Ignition delay-time study of fuel-rich CH_4/air and CH_4/additive/air mixtures over a wide temperature range at high pressure

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1 Introduction

Flexibility between the conversion and storage of energy will be an important aspect in future energy systems, especially when considering the fluctuating availability of renewable energies. In times of low demand but high availability of energy, an interesting concept is the use of external mechanical or electrical energy in internal combustion engines (ICEs) to convert "cheap" chemicals (e.g., natural gas) into higher-value chemicals so that most of the exergy of the cheap fuels is stored. This production of chemicals typically proceeds at fuel-rich conditions, far away from current operating regimes of ICEs. A fundamental understanding of the chemical kinetics and the availability of validated reaction mechanisms for these conditions are essential for the successful implementation of such processes. However, most of the reaction mechanisms published in the literature are validated preferentially for lean and stoichiometric mixtures, because these conditions are important in ICEs and gas turbines.

To test the performance of existing reaction mechanisms under fuel-rich conditions, we measured the ignition delay times (IDTs) of CH_4/air and CH_4/additive/air mixtures at fuel-rich and engine-typical conditions and compared the results with the predictions of literature reaction mechanisms. Additives (ethanol, dimethyl ether (DME), *n*-heptane (*n*-C_7H_{16})) were used to reduce the IDTs of CH_4 so that engines can be used in the HCCI mode without preheating the reactants.

2 Experimental setup

The IDT measurements were performed in a shock tube with a constant inner diameter of 90 mm and lengths of the driver and driven sections of 6.4 and 6.1 m, respectively. Allowable post-ignition peak pressures are 500 bar and the maximum test time is extended up to 16 ms by driver-gas tailoring. Helium was used as the main driver gas component and Ar was added to match the acoustic impedance of the driver gas with the one of the test gas. The driver gas was mixed in situ by using two high-pressure mass flow controllers. Test gas mixtures were prepared manometrically in a mixing vessel and stirred for one hour to ensure homogeneity. DME was purified before use by freezing with liquid nitrogen and removing remaining gases by pumping.

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The temperature T_5 and pressure p_5 behind the reflected shock were computed from the incident shock velocity using a one-dimensional shock model with an estimated temperature uncertainty of < 15 K. The shock velocity was measured over two intervals using three piezoelectric pressure transducers. Bandpass-filtered (431±5 nm) emission from CH* chemiluminescence was monitored through a window in the sidewall 15 mm from the end flange with a Hamamatsu 1P28 photomultiplier tube. The pressure was recorded at the same position using a piezoelectric pressure transducer. IDTs were defined as the interval between the rise in pressure due to the arrival of the reflected shock wave at the measurement port and the extrapolation of the steepest increase in CH* chemiluminescence to its zero level on the time axis.

3 Results and Discussion

IDTs of rich CH_4/air and CH_4/additive/air mixtures ($\phi = 2$) were measured between 700 and 1620 K at a pressure of 30 bar. Additive (ethanol, DME, *n*-heptane) concentrations of 5 mol% of the total amount of fuel (i.e., CH_4 + additive) were used. CH_4/DME/air mixtures ($\phi = 2$) were also studied at 20 bar with DME concentrations of 5 and 20 mol% of the total amount of fuel. The results of the measurements are presented in Figures 1 and 2. In the temperature range above 1000 K the reduction of the IDT by the various additives is about a factor of two independent of the additive used. Below ~1000 K, *n*-heptane is most effective in reducing the IDT followed by DME. Simulations show that CH_4 and CH_4/ethanol mixtures exhibit much longer IDTs in this region due to their low reactivity, which prevented measurement at these conditions. Ignition delay time measurements of Burke et al. [1] with a shock tube and a rapid compression machine (RCM) of a CH_4/DME/air mixture ($\phi = 2$) with 20 mol% DME at 20 bar agree very well with our data (c.f. Figure 2). Our CH_4/DME/air data with 5 mol% DME at 20 bar furthermore agrees very well with RCM measurements of Werler et al. [2], considering the different temperature profiles observed in shock tubes and RCMs.

In order to test their performance under fuel-rich conditions, various literature reaction mechanisms were used to model the measured data. For mixtures containing ethanol, the mechanisms of Zhao et al. [3], Herzler and Naumann [4], Yasunaga et al. [5], and Burke et al. [1] were used. For CH_4/DME mixtures, the mechanisms of Zhao et al. [3], Yasunaga et al. [5] and Burke et al. [1] were used, and for n-C_7H_{16}/CH_4 mixtures, the mechanism of Mehl et al. [6] was used. The data of the CH_4/air mixture were simulated with all of these mechanisms. The simulations are based on the observed pressure increase of 5%/ms for the first 2.8 ms to account for the facility effect. This pressure increase was determined by measurements with inert mixtures, which exhibit no heat release during the measurement time. After the passage of the reflected shock wave through the contact surface no further pressure increase was observed after the first 2.8 ms. The temperature increase was calculated assuming an adiabatic isentropic compression. The maximum increase was found to be less than 30 K. The influence of this temperature increase on the simulated IDTs is shown in Figure 2. Shorter IDTs were observed only for values longer than 2 ms, and the agreement of measurements and simulations is improved for these long IDTs. Figure 2 also shows the differences of the shock-tube and RCM data at similar conditions, which are caused mainly by the different pressure/temperature profiles in these devices. The RCM data are well represented by simulations without temperature increase. At very long IDTs in RCMs the heat losses to the walls become more important so that too short IDTs are predicted when assuming constant temperature.

A comparison of experimental and simulated IDTs for the CH_4/air mixture is shown in Figure 3. All tested mechanisms [1, 3-6] with the exception of the mechanism of Zhao et al. [3] below 1200 K agree very well with our measurements. The results of simulations and experiments for the CH_4/ethanol/air mixture are presented in Figure 4. We find quite good agreement of our data with the mechanism of Herzler and Naumann [4], the mechanisms of Burke et al. [1] and Yasunaga et al. [5], especially below 1250 K, whereas the mechanism of Zhao et al. [3] predicts too long IDTs over the whole temperature range.

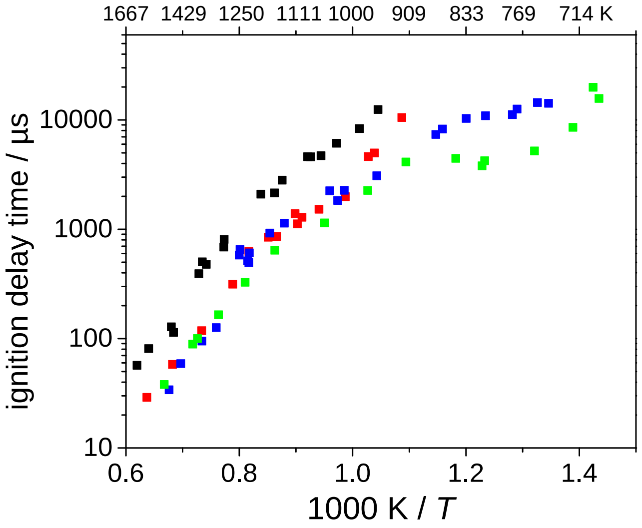

Figure 1. Measured IDTs of CH_4/air and CH_4/additive/air mixtures ($\phi = 2$) at 30 bar. Additive concentrations of 5 mol% of the fuel were used. Black squares: CH_4, red squares: CH_4/ethanol, blue squares: CH_4/DME, green squares: CH_4/*n*-heptane.

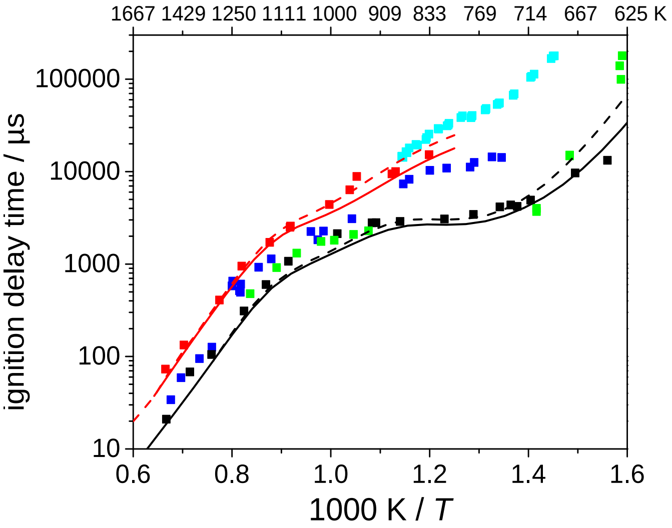

Figure 2. Measured and calculated IDTs of CH_4/DME/air mixtures ($\phi = 2$) at 20 and 30 bar. Symbols: experiments. Blue squares: $[CH_4]/[DME] = 19/1$ and 30 bar, red squares: $[CH_4]/[DME] = 19/1$ and 20 bar, black squares: $[CH_4]/[DME] = 4/1$ and 20 bar, green squares: shock-tube and RCM data of Burke et al. [1] with $[CH_4]/[DME] = 4/1$ and 20 bar, cyan squares: RCM data of Werler et al. [2] with $[CH_4]/[DME] = 19/1$ and 20 bar. Lines: Simulations with the mechanism of Yasunaga et al. [5]. Full lines: simulations considering the gasdynamic pressure increase, dashed lines: simulations considering only temperature increase due to heat production by reactions.

Figure 5 shows a comparison of our experiments with simulations for a CH_4/DME/air mixture ($\phi = 2$) at 30 bar with $[CH_4]/[DME] = 19/1$. Very good agreement is achieved with the mechanism of Yasunaga et al. [5]. The mechanism of Burke et al. [1] also predicts our experiments well, whereas the mechanism of Zhao et al. [3] predicts too long IDTs over the whole temperature range, similar to the situation for CH_4/ethanol/air mixtures. The comparison of experiments and simulations for a CH_4/DME/air mixture ($\phi = 2$) at 20 bar with $[CH_4]/[DME] = 19/1$ shows trends analogous to 30 bar, see Figure 6. For a higher DME content ($[CH_4]/[DME] = 4/1$) the experiments at 20 bar agree very well with the simulations using the mechanism of Burke et al. [1], see Figure 6, except in the temperature range from 800 K to 900 K, where the simulations slightly overpredict the experimental IDTs. For these experiments, the mechanisms of Zhao et al. [3]/Yasunaga et al. [5] agree very well with our experiments except between ~800–1100 K, where too long/too short IDTs are predicted.

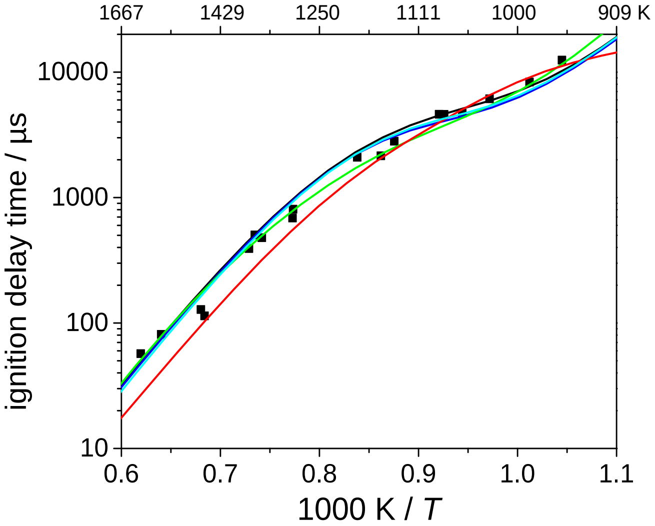

Figure 3. Measured and calculated IDTs of a CH_4/air mixture ($\phi = 2$) at 30 bar. Black squares: experiments. Simulations with the mechanisms of Burke et al. [1]: black line, Yasunaga et al. [5]: blue line, Herzler and Naumann [4]: green line, Zhao et al. [3]: red line, Mehl et al. [6]: cyan line.

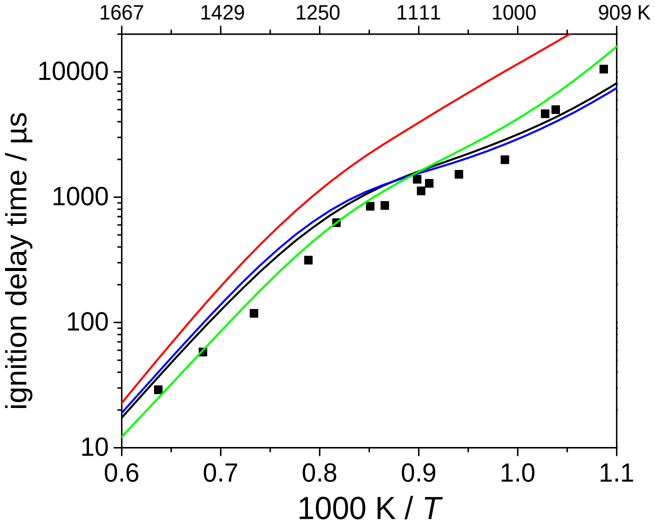

Figure 4. Measured and calculated IDTs of a CH_4/ethanol/air mixture ($\phi = 2$, $[CH_4]/[\text{ethanol}] = 19/1$) at 30 bar. Black squares: experiments. Simulations with the mechanisms of Burke et al. [1]: black line, Yasunaga et al. [5]: blue line, Herzler and Naumann [4]: green line, Zhao et al. [3]: red line.

Figure 7 shows a comparison of measured IDTs for the CH_4/n-C_7H_{16}/air mixture ($\phi = 2$) at 30 bar with $[CH_4]/[n\text{-}C_7H_{16}] = 19/1$ with simulations using the mechanism of Mehl et al. [6]. Overall, the agreement is very good, but the experiments show a slightly stronger NTC behavior in the temperature range from 730 K to 900 K, where the model overpredicts the measured IDTs.

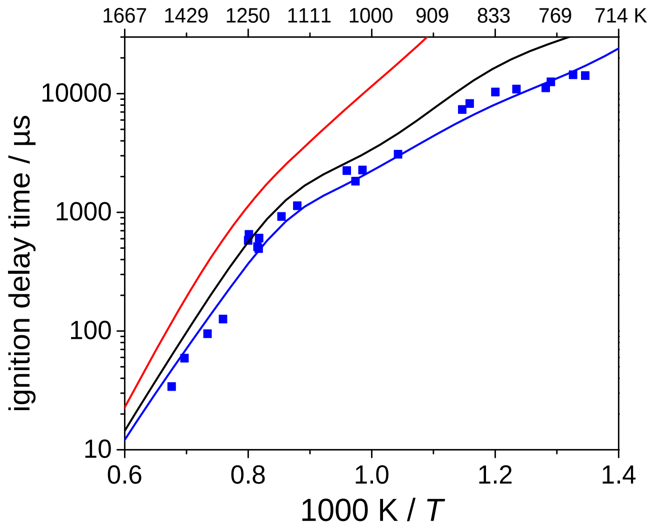

Figure 5. Measured and calculated IDTs of a CH_4/DME/air mixture ($\phi = 2$) at 30 bar with $[CH_4]/[DME] = 19/1$. Black squares: experiments. Simulations with the mechanisms of Burke et al. [1]: black line, Yasunaga et al. [5]: blue line, Zhao et al. [3]: red line.

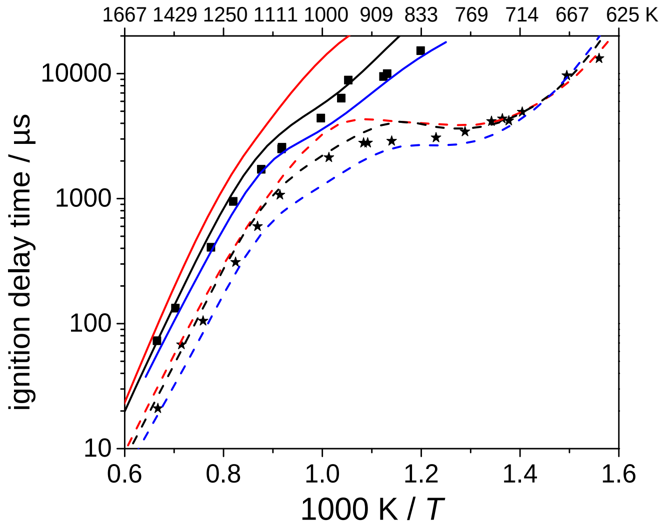

Figure 6. Measured and calculated IDTs of CH_4/DME/air mixtures ($\phi = 2$) at 20 bar. Black squares: experiments with $[CH_4]/[DME] = 19/1$, black stars: experiments with $[CH_4]/[DME] = 4/1$. Solid lines: simulations with $[CH_4]/[DME] = 19/1$, dashed lines: simulations with $[CH_4]/[DME] = 4/1$. Simulations with the mechanisms of Burke et al. [1]: black lines, Yasunaga et al. [5]: blue lines, Zhao et al. [3]: red lines.

4 Conclusions

Ignition delay times of rich CH_4/air and CH_4/additive/air mixtures ($\phi = 2$) were measured in the temperature range of 700 to 1620 K at pressures of 20 and 30 bar. Ethanol, dimethyl ether and *n*-heptane were used as additives. Our results show that *n*-heptane is most effective in increasing the reactivity of the fuel, i.e., in lowering the ignition delay time. Comparison of our results with simulations based on different literature mechanisms shows that these mechanisms, originally mostly validated for lean and stoichiometric conditions, are also well-suited for fuel-rich conditions, demonstrating their potential for modeling the production of chemicals in ICEs at these conditions.

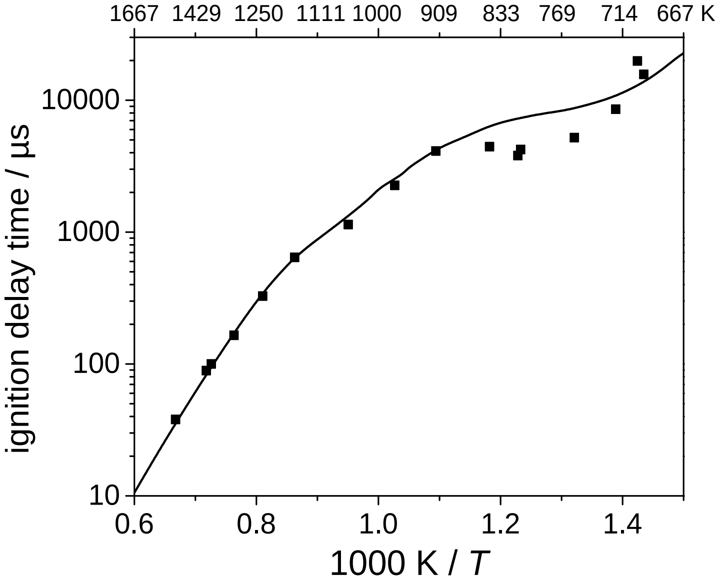

Figure 7. Measured and calculated IDTs of a CH_4/n-C_7H_{16}/air mixture ($\phi = 2$) at 30 bar with $[CH_4]/[n\text{-}C_7H_{16}] = 19/1$. Squares: experiments. Line: simulation with the mechanism of Mehl et al. [6].

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