High-pressure shock-tube study of the ignition of fuel-rich CH_4/air and CH_4/additive/air mixtures over a wide temperature range

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Abstract
Ignition delay times of rich CH_4/air and CH_4/additive/air mixtures ($\phi = 2$) were measured between 700 and 1620 K at pressures of 20 and 30 bar. Ethanol, dimethyl ether, propene 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.

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 fuel-rich conditions are essential for the successful implementation of such processes. However, most of the reaction mechanisms published in the literature were 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 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 these mechanisms. Additives (ethanol, propene, dimethyl ether (DME), *n*-heptane) were used to reduce the ignition delay times of CH_4 so that engines can be used in the HCCI mode without preheating the reactants.

Experimental setup

The ignition delay time 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 15 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. The driver gas composition is dependent on the test gas mixture composition and the Mach number and was calculated prior to the experiment. For the calculation, formulas by Oertel [1] and Palmer and Knox [2] were used.

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.

The temperature T_5 and pressure p_5 behind the reflected shock waves 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. Ignition delay times 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, see Figure 1, which shows a typical experimental result.

Results and discussion

Ignition delay times of rich ($\phi = 2$) CH_4/air and CH_4/additive/air mixtures were measured between 700 and 1620 K at a pressure of 30 bar. Additive (ethanol, propene, 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 2 and 3. In the temperature range above 1000 K the reduction of the ignition delay time by the various additives is about a factor of two independent of the additive used. Only propene shows a significantly smaller influence on the reactivity in this temperature range. Below ~1000 K, *n*-heptane is most effective in reducing the ignition delay time followed by

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DME. Simulations show that CH_4, CH_4/ethanol and CH_4/propene mixtures exhibit much longer ignition delay times in this region due to their low reactivity at these temperatures, which prevented measurements at these conditions. Ignition delay time measurements of Burke et al. [3] using 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 3). Our CH_4/DME/air data with 5 mol% DME at 20 bar furthermore agree very well with RCM measurements of Werler et al. [4], considering the different temperature profiles observed in shock tubes and RCMs.
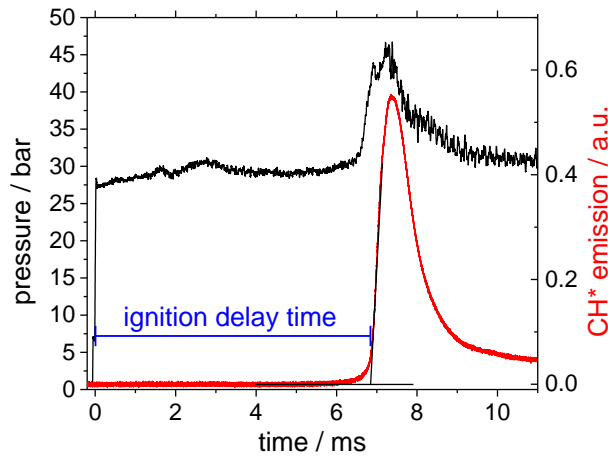
Fig. 1. Measured pressure and CH* emission profile of a CH_4/propene/air mixture ($\phi = 2$) at 27.6 bar and 960 K. $[CH_4]/[C_3H_6] = 95/5$. Black line: pressure, red line: CH* emission.

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. [5], Herzler and Naumann [6], Yasunaga et al. [7], and Burke et al. [3] were used. The same mechanisms with the exception of the mechanism of Zhao et al. [5], which does not include reactions of propene, were used for the methane/propene mixtures. For CH_4/DME mixtures, the mechanisms of Zhao et al. [5], Yasunaga et al. [7] and Burke et al. [3] were used, and for n-heptane/CH_4 mixtures, the mechanism of Mehl et al. [8] 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 2.6 ms to account for this 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 of driver and test gas, no further pressure increase was observed after the first 2.6 ms, see Figure 1. A comparison of simulations considering this gasdynamic pressure increase and simulations with a constant pressure assumption considering only heat release by the chemical reactions is

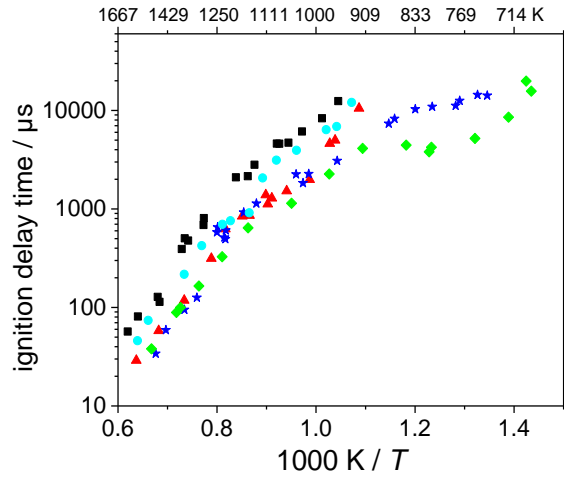shown in Figure 4 for a CH_4/DME/air mixture ($\phi = 2$) with 20 mol% DME at 20 bar.

Fig. 2. Measured ignition delay times 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: methane, red triangles: methane/ethanol, blue stars: methane/DME, green diamonds: methane/n-heptane, cyan circles: methane/propene.
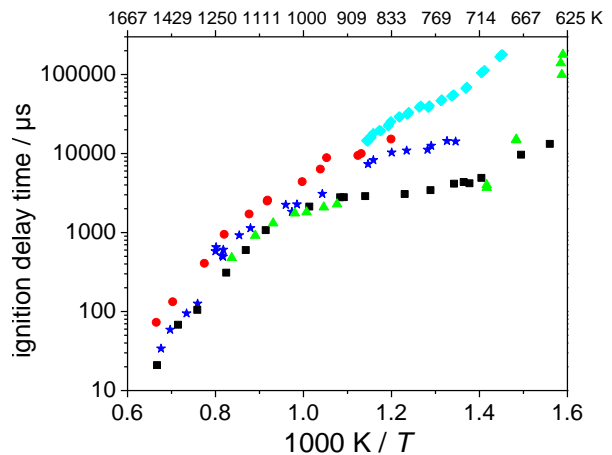

Fig. 3. Measured ignition delay times of CH_4/DME/air mixtures ($\phi = 2$) at 20 and 30 bar. Blue stars: $[CH_4]/[DME] = 19/1$ and 30 bar, red circles: $[CH_4]/[DME] = 19/1$ and 20 bar, black squares: $[CH_4]/[DME] = 4/1$ and 20 bar, green triangles: shock-tube and RCM data of Burke et al. [3] with $[CH_4]/[DME] = 4/1$ and 20 bar, cyan diamonds: RCM data of Werler et al. [4] with $[CH_4]/[DME] = 19/1$ and 20 bar.
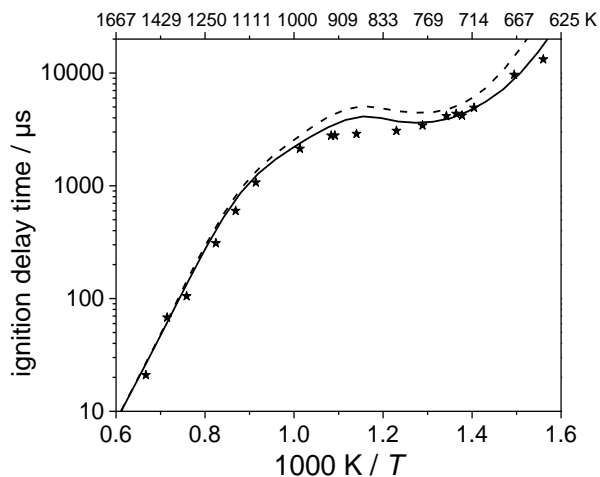
Fig. 4. Measured and calculated ignition delay times of a CH_4/DME/air mixture ($\phi = 2$, $[CH_4]/[DME] = 4/1$) at 20 bar. Black stars: experiments. Simulations are based on the mechanism of Burke et al. [3]. Solid line: simulation considering temperature increase by gas-dynamic effects and heat release of chemical reactions, dashed line: constant pressure simulation considering heat release only by chemical reactions.

The differences between the two simulations increase with larger ignition delay times and lower temperatures. For temperatures above 700 K the calculated ignition delay times are up to 20% longer if no gas-dynamic temperature increase is considered. For all mixtures and mechanisms the simulations with the gas-dynamic temperature increase show a better agreement with the experiments.

A comparison of experimental and simulated ignition delay times for the methane/air mixture is shown in Figure 5. All tested mechanisms [3, 5-8] with the exception of the mechanism of Zhao et al. [5] at temperatures above 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 6. We find quite good agreement of our data with the mechanisms of Herzler and Naumann [6], Burke et al. [3] and Yasunaga et al. [7], especially at temperatures below 1250 K, whereas the mechanism of Zhao et al. [5] predicts too long ignition delay times over the whole temperature range.

Figure 7 shows simulations and experiments for the CH_4/propene/air mixture. We find quite good agreement of our data with the mechanisms of Herzler and Naumann [6], Burke et al. [3] and Yasunaga et al. [7]. The mechanism of Burke et al. [3] achieves the best agreement with the experiments.
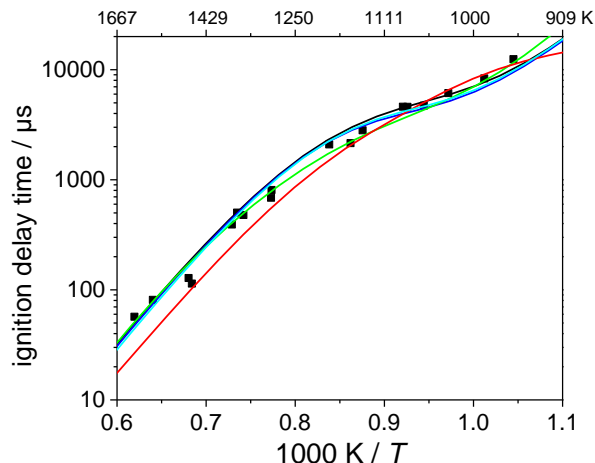

Fig. 5. Measured and calculated ignition delay times of a CH_4/air mixture ($\phi = 2$) at 30 bar. Black squares: experiments. Simulations with the mechanisms of Burke et al. [3]: black line, Yasunaga et al. [7]: blue line, Herzler and Naumann [6]: green line, Zhao et al. [5]: red line, Mehl et al. [8]: cyan line.
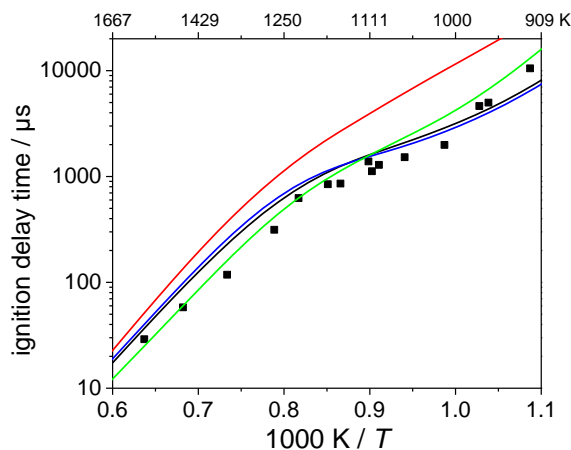

Fig. 6. Measured and calculated ignition delay times of a CH_4/ethanol/air mixture ($\phi = 2$, $[CH_4]/[ethanol] = 19/1$) at 30 bar. Black squares: experiments. Simulations with the mechanisms of Burke et al. [3]: black line, Yasunaga et al. [7]: blue line, Herzler and Naumann [6]: green line, Zhao et al. [5]: red line.

Figure 8 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. [7]. The mechanism of Burke et al. [3] also predicts our experiments well, whereas the mechanism of Zhao et al. [5] predicts too long ignition delay times 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 9. For a higher DME content ($[CH_4]/[DME] = 4/1$) the experiments at 20 bar show a very good agreement with the simulations using the mechanism of Burke et al. [3], see Figure 9. Only in

the temperature range from 800 K to 900 K the simulations predict longer ignition delay times compared to the experiments. For these experiments, the mechanisms of Zhao et al. [5] / Yasunaga et al. [7] agree very well with our experiments with the exception of the temperature range of ~800-1100 K, where too long / too short ignition delay times are predicted.
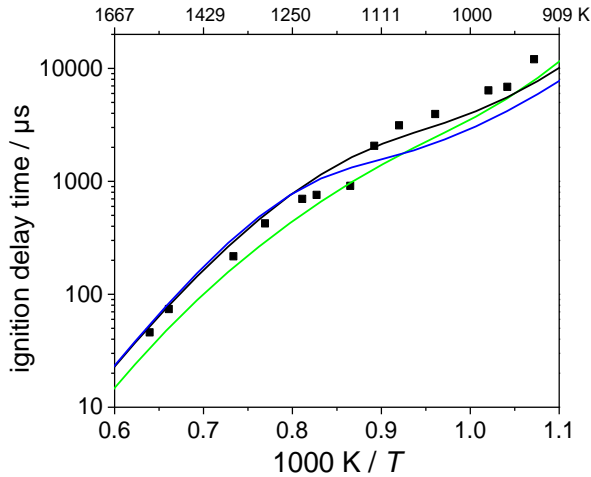
Figure 10 shows a comparison of measured ignition delay times for the $CH_4/n\text{-}C_7H_{16}$/air mixture ($\phi = 2$) at 30 bar with $[CH_4]/[n\text{-}C_7H_{16}] = 19/1$ with simulations using the mechanism of Mehl et al. [8]. Overall, the agreement is very good, but the experiments show a slightly stronger NTC behavior in the temperature range from 730 K to 900 K, where the model overpredicts the measured ignition delay times.

Fig. 7. Measured and calculated ignition delay times of a CH_4/propene/air mixture ($\phi = 2$, $[CH_4]/[\text{propene}] = 19/1$) at 30 bar. Black squares: experiments. Simulations with the mechanisms of Burke et al. [3]: black line, Yasunaga et al. [7]: blue line, Herzler and Naumann [6]: green line.
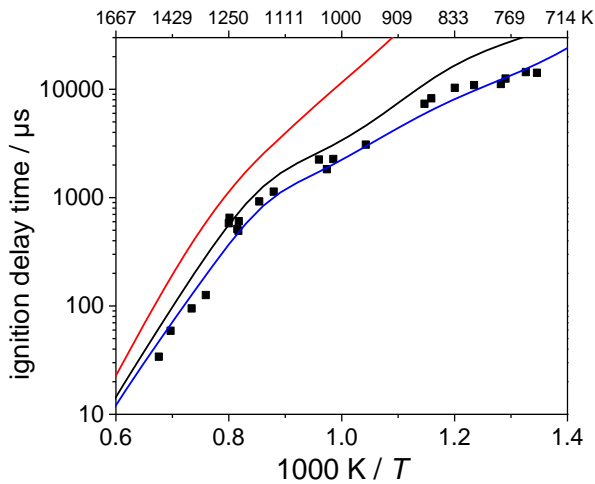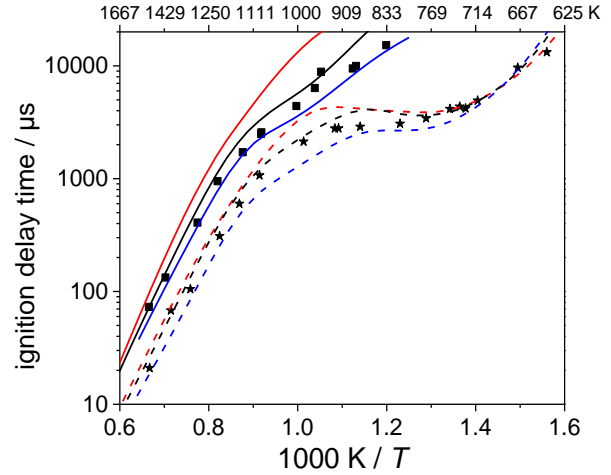

Fig. 9. Measured and calculated ignition delay times of CH_4/DME/air mixtures ($\phi = 2$) at 20 bar. Black squares: experiments with $[CH_4]/[DME] = 19/1$, black stars: experiments with $[CH_4]/[DME] = 4/1$. Solid lines: simulations with $[CH_4]/[DME] = 19/1$, dashed lines: simulations with $[CH_4]/[DME] = 4/1$. Simulations with the mechanisms of Burke et al. [3]: black lines, Yasunaga et al. [7]: blue lines, Zhao et al. [5]: red lines.
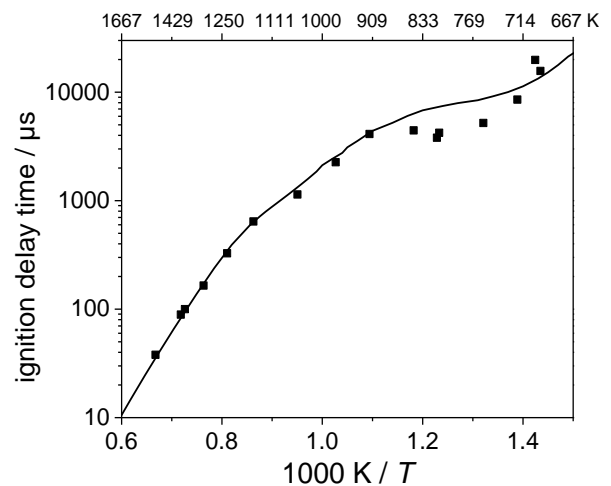

Fig. 8. Measured and calculated ignition delay times of a CH_4/DME/air mixture ($\phi = 2$) at 30 bar with $[CH_4]/[DME] = 19/1$. Black squares: experiments. Simulations with the mechanisms of Burke et al. [3]: black line, Yasunaga et al. [7]: blue line, Zhao et al. [5]: red line.

Fig. 10. Measured and calculated ignition delay times of a $CH_4/n\text{-}C_7H_{16}$/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. [8].

Conclusions

Internal combustion engines can be used in times of low demand but high availability of energy 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. For the development of such concepts validated reaction mechanisms must be available for these conditions. Therefore, we measured the ignition delay times of rich CH_4/air and CH_4/additive/air mixtures ($\phi = 2$) in the temperature range of 700 to 1620 K at pressures of 20 and 30 bar in a high-pressure shock tube. Ethanol, propene, 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. A more reactive fuel is necessary to use the ICEs in the homogeneous charge compression ignition (HCCI) mode without preheating the reactants. 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.

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