

# Comparison of the autoignition characteristics of *n*-heptane, methylcyclohexane and toluene

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**Abstract:** The autoignition characteristics of three C<sub>7</sub> hydrocarbon fuels, *n*-heptane, methylcyclohexane and toluene, were comparatively investigated. Ignitions were performed behind the reflected shock waves in a shock tube. The ignition delay times of these fuels were measured at the same ignition conditions with constant fuel mole fraction of 1.0%, equivalence ratio of 1.0, ignition pressure of  $1.0 \times 10^5$  Pa (one more  $2.0 \times 10^5$  Pa for *n*-heptane) and temperatures of 1 166—1 662 K. The correlation formula of ignition delay dependence of three fuels on ignition conditions was deduced separately. Results show that the ignition delay time of *n*-heptane is the shortest while that of toluene is the longest at the same ignition conditions. The ignition delay time of methylcyclohexane is most sensitive to the temperature while that of *n*-heptane is the least. The comparison of current ignition delay times with the predictions of available chemical kinetic reaction mechanisms has been presented to validate the reliability of mechanisms. The important chemical reactions during the ignition process have been obtained from the sensitivity analysis.

**Key words:** hydrocarbon fuels; ignition delay time; chemical shock tube;  
kinetic mechanism; sensitivity analysis

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For aero-vehicles, practical fuels such as Jet A and RP-3 kerosenes, contain many types of hydrocarbon species. These compounds can be classified by molecular structure and grouped into categories: alkanes, cycloalkanes, aromatics, alkenes, naphthalenes, and oxygenated hydrocarbons<sup>[1]</sup>. Due to the chemical complexity of practical fuels, efforts have been made to develop surrogate mixtures containing a limited number of representative compounds from the various hydrocarbon classes (normal alkanes, cycloalkanes, alkenes, aromatics, naphthalenes) to mimic the properties of real fuels<sup>[2-3]</sup>. *n*-heptane, methylcyclohexane (MCH) and toluene contribute a significant portion of practical fuels.

In order to develop the surrogate mixtures of practical fuels, these three C<sub>7</sub> fuels are often chosen as the representatives of *n*-alkane, cycloalkane and aromatic, respectively<sup>[4]</sup>.

Since autoignition characteristics of fuels are important for the design of aero-engine combustors, the comparative study of the ignition delay times of *n*-heptane, MCH, and toluene is very necessary. This study can provide us a better understanding of ignition characteristics of these fuels and get experimental data for the development of corresponding comprehensive chemical reaction mechanisms.

Previous measurements of ignition delay times for *n*-heptane, MCH, and toluene have

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been performed in shock tubes<sup>[5-10]</sup>, rapid compression machines (RCM)<sup>[11]</sup> and jet stirred reactors<sup>[12]</sup>. In addition to the previous experimental investigations for ignition delay times of these three fuels, there have been many kinetic modeling studies<sup>[5, 11, 13-17]</sup>. However, many of these efforts have been dedicated to *n*-heptane and experiments were performed at high pressures. Only a few studies concern the ignition of MCH and toluene, especially at condition of atmosphere pressure. Therefore, the aim of this work is to experimentally explore the relative high temperature ignition behavior of these three hydrocarbon species around atmosphere pressure, and investigate the chemical kinetic reaction mechanisms for these fuels.

1 Experimental method

The experimental setup is shown in Fig. 1. Experiments were carried out behind the reflected shock waves in a stainless steel shock tube with a constant inner diameter of 10.0 cm. The shock tube includes a 5.0 m driven section and a 4.0 m driver section. The shock tube technique used is characterized by a very rapid heat up of the experiment gas coupled with adiabatic and diffusion-free reaction conditions. It is well suited to measure ignition delay times less than about 10 ms<sup>[6]</sup>. The shock tube and delivery lines were pumped to pressures less than 10 Pa by a vacuum pump system. Fuel/O<sub>2</sub>/Ar mixtures were prepared in a 40 L mixing tank. The con-

centration of fuels is kept to 1.0% and diluted in argon, with an equivalence ratio ( $\Phi$ ) of 1.0. The details of the facility have been described elsewhere<sup>[18-19]</sup>.

The light emission during the combustion process was exported by a quartz fiber, which located at the same cross section of the last pressure transducer, 15 mm to the endwall. The CH<sup>+</sup> chemiluminescence at 431 nm was measured by a monochromator coupled with a photomultiplier tube. The pressure and light signals were transferred and recorded by two digital phosphor oscilloscopes ( Tektronix TDS5054B and DPO5054 ). The incident shock speeds were measured using four piezo-electric pressure transducers (PCB 113B) spaced over the last 75 cm of the shock tube.

The ignition temperatures and pressures of the reflected shock waves were calculated by the one-dimensional normal shock equations using the measured initial temperature and pressure in the driven section, the incident shock speed, and the chemical thermodynamic properties of the reactant mixtures. Due to the uncertainty in the incident shock wave speed measurements, the uncertainty in determining the ignition delay time from the pressure and emission, and the uncertainty in temperature and pressure change by non-ideal gas dynamic effects, the ignition delay time uncertainty is estimated to be less than  $\pm 20\%$  in current work. A typical example of ignition delay measurement is shown in Fig. 2.

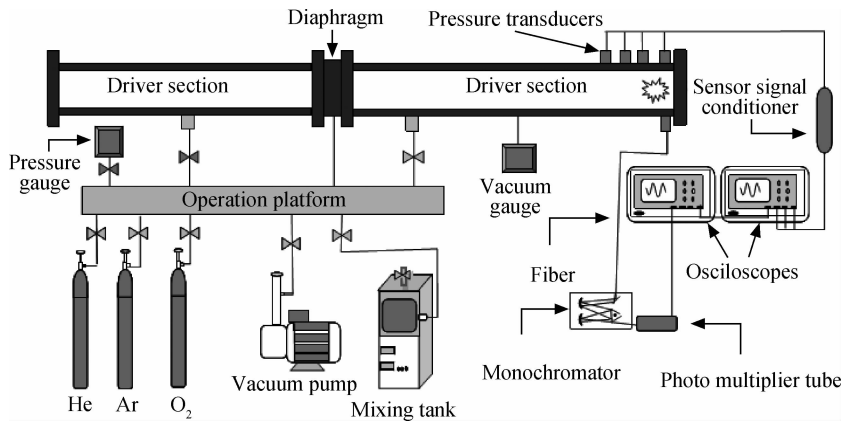


Fig. 1 Experimental setup

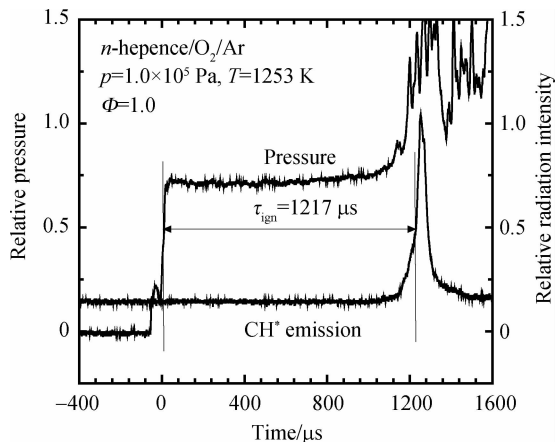
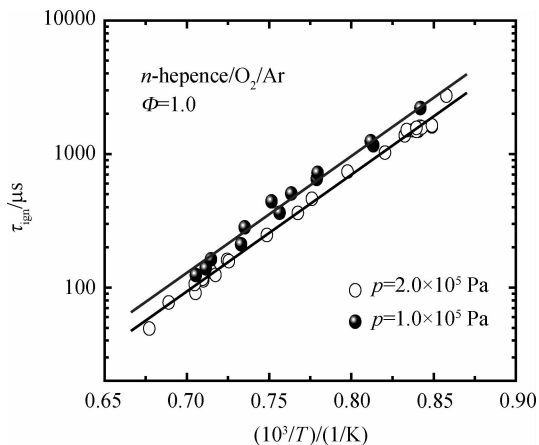


Fig. 2 Example of ignition delay time measurement

Fig. 3 Ignition delay times of *n*-heptane

## 2 Results and discussion

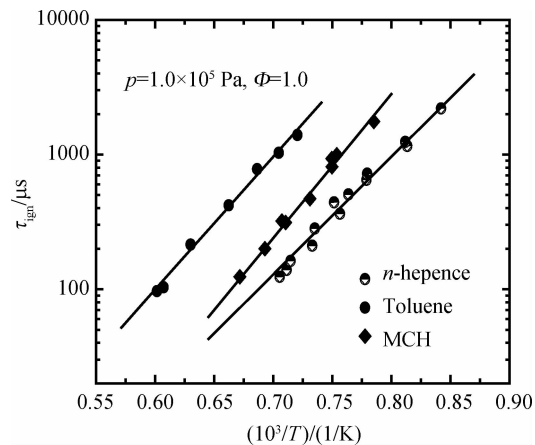
### 2.1 Experimental results

The ignition delay results of *n*-heptane/O<sub>2</sub>/Ar mixtures are shown in Fig. 3. It clearly depicts that the ignition delay times of *n*-heptane show distinct variations with pressure and temperature, an increase in the pressure or temperature results in a decrease in the measured ignition delay times. Species concentrations increase with increasing in pressure, then the chemical reaction rate increases, as a result, the ignition delay time decreases. The chemical reaction rate increases for increasing temperature, this also results in the ignition delay time decreases. The slopes of experimental data at  $1.0 \times 10^5$  Pa, and  $2.0 \times 10^5$  Pa conditions are identical, so correlation formula for the ignition delay times can be obtained as below by linear regression analysis ( $r^2$  is the correlation coefficient).

$$\textit{n-heptane} \quad \tau_{\text{ign}} = 9.80 \times 10^{-5} p^{-0.463} e^{167340/(RT)} \quad (r^2 = 0.994) \quad (1)$$

where  $\tau_{\text{ign}}$  is the ignition delay time in  $\mu\text{s}$ ,  $p$  is the ignition pressure in  $10^5$  Pa,  $T$  is the ignition temperature in K, and  $R(8.314\text{J}/(\text{mol} \cdot \text{K}))$  is the universal gas constant. The lines in Fig. 3 are fitted results at respective pressure.

The ignition pressures of toluene and MCH are around  $1.0 \times 10^5$  Pa, experimental results are comparatively shown in Fig. 4, as well as the results of *n*-heptane. Correlation formula for the ignition delay times of toluene and MCH are ob-

Fig. 4 Ignition delay times of C<sub>7</sub> fuels

tained separately, as below:

$$\text{MCH} \quad \tau_{\text{ign}} = 7.95 \times 10^{-6} e^{204560/(RT)} \quad (r^2 = 0.991) \quad (2)$$

$$\text{Toluene} \quad \tau_{\text{ign}} = 1.32 \times 10^{-4} e^{188830/(RT)} \quad (r^2 = 0.991) \quad (3)$$

Fig. 4 shows that under the same ignition conditions, the ignition delay times of toluene are the longest while those of *n*-heptane are the shortest. The slopes of the lines in Fig. 4 represent the global activation energies of the fuels, the global activation energies of *n*-heptane, MCH and toluene were fitted to be 167, 205, 189 kJ/mol, respectively, indicating that the ignition of MCH is most sensitive to the temperature, while that of *n*-heptane is the least. The causes of this behavior will be discussed in the next section.

### 2.2 Discussion

During the oxidation processes, toluene

needs to via ring open bybond cleavage of C=C bond, while MCH via ring open by bond cleavage of C-C bond to form small species. *n*-heptane is a straight-chain alkane, there is no ring open process during the oxidation. Thus, the ignition delay time of toluene being the longest while that of *n*-heptane being the shortest is partially caused by these different bond cleavage modes. To investigate the phenomenon further, the chemical kinetic reaction mechanism analysis was discussed below.

The obtained experimental data were used here to validate the reliabilities of corresponding chemical kinetic mechanisms. Andrae et al.<sup>[14]</sup> proposed a semi-detailed mechanism for toluene reference fuels, where skeletal mechanisms for *n*-heptane were added to a detailed toluene sub-mechanism. Ranzi<sup>[15]</sup> constructed a detailed chemical kinetic mechanism for surrogates of real fuels. JetSurF 2.0<sup>[16]</sup> is a high-temperature chemical kinetic model of *n*-alkane (up to *n*-dodecane), cyclohexane, and methyl-, ethyl-, *n*-propyl and *n*-butyl-cyclohexane oxidation. The model is being developed through multi-university research collaboration. Pitz et al.<sup>[11]</sup> developed a kinetic mechanism of MCH for the low and high temperature chemistry. Blanquart et al.<sup>[17]</sup> presented a chemical mechanism for the high temperature combustion of a wide range of hydrocarbon fuels, including aromatic chemistry. For the purpose of comparison with experiments, the shock tube ignition process is modeled using a reflected shock tube reactor with Chemkin 2.0<sup>[20]</sup>. Fig. 5(a) shows that all mechanisms successfully predict the global activation energy of *n*-heptane. However, the ignition delay times are overestimated by a amount of about 40% by JetSurF 2.0<sup>[16]</sup>. The prediction of Ranzi et al.<sup>[15]</sup> is close to the experimental results, and pitz et al.<sup>[11]</sup> mechanism is in fairly good agreement with measured ignition delay times. Fig. 5 (b) shows that the Ranzi et al.<sup>[15]</sup> mechanism can successfully predict the global activation energy of MCH, however, the ignition delay times are about 20% underestimated. Pizi et al.<sup>[11]</sup>

mechanism is in agreement with the measured ignition delay times. Fig. 5 (c) shows that for toluene at  $1.0 \times 10^5$  Pa, the prediction of Andrae et al.<sup>[14]</sup> mechanism is far away from the measured ignition delay times. Ranzi et al.<sup>[15]</sup> mechanism underestimates the ignition delay times. Blanquart et al.<sup>[17]</sup> mechanism is in good agreement

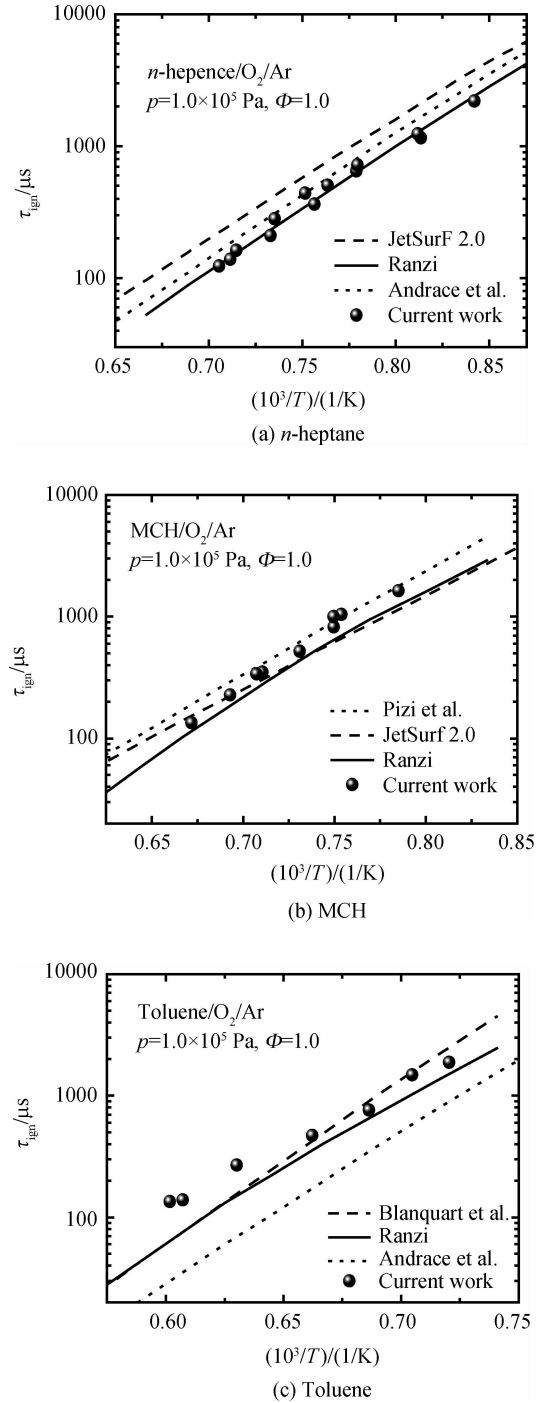


Fig. 5 Comparison of *n*-heptane, MCH and toluene ignition delay times with corresponding mechanism predictions

with the measured ignition times at relative low temperatures. However, all mechanisms underestimate the ignition delay times of toluene at relative high temperatures.

As Andrae et al.<sup>[14]</sup>, Pitz et al.<sup>[11]</sup>, and Blanquart et al.<sup>[17]</sup> mechanisms can successfully predict the ignition delay times of *n*-heptane, MCH and toluene respectively, sensitivity analyses of these fuels were performed using corresponding mechanisms to assess the chemical reactions with the main influence. The percentage change in the ignition delay  $100 \times [\tau_{\text{ign}}(2k_i) - \tau_{\text{ign}}(k_i)]/\tau_{\text{ign}}(k_i)$  is taken as the sensitivity of each reaction<sup>[21]</sup>. A positive sensitivity coefficient implies that ignition delay increases with increasing rate constant of a particular reaction. Results of the sensitivity analysis are shown in Fig. 6, where A<sub>1</sub> is Benzene, A<sub>1</sub>CH<sub>3</sub> is toluene, A<sub>1</sub>CH<sub>2</sub> is benzyl radical and A<sub>1</sub>CH<sub>2</sub>O is benzyl alcohol radical.

Chemical mechanism analysis shows that the reaction  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$  plays an important role in the ignition processes, and exhibits the highest sensitivity, leading to the decrease of the

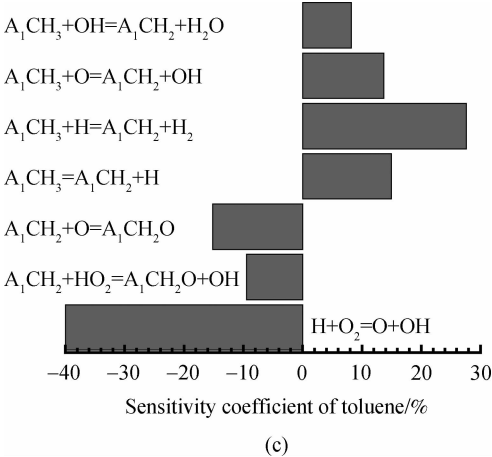
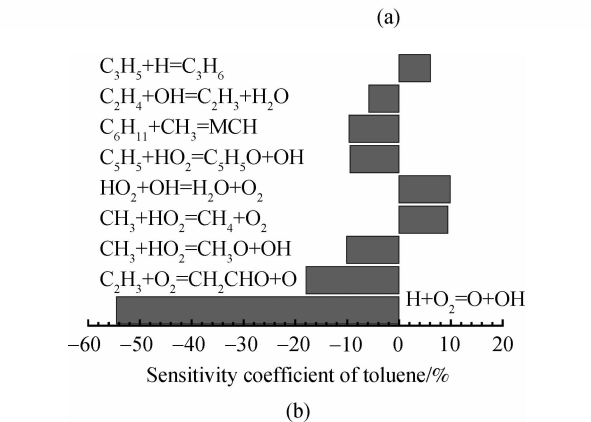
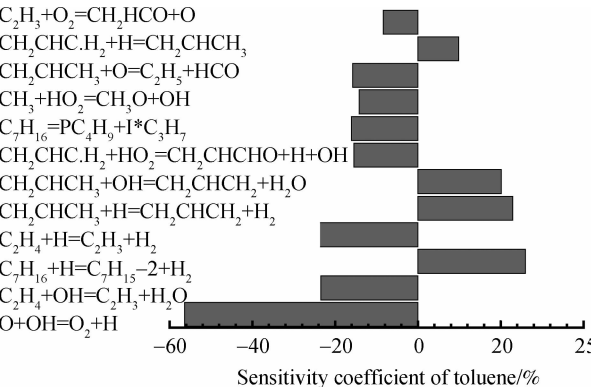


Fig. 6 Sensitivity analyses for *n*-heptane, MCH and toluene

ignition delay for toluene, MCH and *n*-heptane. However, the other key reactions for the fuels are quite different. Sensitivity results indicate that reactions involving H and OH, the decomposition and H-abstraction reactions of *n*-heptane, reactions involving ethane and allyl radicals are important for *n*-heptane at the experimental conditions. The chemical reactions involving OH, HO<sub>2</sub>, CH<sub>3</sub> and C<sub>2</sub>H<sub>3</sub> radicals make major contributions to the ignition delay times for MCH, such as the consumption reaction of CH<sub>3</sub> with HO<sub>2</sub> and oxidation reactions of C<sub>2</sub>H<sub>3</sub> with O<sub>2</sub>. The important reactions for toluene are benzyl radical oxidation, toluene decomposition reaction and reactions of toluene with H, O and OH radicals, they have opposite effects on the ignition delay. In these fuels, These different reactions and bond cleavage modes lead to the different ignition delay times of these three fuels at the same conditions.

### 3 Conclusions

Ignition delay times of *n*-heptane, MCH and toluene have been studied behind shock waves around atmosphere. An increase in the pressure or temperature results in a decrease in the measured ignition delay times. The magnitudes of ignition delay times follow the order *n*-heptane<MCH<toluene at the same ignition conditions, and the magnitudes of the global activation energies are in the order of *n*-heptane<

toluene < MCH. The complete data set greatly extends the chemical kinetic modeling targets available for toluene, MCH and *n*-heptane at low-pressure conditions.

The different ignition delay times of *n*-heptane, MCH and toluene indicate that the dominant chemistry in each ignition process is different. Sensitivity analyses show that reaction  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$  exhibits the highest sensitivity for all these fuels, leading to the decrease of the ignition delay. However, the other main sensitive reactions and the bond cleavage mode for each fuel are quite different, resulting in the difference of the ignition delay times of these three fuels.

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