A Rapid Compression Machine Study of Diethyl Ether Autoignition

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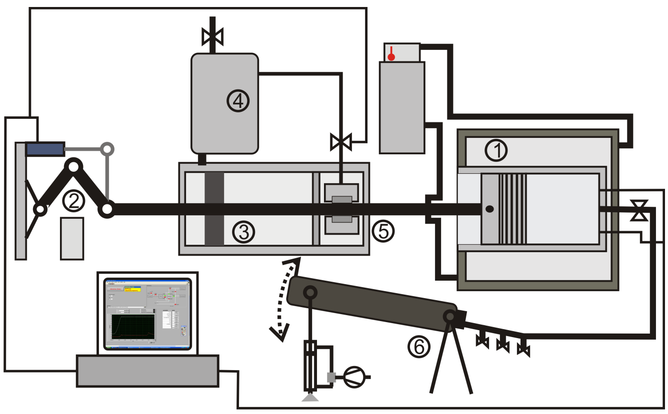
1 Introduction

The depletion of fossil fuels attracts increased attention on fuel alternatives for power generation and the transport sector. The combustion behavior of these fuels in engines is often not well known. Diethyl Ether (DEE) has been used for a long time as a cold start-aid. Investigations on DEE as an ignition enhancer for several fuels in diesel engines as well as in HCCI engines are widespread [1–3]. DEE itself is considered to be a good compression ignition fuel as well [4].
Beside its use in internal combustion engines, its large ignitability makes DEE also interesting for investigations on safety-relevant ignition processes on hot surfaces and in free jets. Therefore the ignition behavior of DEE in the temperature range below 1000 K is of great interest. Furthermore, the ignition delay time of a fuel is an important quantity for the validation of kinetic models. Despite these many applications, the properties of DEE are still not well studied in the low temperature range.
Yasunaga et al. already studied the pyrolysis and oxidation of DEE behind shock waves in a temperature range between 900 K and 1900 K. A detailed chemical kinetic model was assembled for this temperature range, identifying the most important reactions [5]. Inomata et al. carried out measurements on ignition delay times in a temperature range of 500 K to 650 K and a pressure range of 10 - 15 bar. The measurements were done with a DEE/oxygen mixture, diluted with nitrogen and carbon dioxide ($DEE/O_2/N_2+CO_2$:0.03/0.195/0.775). Furthermore, they investigated the influence of DEE on the ignition delay time of toluene in a temperature range from about 700 K to 850 K [6]. An experimental and numerical study on oscillatory cool flames of DEE/air mixtures was presented by Griffiths et al. to investigate the low temperature oxidation [7]. Burning velocities of DEE were investigated by Gillespie et al [8] using the heat flux method. Gibbs et al. used a Bunsen burner cone with the apex-cone method and Zhang et al. used a spherically propagating flame in a cylindrical vessel and high speed Schlieren photography to investigate burning velocities [9], [10].
Since there is no wide range low-temperature autoignition study for DEE, the purpose of this study is to provide a set of ignition delay data for the validation of a low temperature reaction mechanism. The measurements were conducted in a Rapid Compression Machine in a temperature range from 500 - 850 K and for pressures between 2.5 and 13 bar, as well as for different fuel/air equivalence ratios, ϕ = 0.5, 1 and 2.

2 Rapid Compression Machine

Rapid Compression Machines (RCMs) are common devices for the investigation of ignition delay times and chemical kinetics, predominantly in the low-temperature range [12–14].
In the present study, a RCM with a pneumatically driven piston is employed (Fig.1). A creviced piston is used to suppress the corner vortex and ensures a better defined homogeneous zone within the combustion chamber [12–14]. The piston shape was designed according to the suggestions of Würmel et al. The design was optimized for post-compression pressures above 6 bar [14]. Due to the very short ignition delay times of DEE at higher pressures the experiments in this study were conducted at lower pressures to provide data for a wide temperature range.
To avoid blow-by, the piston is sealed by four compression rings and two additional quad-ring sealings. The piston is pneumatically moved in a cylinder liner, which is closed by a cylinder head with a flat surface. The cylinder head is equipped with temperature and pressure sensors, and features inlet and outlet ports, allowing to fill in the reactant mixture, to evacuate the chamber and to take gas samples. To ensure a homogeneous and constant temperature distribution, the cylinder liner and the cylinder head are surrounded by an oil bath (1), which allows to adjust the initial charge temperature between T_0 = 288 K and 473 K. The RCM can be operated at compression ratios up to 15; the ratio can be modified by applying different piston attachments or by shortening the stroke length.
After reaching top dead center (TDC), the piston is held fixed by a knee lever (2) connected to the driving rod of the pneumatic actuator (3). To keep the driving pressure constant, an air tank is connected to the pneumatic actuator (4). A pneumatic clamp (5) on the driving rod prevents the driver piston from moving when the tank is pressurized.
A large vessel (6) is used to prepare and to store the test gas mixture. The relative amount of each component in the vessel is determined from its measured partial pressure. With the large quantity of stored test gas mixture, many RCM shots can be performed with exactly the same charge. To prevent a density stratification, the vessel is moved around the horizontal by a pneumatic actuator. Additionally, a magneto-coupled stirrer mixes the gas inside the vessel.



Bore	82.05 mm
Stroke	77 - 80 mm
Compression time	15 - 25 ms
Compression ratio	8 - 15
Driving pressure	3 - 10 bar

Figure 1: Schematic diagram and parameters of the Rapid Compression Machine

3 Experimental

Investigations were performed for a wide temperature range, 500 - 850 K, and a pressure range of 2.5 - 13 bar. Different equivalence ratios, ϕ = 0.5, 1, 2 with molar compositions: DEE/O_2/N_2 = 1.72/20.64/77.64, 3.38/20.29/76.33, 6.54/19.63/73.83 were studied. The temperature after compression was varied by using different initial temperatures, by altering the compression ratio and by changing the composition of the diluent inert gas. To obtain post-compression temperatures below 565 K, 50% of the nitrogen was replaced by carbon dioxide. The post compression pressure was adjusted by varying the initial pressure in the reaction chamber.

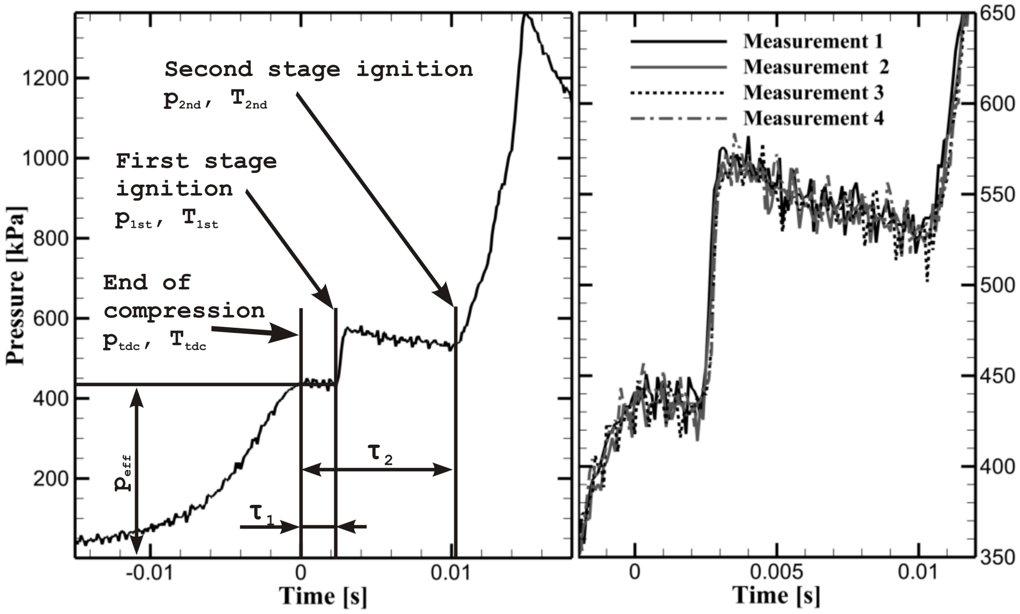


Figure 2: Left diagram: Pressure traces illustrating the definitions of ignition delay times, temperatures and pressures. Right diagram: Detail of the pressure trace of four measurements showing the high repeatability of experiments.

Figure 2 shows a typical pressure trace from an RCM-experiment with a two stage ignition. Due to the low overall pressure a slight noise in the pressure traces is visible. All measurement data show the same smooth and continuous increase of pressure during the compression process ($t < 0$). Within 10 ms the bulk of compression takes place. Afterwards, a decrease of pressure follows due to heat losses. A small pressure increase arises provoked by the first ignition, after the first ignition delay time τ_1. The pressure further decreases until the second ignition appears. The time between the end of compression and the last pressure increase is taken here as the overall ignition delay time τ_2. Due to heat losses and pre-ignition chemical reactions, neither temperature nor pressure are constant after the compression. To assign a pressure and a temperature to an ignition event (and the corresponding ignition delay), an effective temperature and pressure are used here. The effective pressure is defined as the time-averaged pressure between the end of the compression and the pressure increase due to ignition [11]. If two stage ignition occurs, only the averaged pressure between TDC and first increase of pressure is used.

$$p_{\mathrm{eff}} = \frac{1}{t_{1\mathrm{st}} - t_{\mathrm{tdc}}} \int_{t_{\mathrm{tdc}}}^{t_{1\mathrm{st}}} p \, \mathrm{d}t \tag{1}$$

The reference temperature T_{eff} is then calculated from p_{eff} and the initial temperature and pressure (T_0, p_0), assuming the existence of an isentropic core, by solving the equation

$$\int_{T_0}^{T_{\mathrm{eff}}} \frac{\gamma}{\gamma - 1} \frac{\mathrm{d}T}{T} = \log \frac{p_{\mathrm{eff}}}{p_0} \quad . \tag{2}$$

For the calculation, the (temperature-dependent) ratio of specific heats γ is determined from a thermodynamical database [15].

4 Results

The influence of pressure on ignition delay time is shown in figure 3, by experimental data from rapid compression experiments by Inomata et al. [6], from shock tube experiments by Yasunaga et al. [5], and from this study.

Based on the experimental uncertainties of the initial conditions (T_0, p_0, ϕ_0) and the determination of the effective pressure (p_{eff}), the resulting uncertainty in the effective temperature is 8 K at a mean temperature of T_{eff} = 733 K.

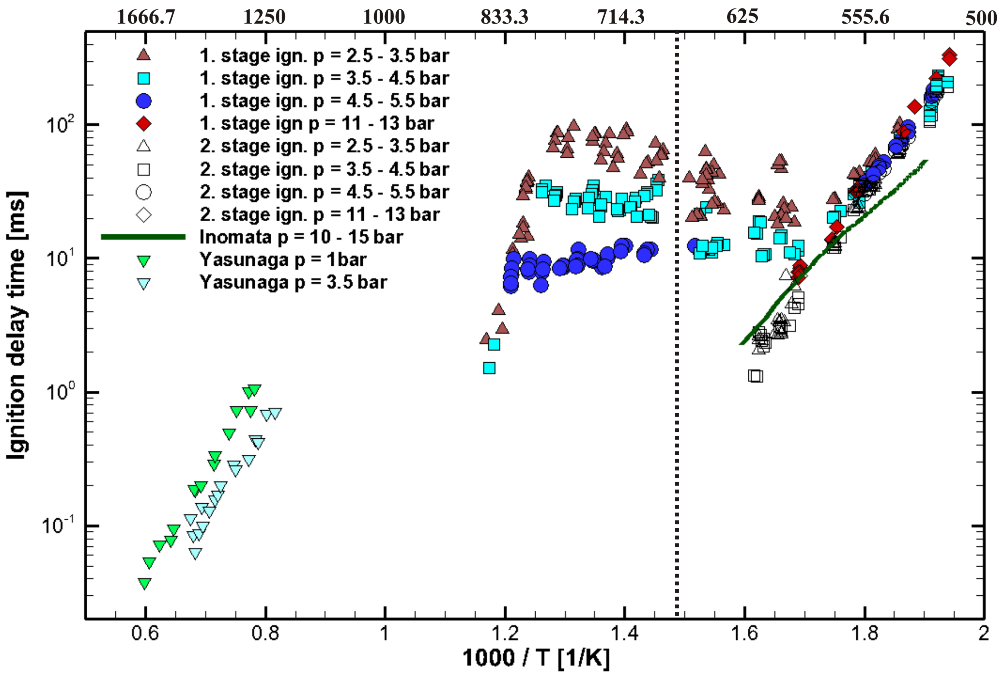


Figure 3: Influence of pressure on ignition delay times of DEE for an equivalence ratio of ϕ = 1. Open symbols represent first stage- and filled symbols overall ignition delay times. Measurements by Inomata et al.: similar composition [6]. Measurements by Yasunaga et al. (shock tube experiments): 1 % DEE in Ar with 6% O_2 [5].

Above 833 K, a steep decrease of the ignition delay time with increasing temperature is indicated by our RCM-data. This is qualitatively also found in the shock tube experiments of Yasunaga et al [5]. In the temperature range from 600 K to 833 K, there was only a weak effect of temperature on ignition delay; at low pressures, a slight negative temperature coefficient (NTC) behavior was observed (the ignition delay increased with temperature). However, ignition delay depended strongly on pressure in this temperature range, with ignition delays near 5 bar up to 10 times (at $T \approx 770$ K) smaller than those near 3 bar. The pressure-dependence is particularly strong at low pressures (2.5-3.5 bar), causing the comparatively large scatter for these data compared to the data for higher pressures (3.5 - 5.5 bar). Below about 665 K (on the right side of the dotted line), a two stage ignition was detected. The data points of the first-stage ignition delay in the temperature range between 625 K and 665 K are not depicted in figure 3. Their first-stage ignition delay is in the range < 1 ms, rendering those measurements unreliable in the RCM. The first stage ignition delay increases with decreasing temperature; in the investigated range, pressure was only of weak influence on the first ignition delay time. Between 590 K and 665 K, the overall ignition delay time decreases slightly and still shows a dependence on pressure, as for higher temperatures. Below 590 K the delay time increases in the same magnitude as the first stage ignition.

At higher pressures and temperatures above 600 K the autoignition of DEE is too fast to be reliably measured with the employed RCM. However, measurements were conducted at pressures above 10 bar in the same low temperature range as the measurements of Inomata et al. [6]. A comparison between the data shows a good agreement at temperatures above 570 K. Below 570 K, the detected ignition delay is longer than those of Inomata et al. [6]. In this range, the high pressure does not affect the delay time; the ignition delay is in this range determined mostly by temperature. In our study, a two stage ignition at this high pressure was observed below 550 K.

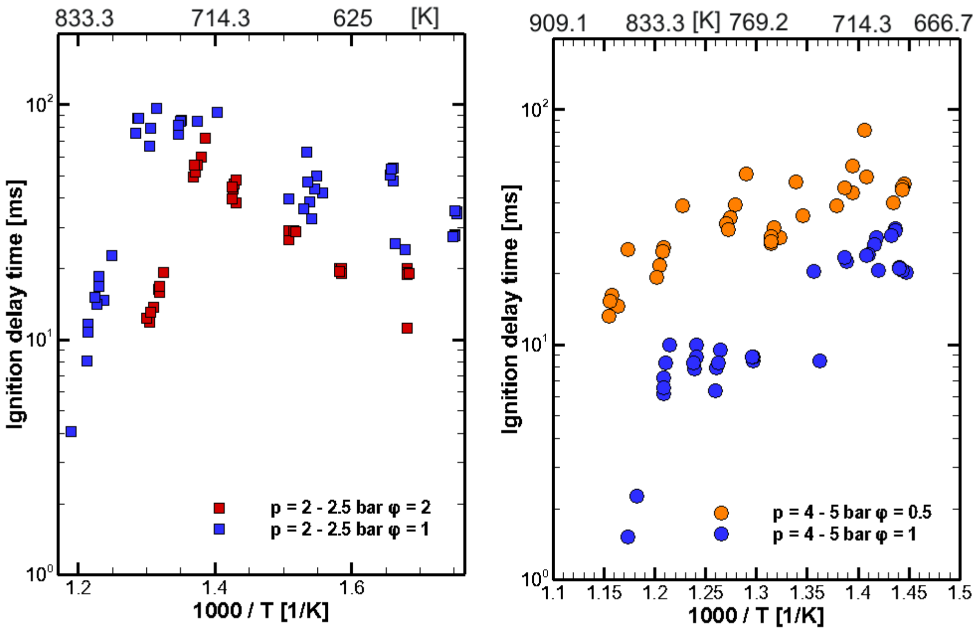


Figure 4: Influence of equivalence ratio on ignition delay times of DEE

The effect of equivalence ratio on the ignition delay time is depicted in figure 4. Data for lean and rich mixtures are compared to the stoichiometric case within the same pressure range. With the rich mixture, a faster ignition was observed, while the lean mixture displayed slower ignition than stoichiometric. The rich and lean mixture could not be compared at the same pressures, because the lean mixture did not ignite at all at low pressures, while at high pressures, the ignition delay times of the rich mixture were too short to allow a reliable evaluation (i.e., assignment of an effective temperature) with the RCM.

5 Summary and conclusion

Ignition delay times of Diethyl Ether (DEE)/air mixtures were measured in a rapid compression machine in the temperature range from 500 K to 850 K and a pressure range from 2.5 to 13 bar. It was found that DEE ignition delay displays a pronounced region (600 K to 833 K) of quite low temperature sensitivity, and at lower pressures, even a slight negative temperature coefficient (NTC) behavior. At very high and very low temperatures, the ignition delay showed an Arrhenius-like decrease with increasing temperature. Two-stage ignition was observed in the temperature range from 500 K to 665 K.

The measured data are intended for use as a validation case for a low-temperature DEE mechanism, which is currently developed by another group. All raw-data and pressure-traces are available in tabular form. If you are interested please contact the corresponding author.

Further work will refine the measurement evaluation, in particular assessing the influence of the heat-loss in the RCM, especially at lower pressures.

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