured for 10 min after injecting 5, 10 and 20 μL of liquid JP-10 as shown in Fig.2. These results show the adsorption equilibriums are almost reached in 5 min and completely reached in 10 min. If the adsorption could be negligible and a full evaporation is achieved, then 10 μL of liquid JP-10 would yield a theoretic vapor pressure of about 70 Pa at 70 °C. The adsorbance could be expressed as the difference between the theoretic and equilibrium vapor pressures, thus the adsorbance accounts for 53% of the theoretic vapor pressure for the 10 μL sample, indicating the occurrence of a high degree of fuel vapor adsorption.
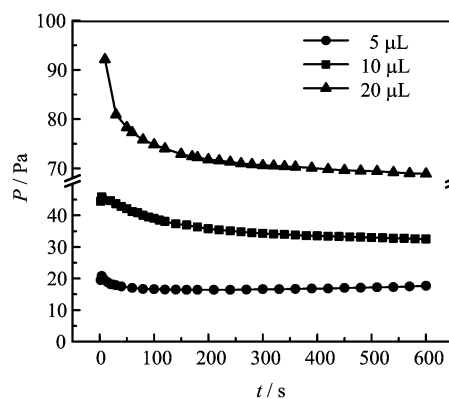

FIG. 2 Adsorption curves of JP-10.

After the driven section was evacuated to the ultimate pressure, a quantity of liquid JP-10 was injected into the driven section after which the JP-10 pressure was measured 5 min after the fuel evaporated and adsorbed. Furthermore, a mixture of O_2 (99.995% pure) and Ar (99.99% pure) as diluent was added into the driven section, an additional time of 5 min was allowed

for the gases to mix fully, and the final total pressure was measured 10 min after injecting JP-10. Our experience shows that 5 min is sufficient to mix the gases fully. Thus the JP-10 concentrations could be determined by using the direct pressure measurements based on the adsorption curves. The time interval of 10 min from injecting JP-10 to the diaphragm rupture was specified to ensure both achievement of JP-10 adsorption equilibrium and homogeneity of the test mixture. The driver section was filled with N_2 and He at a required ratio as the tailored interface operation is achieved. To mix the added gases fully, an alternate addition procedure of the mixture components was employed. After initially adding He to approximately half of the desired pressure and subsequently N_2 to the desired pressure, the driver section was filled with the remaining He to the desired final pressure. It has been shown that the instability of the shock speed can be avoided by employing such an addition procedure. JP-10 was used without purification. The chromatogram of the sample showed the JP-10 was 98.5% pure.

Experiments were performed over the pressure range of 151-556 kPa and the temperature range of 1000-2200 K. The total pressure and the emission of OH radical at 306.5 nm or CH radical at 431.5 nm in the reflected shock region were recorded after the bursting of the diaphragm. The radical emission was used as the marker to identify the ignition time.

An example of pressure and OH emission data is shown in Fig.3. P_5 indicates the passing of the reflected shock and the pressure evolution, and I_{OH} indicates the OH emission evolution in the reflected shock region. It can be seen that the abrupt increases in pressure and emission occur at the same time, and the onset of ignition is unequivocal, especially compared to the more conventional determination from the abrupt increase in pressure [15,16]. The ignition delay time is defined as the time interval between the passing of the reflected shock and the onset of ignition, which is usually determined by fitting a straight line to the initial rapid
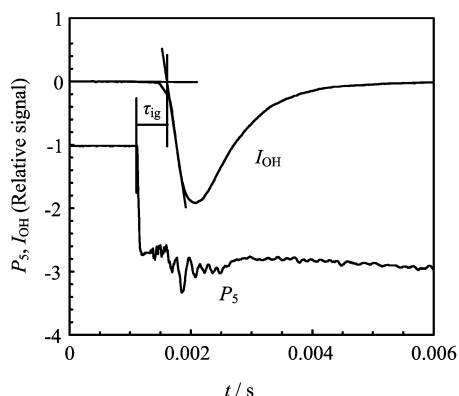

FIG. 3 Example of OH emission and pressure data. Reflected shock conditions: 1280 K, 0.12%JP-10, 6.7%O_2 and 93.1%Ar.

rising portion of the emission and extrapolating until it intersects with zero, as shown in Fig.3.

In the current study, emission measurements were made both for OH radical at 306.5 nm and for CH radical at 431.5 nm. The resulting comparison of the two diagnostic methods for ϕ=1.0 case as an example is shown in Fig.4. The results of experiments show that the two diagnostic methods yield no distinct difference in the ignition times.
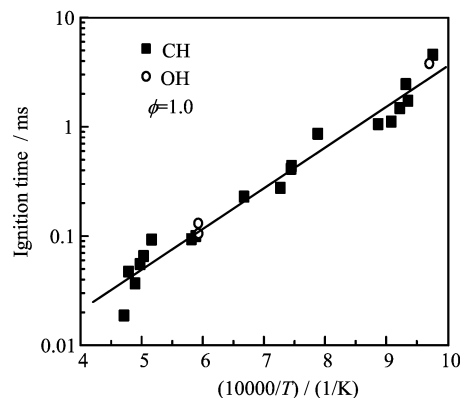

FIG. 4 Comparison of the results by tracing CH and OH emission signals.

III. RESULTS AND DISCUSSION

Ignition times were measured for four different fuel/O_2/Ar mixtures with stoichiometric ratios of 2.0, 1.0, 0.5 and 0.25, respectively. The initial compositions of the diluent gases and the injection volumes of JP-10 are given in Table I. The experiments for ϕ=1.0 were measured by using CH emission, whereas the experiments for the other ϕ were measured by using OH emission.

TABLE I Initial composition

No.	Composition of diluent gas	Injection volume of JP-10/μL	ϕ
1	96.40%Ar+3.60%O_2	20	2.0
2	96.65%Ar+3.35%O_2	10	1.0
3	93.28%Ar+6.72%O_2	10	0.5
4	93.28%Ar+6.72%O_2	5	0.25

JP-10 ignition delay time data are shown in a logarithmic plot of the ignition time *vs* the reciprocal temperature in Fig.5. Clearly, the slopes of the ignition curves decrease with increasing ϕ, suggesting that the ignition activation energy exhibits a systematic decrease with increasing stoichiometric ratio ϕ. If an expression of the form $\tau=AP^n\exp(B/T)$ is used to correlate the data, where P is the total pressure behind the reflected shock and in atmospheres, we have n=−1.95, −0.76,

0.34 and -0.18, and B=11900, 11032, 9585 and 6482 K, with an R^2 value of 0.889, 0.992, 0.984 and 0.993, for the data sets of ϕ=0.25, 0.5, 1.0 and 2.0, respectively.
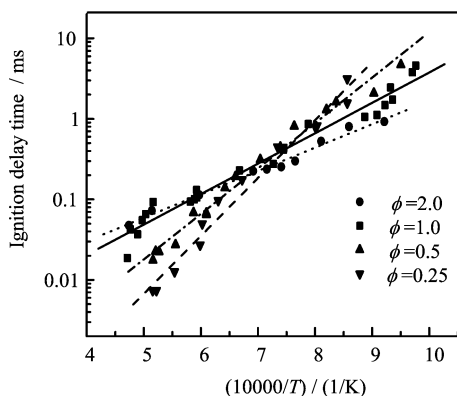

FIG. 5 Ignition time data.

Furthermore, over the temperature range studied here, all ignition curves intersect with each other approximately at 1400 K. The transition temperature of 1400 K divides the experimental temperature range into higher and lower temperature regions. For higher temperatures, the JP-10 ignition time decreases as ϕ is decreased. On the contrary, for lower temperatures, the JP-10 ignition time decreases as ϕ is increased. This suggests that there is a transition in the chemical mechanism, probably the result of the competition between the nonoxidative and oxidative pyrolytic decompositions of JP-10. This phenomenon has not been seen in earlier studies, probably because of their narrower temperature range. Considering this feature of the current results, a least square analysis was performed for the higher and lower temperature ranges, respectively, to correlate the JP-10 ignition time data with temperature and concentrations of JP-10 and oxygen based upon the expression of an average activation energy.

For the higher temperature range of 1400-2120 K, the correlations were obtained with an R^2 value of 0.897 in the following forms

$$\tau = 5.66 \times 10^{-11}[\text{JP--10}]^{0.52}[\text{O}_2]^{-1.20} \exp\left(\frac{95733}{RT}\right) \quad (1)$$

$$\tau = 9.84 \times 10^{-5} P^{-0.63} X_{\text{O}_2}{}^{-0.64} \phi^{0.52} \exp\left(\frac{86851}{RT}\right) \quad (2)$$

For the lower temperature range of 1000-1400 K, the correlations were obtained with an R^2 value of 0.948 in the following forms

$$\tau = 1.25 \times 10^{-6}[\text{JP--10}]^{-0.35}[\text{O}_2]^{0.53} \exp\left(\frac{81643}{RT}\right) \quad (3)$$

$$\tau = 3.91 \times 10^{-8} P^{0.18} X_{\text{O}_2}{}^{0.16} \phi^{-0.31} \exp\left(\frac{83350}{RT}\right) \quad (4)$$

where τ is in seconds, P is in Pa, X_{O_2} is the oxygen mole fraction, ϕ is the stoichiometric ratio, [JP-10] and

[O_2] are in mol/cm^3, and the activation energy is in J/mol. In Eqs.(1) and (3), the ignition time is expressed in terms of the temperature and the fuel and oxygen concentrations, whereas in Eqs.(2) and (4) the correlation of the ignition time with more practical parameters, pressure and stoichiometric ratio, is explicitly expressed.

Using Eq.(1) for the higher temperature range, it can be determined that the effect of fuel and oxygen concentrations on the JP-10 ignition time is strong, and the JP-10 concentration power dependence is a relatively large positive value, and the oxygen concentration power dependence is a relatively large negative value. For the lower temperature range, however, Eq.(3) shows that the effect of fuel and oxygen concentrations on the JP-10 ignition time is weak compared to higher temperatures. In fact, the JP-10 concentration power dependence is a negative value and the oxygen concentration power dependence is a positive value for the lower temperature range. It is found that the activation energy varies only slightly for the lower and higher temperature ranges.

To compare the current work with the earlier shock tube studies at similar conditions, the stoichiometric ignition time data are shown in Fig.6 along with the data from Davidson et al. [12], Colket and Spadaccini [17], and Mikolaitis et al. [13]. The ignition times in the current study appear to be shorter than those obtained by Davidson et al., longer than those by Mikolaitis et al., and in fair agreement with the Colket and Spadaccini data in the common temperature region. When correlating the data using the form $\tau = AP^n \exp(B/T)$, we obtain activation energies of B=26179, 22490, 15065 and 9585 K for the data from Davidson et al., Colket & Spadaccini, Mikolaitis et al., and the current work, respectively. The activation energy of the current work is smaller than that from Mikolaitis et al., and much lower than those from Davidson et al., and Colket and Spadaccini. Ryan et al. performed an ignition study of JP-10 in a constant-volume bomb at 590-855 K and
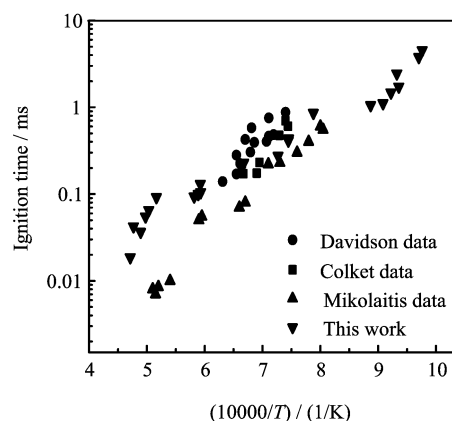

FIG. 6 Comparison of the current work with the earlier studies for stoichiometric ignition time data.

2.5-3.0 MPa [18], and derived an activation energy of B=11000 K, very close to the value in the current study. However, the test conditions in the Ryan *et al.* study were different from those studied here. The difference in the activation energy may be due in part to the different ignition time definitions employed. In the Davidson *et al.* study, the onset of ignition was defined from the peak CH emission signal, whereas for the Colket and Spadaccini and current studies, the onset of ignition was based on the initial rapid rise in the CH or OH emission trace. Generally, peak signal measurements lead to a higher activation energy than those based on the signal initial rapid rise [19]. On the other hand, the adsorption effect on the shock tube wall was taken into account only in the Davidson *et al.* and current studies. The premixed mixture composition was manometrically measured in the Colket and Spadaccini study. Based on the injection volume of JP-10, Mikolaitis *et al.* determined the gas mixture composition in shock tube. Davidson *et al.* tried measuring JP-10 concentration by using *in situ* laser absorption, and the results showed that the laser absorption concentration measurement differed from the conventional mixing assembly manometric measurement by typically ±5%. However, the adsorption effect was significant in the current study (see Fig.2). Therefore, the stoichiometric data in the earlier studies should correspond to those data at somewhat lean conditions in the current study, which lead to a higher activation energy. In addition, more striking are the similarities of the ignition time sensitivities for the different investigators. The correlations obtained by Davidson *et al.* and Colket and Spadaccini exhibit the fuel and oxygen concentration dependences of 0.67 and −1.27, and 0.40 and −1.20, respectively, which are very close to those values of 0.52 and −1.20 observed for the higher temperature range in the current study. To explain the observed behavior and further validate the correlations presented in the current study, it is recommended that further work involve the comparisons of the simulated ignition times with a chemical kinetic model to those found experimentally.

IV. CONCLUSION

JP-10 ignition delay times were measured in a preheated shock tube over the pressure range of 151-556 kPa, temperature range of 1000-2200 K, fuel concentrations of 0.1%-0.55% mole fraction, and stoichiometric ratios of 0.25, 0.5, 1.0, 2.0. In the current experiments, the adsorption of JP-10 in shock tube was taken into account, and JP-10 concentration was determined by measuring the vapor pressure with a high-precision vacuum gauge and using the adsorption curves, to remedy the difficulty in determining the gaseous concentrations of heavy hydrocarbon fuels arising from the adsorption on the shock tube wall. These measured ignition delay times are correlated with the temperature and the concentrations of JP-10 and oxygen. The experimental data show there are the different dependency relationships for the lower and higher temperature ranges. The transition temperature is about 1400 K. For the higher temperature range of 1400-2120 K, the JP-10 concentration dependence of the ignition time is a relatively large positive value, whereas the oxygen concentration dependence is a relatively large negative value. In contrast, for the lower temperature range of 1000-1400 K the JP-10 concentration dependence of the ignition time is a negative value and the oxygen concentration dependence is a positive value.

V. ACKNOWLEDGMENT

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