Autoignition of gasoline surrogates mixtures at intermediate temperatures and high pressures

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Abstract

Ignition times were determined in high-pressure shock-tube experiments for various stoichiometric mixtures of two multicomponent model fuels in air for the validation of ignition delay simulations based on chemical kinetic models. The fuel blends were n-heptane (18%)/isooctane (62%)/ethanol (20%) by liquid volume (14.5%/44.5%/41% by mole fraction) and n-heptane (20%)/toluene (45%)/isooctane (25%)/diisobutylene (10%) by liquid volume (17.5%/55%/19.5%/8.0% by mole fraction). These fuels have octane numbers comparable to a standard European gasoline of 95 RON and 85 MON. The experimental conditions cover temperatures from 690 to 1200 K and pressures at 10, 30, and 50 bar. The obtained ignition time data are scaled with respect to pressure and compared to previous results reported in the literature.

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1. Introduction

Autoignition is of critical importance in internal combustion (IC) engines, since it causes knock, which limits efficiency, in spark ignition (SI) engines and is the mechanism by which heat release occurs in compression ignition (CI) and homogeneous charge compression ignition (HCCI) engines. Autoignition is determined by the evolution of pressure and temperature in the fuel/air mixture with time and by the fuel. Practical fuels are complex mixtures of hydrocarbons and their autoignition characteristics must be described by empirical measures such as research and motor octane numbers, RON and MON, which are not always adequate [1]. Ideally, autoignition would be described by comprehensive chemical kinetics as the pressure and temperature evolve with time. However, such mechanisms applicable to IC engines have only been developed for a very few simple fuels [2]. Nevertheless, the empirical knowledge gained about the autoignition of practical fuels needs to be understood in terms of fundamental chemical kinetics. This requires the development of chemical kinetic schemes for fuel mixtures that are more like practical fuels. The development and refinement of such schemes depend critically on the availability of experimental data, particularly on ignition delay times.

In a previous study, we investigated the ignition delay time of mixtures containing 35% n-heptane and 65% toluene by liquid volume (fuel A) behind reflected shock waves in the temperature range 620 ≤...
In a companion paper by Andrae et al. \[4\], the results of this study were used to develop a detailed chemical kinetics model. Experimental data for many gasoline surrogates have been used to develop kinetic models \[5–7\].

In this work we present ignition delay times measured in the shock tube for two other fuel mixtures, B and C, described in Table 1. Of the new fuel components used, diisobutylene is a common olefin and ethanol is the main biofuel component in practical gasolines. In particular, the 2-4-4 trimethyl-1-pentene isomer of diisobutylene was used. The ethanol used was 99% pure and the other components used were of ASTM grade purity.

### 2. Experimental

The experiments were carried out in a heated high-pressure shock tube with an internal diameter of 90 mm. The details of the apparatus and the experimental procedure used are the same as described in \[3\]. The experiments were conducted in the temperature range of $690 \leq T \leq 1200$ K at pressures of about 10, 30, and 50 bar and at equivalence ratio $\phi = 1$. These conditions are relevant for internal combustion engines. Postreflected shock temperature $T_5$ is determined from the shock-wave velocity using a one-dimensional shock-tube model (the shock-tube code of the CHEMKIN package).

### 3. Results and discussion

The measured ignition delay, $\tau$, is listed in Table 2 along with the pressure $p$ and temperature $T$. At lower temperatures than shown in Table 2 no ignition was observed during the maximum test time of 15 ms.

The ignition delay for fuel B is shown as a function of temperature in Fig. 1. As in \[3\], we assume that

$$\tau = A \exp(B/T) \cdot p^{-x}, \quad (1)$$

where $x$ is the pressure exponent. Multiple linear regression analysis using $\ln(\tau)$ as the dependent variable and $(1/T)$ and $\ln(p)$ as the independent variables.
helps to identify the value of $x$ as 0.76 using all the data listed in Table 2 for fuel B. In Fig. 2, $\tau_{30}$, the ignition delay time scaled to 30 bar, is plotted against $1000 \, K / T$; $\tau_{30} = \tau (30 \, \text{bar} / p)^{-0.76}$ for fuel B.

The measured ignition delay time for fuel C is shown as a function of temperature in Fig. 3. An analysis similar to that described above identifies the pressure exponent, $x$, to be 0.65 for these data. In Fig. 4, $\tau_{30} = \tau (30 \, \text{bar} / p)^{-0.65}$ is plotted as a function of temperature for fuel C.

A comparison of the results for the different fuels investigated in this work with data from the literature [3,8] normalized with their respective scaling factors is shown in Fig. 5. All data are under stoichiometric conditions except the data of fuel A containing 35% $n$-heptane and 65% toluene by liquid volume (cross) with $\phi = 0.3$ from [3]. The corresponding fuels from the work of Gauthier et al. [8] are gasoline and two gasoline surrogates containing isooctane, toluene, and $n$-heptane in the following proportions: surrogate A 63/20/17% and surrogate B 69/14/17% by liquid volume. The gasoline in [8] has a $(\text{RON} + \text{MON})/2$ value of 87; we estimate the RON to be 92. We also estimate the RON/MON for gasoline surrogate A and B from [8] to be 89/84 and 87/84 respectively, using a blending program proprietary to Shell.

The power-law pressure dependence is $p^{-0.83}$ for surrogate A, $p^{-0.96}$ for surrogate B, and $p^{-1.06}$ for gasoline, as given in Fig. 13 of [8]. The pressure scaling of $n$-heptane (circles) was determined to be $p^{-1.64}$ by Gauthier et al. in Fig. 11 of [8]. If we use the same procedure as in the present work and estimate a single value of $x$ for each fuel using the data listed in Table 4 of [8], the values of $x$ for $n$-heptane,
surrogate A, surrogate B, and gasoline are 1.32, 0.8, 0.88, and 1.0, respectively. The pressure-scaling exponent, \(x\), appears, in general, to be much larger for paraffinic fuels than for nonparaffinic fuels [1]. This experimental observation is consistent with the observation that the difference between paraffinic and nonparaffinic fuels in HCCI engines [9] and knocking SI engines [10] could be explained only by assuming such a difference in the pressure dependence of autoignition delay times between such fuels. In these engine experiments the same gasoline could match widely different primary reference fuels for autoignition behavior depending on the pressure and temperature history. However, for stoichiometric mixtures, the difference in autoignition delay at a fixed pressure of 30 bar between different gasoline fuel surrogate blends and gasoline considered in Fig. 5 is small for the high-temperature range above about 1000 K. In

the Livengood–Wu integral approach to autoignition [9,10], where the reciprocal of the ignition delay is integrated over time, the high-temperature range is the most important, since it contributes most to the integral. However, the pressure exponents are different, particularly for \(n\)-heptane compared to other fuels. Chemical kinetic models should be able to adequately explain such pressure effects if they are to elucidate how practical fuels behave in internal combustion engines, where pressure and temperature in the unburnt mixture vary over a wide range. In Fig. 5 fuel A (open diamonds) seems to have a slightly longer ignition delay at the same temperature than the other fuels. This is in fact consistent with its observed behavior in HCCI tests at high temperature, where it was more resistant to autoignition than expected from its octane index [11].

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**Fig. 3.** Ignition delay times for a stoichiometric mixture of fuel C in air at pressures of about 10 (diamonds), 30 (squares), and 50 bar (triangles). The lines connect the data points to illustrate the trends.

**Fig. 4.** Ignition delay times for stoichiometric mixtures of fuel C in air at pressures of about 10 (diamonds), 30 (squares), and 50 bar (triangles) normalized to 30 bar using \((30\ \text{bar}/p)^{-0.65}\). The solid line shows the trends of the data.
Fig. 5. Comparison of the ignition-delay times for the different fuels from this work with ignition delay times from the literature [5,8]. All data are normalized to 30 bar using the respective scaling factors $x$. All data are at $\phi = 1$ except (+).

We have used one value for the pressure exponent $x$ for each fuel over the entire temperature range. It is likely that the pressure dependence of ignition delay is different in different pressure and temperature ranges. For instance, Yates et al. [12] have suggested using three different values for each fuel. However, we do not have sufficient data to resolve such details. It is also difficult to know how exactly these different temperature ranges are to be defined, though the approach used by Yates et al. [12] does not require this to be done explicitly. Nevertheless, for the data set in this work, the pressure effects can be adequately explained with a single value of $x$ for each fuel.

However, the value of the pressure exponent, $x$, seems to be different for these different fuels.

- The experimental findings from this survey will be used in future work to validate kinetic models for the autoignition of fuel blends containing diisobutylene and ethanol.

4. Conclusions

Ignition delay times of stoichiometric mixtures of two surrogate fuels consisting of $n$-heptane (18%)/isoctane (62%)/ethanol (20%) and $n$-heptane (20%)/toluene (45%)/isoctane (25%)/diisobutylene (10%) by liquid volume have been measured in a high-pressure shock tube behind the reflected wave at pressures of 10, 30, and 50 bar and at temperatures of $690 \leq T \leq 1230$ K. It is possible to scale the data for a given fuel at different pressures by multiplying the autoignition delay by $p^{-x}$, where $p$ is the pressure and $x$ is found from analysis of the data.

- The data for the two gasoline surrogates are in good agreement with the literature data for other gasoline surrogates, at high temperatures at a fixed pressure, even though the RON varies between 87 and 95 across these different fuels.

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References

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