Ignition delay times of methane/diethyl ether blends measured in a rapid compression machine (RCM)

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1 Introduction

Recently the use of methane-based fuels or hydrogen in compression ignition (CI) engines has grown. A general strategy to wider the operation conditions for these fuels in CI engines is to operate them in a dual fuel mode, where a substance of higher reactivity is added to promote the auto-ignition of the gaseous fuels [1, 2]. By adding diethyl ether (DEE), a wider operation range could be observed including positive effects concerning efficiency and pollutants [1, 2]. Also for polygeneration processes, where homogeneous charge compression ignition engines shall be used to produce higher-value chemicals from natural gas by partial oxidation, the addition of small amounts of reactive substances to enhance reactivity is favorable [3, 4].

Despite the interest in using diethyl ether as ignition enhancer in combustion engines, there are, to our best knowledge no fundamental studies on the auto-ignition of methane/DEE-mixtures. However, there are numerous studies on the ignition of the pure substances. Ignition delay times of pure methane/air-mixtures have widely been studied in shock tubes and in rapid compression machines (RCM) [5-7]. Furthermore, there are studies on ignition delay times of pure DEE/air-mixtures in a wide range of temperatures and pressures [8, 9]. According to the need of fundamental data to develop and validate reaction mechanisms for the investigation of the interaction of dual fuel systems containing substances of strongly differing reactivity, in this study ignition delay times (τ_{1G}) of mixtures containing methane and DEE are measured in a RCM.

The investigated range of conditions spans temperatures at the end of compression (EOC) from $T_{EOC} = 515$ K to 925 K, pressures from $p_{EOC} = 10$ bar to 20 bar, equivalence ratios from $\phi = 1$ to 2, and amounts of DEE in the DEE/CH₄ blend from 5 mol-% to 10 mol-%. In the investigated range of conditions, the blends show some negative temperature coefficient (NTC) behavior that they "inherit" from DEE.

The experimentally obtained data were used for comparison with a recently published reaction mechanism for pure DEE/air-mixtures, which was developed by Eble et al. to describe the low temperature combustion including the NTC behaviour of DEE with its two-stage ignition phenomena [10]. A second mechanism from Sakai et al. [11], also developed for pure DEE/air mixtures, is used as well. This work **Correspondence to: robert.schiessl@kit.edu** 1

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will explain the experimental procedure, present the measured ignition delay times, and study the promoting effect of DEE on methane auto-ignition and in which regimes the mechanisms can reproduce the ignition delay time, despite the fact that they are originally not made for $CH_4/DEE/air$ -mixture with a low ratio of DEE/CH₄ (5 mol-% to 10 mol-% DEE of fuel).

2 Experimental Setup

A rapid compression machine (RCM) was used to measure the ignition delay times of methane/DEE/airmixtures. The experimental setup of the experiment was described in detail in a previous publication [8]. In the following, a brief description of the experiment will be given before the obtained reproducibility and the relative error are discussed.

The RCM is a piston cylinder device, in which a piston is driven pneumatically into the combustion chamber to compress the gas mixture. A knee lever system is used to stop and fix the piston at top dead center (TDC) mechanically. At the time where the piston reaches TDC, the knee lever impinges onto a bumper where it is kept in its craned position to preserve isochoric conditions in the cylinder.

The in-cylinder pressure is monitored by a quartz pressure transducer (Kistler 6061 B). The transducer is protected against thermal shocks by a double membrane. Beside the possibility to measure the pressure trace, the piston-position is measured by a potentiometric position sensor (Burster type 7812) connected to the piston rod. Additionally, the chemiluminescence of CH*-radicals is detected though a band-pass filter (430 nm +/- 5 nm) by a photomultiplier tube module (PMT, Hamamatsu H10722- 210).

To allow well-defined initial conditions, a manometrically prepared homogenous mixture can be filled into the combustion chamber to the desired pressure using solenoid valves monitored by an absolute pressure transducer (Baratron type 121A). The accuracy of the initial pressure in the filling process is ± 0.5 %. A well-defined temperature distribution of the cylinder walls and regulated initial temperature is achieved by a thermostatically controlled oil bath surrounding the combustion chamber.

The ignition delay time in this work is defined as the time between the piston reaches TDC and the inflection point of the pressure rise due to an ignition event (Figure 1). To refer the measured ignition delay times the pressure and the temperature at TDC are used. The pressure is measured directly using the combination of the previously mentioned pressure detectors and the charging amplifier (Kistler 5011B). The combination of the measurement systems gives an uncertainty of ± 0.71 % of reading.

Assuming the validity of the adiabatic core hypothesis, which is best ensured due to a creviced piston shape, the temperature at TDC can be calculated from the pressure at TDC, the initial value of pressure and temperature and the isentropic exponent κ of the investigated gas-mixture. The uncertainty of the temperature determination is calculated again assuming the validity of an adiabatic core for and for an ideal gas by the Gaußian uncertainty propagation for all involved measurement systems and is given in the range of ± 1.33 % of the calculated value.

Figure 1 shows the resulting pressure traces from three experimental RCM "shots" with the same initial conditions (TI = 380 K; pI = 60 kPa; $\phi = 1$; Fuel: 10 mol-% DEE / 90 mol-% CH4). In this case, the average of the three measured ignition delay times is $\overline{\tau_{IG}} = 136.14$ ms. The minimum is $\tau_{IG,min} = 130.97$ ms (blue curve, Experiment 1) and the maximum is $\tau_{IG,max} = 138.87$ ms (red curve, Experiment 3). These three RCM shots in Figure 1 differ with an average relative deviation of 3.8 % from their average. The small shot-to-shot variation even for these very long ignition delay times indicates the good reproducibility of the RCM. As Figure 1 shows exemplarily how the relative deviation is determined for one data set, Figure 2 shows the relative deviations for all experiments used in this work. Thus, along the

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X-Axis each peak represents the relative deviation of one experiment calculated with its ignition delay time over average ignition delay time determined by three RCM shots with the same initial conditions. The experiments are ordered by the pressure deviation. The average relative deviation over all experiments is 2.21 %. With increasing pressure deviation, the relative ignition delay deviation increases. Thus, it can be seen that the ignition delay time is affected to the pressure.



Figure 1: Experiments with same settings, initial Figure 2: Relative deviation of ignition delay time, conditions $T_{I} = 380$ K; $p_{I} = 0.6$ bar, $\phi = 1, 10\%$ DEE

calculated for all experiments used in this work

3 Simulation and comparison of ignition delay times

The measured ignition delay times are compared to simulations based on a homogeneous reactor model [12] applying the previously mentioned reaction mechanisms (Eble et al. [10] and Sakai et al. [11]).

To take the facility effects of the measurements into account an adiabatic core model described in detail by Mittal and Sung [13] was used in the simulations. In this model, the compression and the heat loss are considered by giving the temporal volume change of the adiabatic core as a constraint, thus the adiabatic core hypothesis also has to be valid for the simulations. The temporal volume of the adiabatic core is determined by pressure measurements of "unreactive" mixtures with similar properties of the isentropic exponent and thermal diffusivity as in the measurements of the reactive cases. Therefore, the amount of oxygen in the test mixture is substituted by nitrogen (c.f. [13]).

To quantify agreement between simulation and measurement, as well as to compare the predictive efficiency of the two mechanisms formula (1.1) of Olm et al. is used [14]

$$E = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{N_i} \sum_{j=1}^{N_i} \left(\frac{Y_{ij}^{sim} - Y_{ij}^{exp}}{\sigma\left(Y_{ij}^{exp}\right)} \right)^2.$$
(1.1)

Here, N is the number of data sets (one data set is one defined end of compression temperature/pressure), N_i is the number of experiments per data set, Y_{ij} are calculated by using the natural logarithm of the simulated or measured ignition delay times. $\sigma(Y_{ij}^{exp})$ is the standard deviation of the experiments.

4 **Results and Discussion**

Understanding the influence of DEE on the ignition of CH₄, different fuel-mixtures from stoichiometric to fuel rich conditions were measured. Figure 3 and Figure 4 show comparisons of mixtures with 5 mol-% DEE and 10 mol-% DEE with an end of compression pressure of 10 bar. In Figure 3, stoichiometric

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mixtures and in Figure 4, fuel-rich mixtures ($\phi = 2$) are shown; the equivalence ratios reported here always refer to the overall mixture. All measurements are compared to the respective simulations.

It can be seen, that by doubling the DEE amount in fuel from 5 mol-% to 10 mol-%, the ignition delay time drops by a factor of 5 to 10 in the experiments and by a factor 2 to 5 for simulations at stoichiometric conditions. Fuel rich mixtures are showing a similar behavior.



Figure 3: Ignition delay times of 5 % and 10 % DEE mixtures at an ignition pressure of 10 bar and stoichiometric conditions ($\phi = 1$)

Figure 4: Ignition delay times of 5 % and 10 % DEE mixtures at an ignition pressure of 10 bar and fuelrich conditions ($\phi = 2$)

Since a RCM is not adiabatic, fuels with a long ignition delay time cannot been measured under this end of compression conditions. Under isobaric end of compression conditions, this leads to a minimum measurable temperature. In Figure 3, the 5 mol-% DEE mixture has a minimum end of compression temperature of 840 K. For the higher amount of DEE in fuel, the DEE chemistry becomes more dominant. Thus, an ignition is possible at lower end of compression temperatures at stoichiometric conditions.

For the fuel-rich conditions already the low amount of DEE is sufficient to decrease the ignition temperature drastically, auto-ignition takes place below 600 K. From the shown comparison, it is apparent that both mechanisms well describe the ignition delay times of the fuel mixture with a higher amount of DEE. Both mechanisms describe very similar ignition delay times for the shown properties. For the small addition of DEE at stoichiometric conditions the predicted ignition delay is much shorter than observed experimentally. This appears plausible since both mechanisms are developed for pure DEE/air mixtures [10, 11]; their performance for low-DEE content mixtures is expected to be inferior compared to the high DEE-content case. This is underlined by the behavior of the 10 mol-% DEE mixture as well as the fuel rich 5 mol-% DEE mixture. In contrast, for $\phi = 2$, both mechanisms predict shorter ignition delay times at higher temperatures and longer ignition delay times at lower temperatures, with an intersection with the measurements at around 740 K.

In comparison to Figure 3 and Figure 4, it can be seen in Figure 5, that a small amount of DEE (mol-% on X-Axis) reduces the ignition delay time of CH₄ strongly. Pure methane is measured at a higher ignition temperature ($T_{EOC} = 1100$ K), since there was no ignition at 10bar/850K. However, DEE in contrast, could not be measured at the higher ignition pressure/temperature, caused by a reaction during compression event. All points are simulated with the adiabatic core model. For points of 5 mol-% and 10 mol-% a non-reactive compression was measured. These results are used to calculate the volume trace for

the adiabatic core model. Since both volume traces are very similar, they are also used for the other shown points.

To quantify the pressure influence two sets of experiments are compared in Figure 6 with an end of compression pressure of $p_{EOC} = 10$ bar and 20 bar, respectively. An increase in pressure leads to an accelerated ignition and to ignition at lower temperatures. Both mechanisms again describe a very similar behavior. For the low pressure also at lower temperatures ignition occurs. Again the simulations predict a shorter ignition delay time as measured. The difference decreases for the higher pressure at lower temperatures.



Figure 5: Behavior of different DEE/methane blends $(\phi = 1)$ at 850 K and 10 bar (no ignition of pure methane under these conditions). Pure methane at 1100 K and 10 bar.

Figure 6: Ignition delay times with pressures of 10 bar and 20 bar; stoichiometric ($\phi = 1$) 5 mol-% DEE mixture

The error function from formula (1.1) from Olm et al. [14] is used to evaluation the mechanisms. The lower the result of this error function, the better experimental and simulated ignition delay times match. A value of 0 would be a perfect match. An overall deviation between experiment and simulation by a factor of 2 would lead to an error value of $E \approx 48$. The results are shown in Table 1, whereby the studies are ordered by increasing DEE mole fraction in the whole gas mixture containing working fluid and fuel.

Table 1: Mechanism evaluation results

Experiment/Simulation	E(Eble)	E(Sakai)
5 mol-% DEE ; 10 bar ; $\phi = 1$	343.99	244.05
5 mol-% DEE ; 20 bar ; $\phi = 1$	144.39	91.89
5 mol-% DEE ; 10 bar ; $\phi = 2$	25.59	30.55
10 mol-% DEE ; 10 bar ; $\phi = 1$	20.211	7.39
10 mol-% DEE ; 10 bar ; $\phi = 2$	2.82	12.04
	<i>Experiment/Simulation</i> 5 mol-% DEE ; 10 bar ; $\phi = 1$ 5 mol-% DEE ; 20 bar ; $\phi = 1$ 5 mol-% DEE ; 10 bar ; $\phi = 2$ 10 mol-% DEE ; 10 bar ; $\phi = 1$ 10 mol-% DEE ; 10 bar ; $\phi = 2$	Experiment/Simulation $E(Eble)$ 5 mol-% DEE ; 10 bar ; $\phi = 1$ 343.995 mol-% DEE ; 20 bar ; $\phi = 1$ 144.395 mol-% DEE ; 10 bar ; $\phi = 2$ 25.5910 mol-% DEE ; 10 bar ; $\phi = 1$ 20.21110 mol-% DEE ; 10 bar ; $\phi = 2$ 2.82

5 Summary and Conclusion

The ignition delay time fastens up to a factor of 10 by doubling the amount of DEE from 5 mol-% to 10 mol-%. The end of compression temperature difference between the longest measurable ignition delay time of the 5 mol-% DEE mixture and the same ignition delay time for 10 mol-% DEE mixture is approx.

300 K. Already a 5 mol-% DEE mixture at T_{EOC} = 840 K and 10 bar is ignitable whereas a pure methane mixture would not ignite under these conditions.

Doubling the pressure from $p_{EOC} = 10$ bar to 20 bar, the lowest measurable temperature decreases from $T_{EOC} = 840$ K to 730 K. The ignition delay time decreases by factor 8. A fuel-rich ($\phi = 2$) mixture has a 4 times shorter ignition delay time than a stoichiometric mixture.

A 10 mol-% DEE mixture starts showing a negative temperature coefficient similar to pure DEE. Furthermore, a fuel-rich 5 mol-% DEE mixture shows an almost constant ignition delay time with increasing temperature in the range from $T_{EOC} = 650$ K to 830 K.

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