

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

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## Abstract

Diethyl ether (DEE) is an interesting species for combustion for at least two reasons: On the one hand, it is used as a kind of "worst case" reference substance for studies concerned with the prevention of accidental ignition events. On the other hand, it is also a candidate bio-fuel. For this reason, in this work, auto-ignition of two different CH<sub>4</sub>/DEE-mixtures (90/10 and 95/5 mol-% CH<sub>4</sub>/DEE) are studied in a rapid compression machine (RCM). In the RCM, the gas mixture is compressed in a piston-cylinder device up to 20 bar and held under isochoric conditions at top dead center. Auto-ignition occurs after an ignition delay time (IDT). IDTs are measured for compression temperatures ranging between 515 and 925 K, for both, stoichiometric and fuel-rich mixtures (equivalence ratio  $\phi = 2$ ). The experimental data are compared to results of simulations involving detailed chemistry, as well as to other fuels investigated in the same RCM (results from literature).

**Keywords:** *Ignition delay times, Diethyl ether, DEE, Rapid compression machine, methane*

## 1 Introduction

Diethyl ether (DEE, CH<sub>3</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>3</sub>) is an interesting fuel. With respect to safety engineering, it is extremely flammable, and its vapour/air mixtures can be highly explosive (International Labour Organization, 2002). DEE is therefore often employed as a kind of worst case substance for explosion safety considerations.

Moreover, in compression ignition (CI) engines, the operation range can be extended operating them in a dual fuel mode with DEE as an ignition enhancer (Polat, 2016). As a fuel component, DEE can have several beneficial effects: In CI engines, a wider operation range in comparison to methane (CH<sub>4</sub>) only is observed, as well as a positive effect concerning efficiency and pollutants. For example, hydrogen with DEE (Dhanasekaran and Mohankumar, 2016), as well as bio-gas and DEE (Sudheesh and Mallikarjuna, 2010) are used to promote the auto-ignition. Further, the interest in bio-fuels is growing, and with this, the safety aspect becomes more important as well, such as the auto-ignition behavior (Rajesh Kumar and Saravanan, 2016).

Compared to more conventional fuels or fuel components like e.g. alkanes, there are many studies available investigating the auto-ignition properties: There are studies investigating CH<sub>4</sub>/air-mixtures in shock tubes (ST) and in rapid compression machines (RCM) (Burke et al., 2015b, Gersen et al., 2008, Petersen et al., 1999). Furthermore, there are studies investigating the ignition delay time (IDT) of DEE (Werler et al., 2015a, Inomata et al., 1991). However, there is only little data available combining both, CH<sub>4</sub> and DEE, as a dual fuel, such as (Herzler et al., 2019). As mentioned above, according to engine operation, dual fuel operation has its benefits. For this reason, we investigate mixtures of CH<sub>4</sub>/DEE in a RCM to understand the ignition enhancing effect of DEE on CH<sub>4</sub> in an engine like apparatus. These data can also serve for development and validation of reaction mechanisms.

This work investigates two CH<sub>4</sub>/DEE mixtures, namely a 95/5 and a 90/10 (mol/mol) mixture in a range of end-of-compression temperature from  $T_C = 515$  K to 925 K, and an end-of-compression pressure range of  $p_C = 10$  bar to 20 bar. Both mixtures are investigated under stoichiometric and fuel-rich ( $\phi = 2$ , fuel-air equivalence ratio) conditions. The experimentally obtained data is used for comparison with two reaction mechanisms developed to describe DEE chemistry, published by Eble

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**Table 1:** Mixture compositions (mole-fractions in %)

No.	Fuel	Equivalence ratio	CH <sub>4</sub>	DEE	O <sub>2</sub>	Inert species
1	95/5 CH <sub>4</sub> /DEE	$\phi = 1$	8.28	0.436	19.17	72.12
2	90/10 CH <sub>4</sub> /DEE	$\phi = 1$	7.24	0.805	19.31	72.64
3	95/5 CH <sub>4</sub> /DEE	$\phi = 2$	15.23	0.802	17.63	66.34
4	90/10 CH <sub>4</sub> /DEE	$\phi = 2$	13.40	1.489	17.87	67.24

et al. (2017) and Sakai et al. (2017).

This work outlines the experimental procedure; then, we present the measured IDTs. The results are discussed in terms of the promoting effect of DEE on methane auto-ignition. Predicted IDTs from numerical simulations based on detailed reaction mechanisms are tested against the experimental data; it is assessed in which regimes the mechanisms can reproduce the IDT, despite the fact that they were originally developed for auto-ignition of stoichiometric DEE/air mixtures (Eble et al. (2017): 500 to 900 K / 3 to 5 bar and 900 to 1300 K / 10 to 40 bar; Sakai et al. (2017): 500 to 1300 K / 1 to 40 bar), and not for the CH<sub>4</sub>/DEE/air-mixtures presented in this work with a very small ratio of DEE/CH<sub>4</sub>.

Furthermore, the experimental data are compared to results for other ignition enhancing fuels investigated in the same RCM (results from literature). These fuels are Dimethyl ether (DME), two polyoxymethylene dimethyl ether fuels (OME<sub>2</sub> and OME<sub>3</sub>) and n-heptane (C<sub>7</sub>H<sub>16</sub>). The comparison highlights the strong ignition enhancing effect of DEE, which is significantly larger than for the other fuels.

## 2 Experimental Setup

The auto-ignition behavior of the investigated CH<sub>4</sub>/DEE/air-mixtures is studied in a rapid compression machine (RCM). This machine has been described in detail in previous publications (Drost et al., 2019, Werler et al., 2015a). For this reason, only a brief description of the experimental setup is given in this work.

The RCM is a piston-cylinder device which allows to achieve high temperatures and pressures in a fuel/air mixture by rapid compression, thereby also stimulating chemical reactions. Therefore, the operation is similar to a CI engine, but the RCM allows better defined initial conditions with respect to temperature, pressure, mixture composition and flow field. The volume- and pressure history during and after the compression event is tracked in each experiment; the pressure measurement is split into a measurement of the static/initial pressure and the time dependent in-cylinder pressure measurement. The static initial pressure  $p_0$  is measured with an absolute pressure transducer (MKS Baratron type 121A) with an accuracy of  $U_{p0} = \pm 0.5\%$  of reading (MKS, 2008), whereas the time dependent pressure trace  $p(\tau)$  is monitored by a quartz pressure transducer (Kistler 6061 B) with a linearity of  $U_{p(\tau)} = 0.5\%$  (full scale output, adjusted to 10 bar) (Kistler, 2013). This pressure transducer is optimized against thermo-shocks with a double diaphragm. For reciprocating internal combustion engines with 1500 revolutions per minute (approximately a similar speed as the presented RCM; compression time of 20 - 40 ms) and an indicated mean effective pressure of 9 bar, the thermo shock causes a pressure fluctuation of  $\Delta p = \pm 0.2$  bar (Kistler, 2013).

The time-resolved position of the piston is measured with a potentiometric position sensor (Burster type 8712), which is connected to the piston rod with a non-linearity of  $U_S = 0.1\%$  of full scale (Burster, 2020).

Before a series of RCM-experiments is performed, the mixture is prepared in a mixing vessel by filling in the desired mole fractions of the pure components, as given by their partial pressures. The mixing vessel contains gas for about 10 - 100 RCM experiments, depending on the detailed conditions. The mixtures investigated in this work are summarized in Table 1.

In an experiment, the gas mixture is filled into the initially evacuated RCM combustion chamber. After this, the piston is driven into the cylinder within a compression time of about  $\tau_C = 20$  to 40 ms,

depending on the compression pressure  $p_C$  in the combustion chamber. After reaching top dead center (TDC), the piston is held in fixed position, granting isochoric conditions till the experiment ends. After some ignition delay time (IDT), auto-ignition occurs; the IDT is counted relative to the end of compression (the time when the piston first reaches TDC).

To assign a temperature and pressure to an ignition event and its IDT, the conditions at the end of compression are chosen. The temperature at this time is calculated from the measured pressure ( $p(\tau)$ ), and the initial values of pressure/temperature and the temperature-dependent heat capacities of the investigated gas-mixture, using an isentropic relation.

### 3 Simulations

The simulations in this work are performed with the in-house code HOMREA (Maas and Warnatz, 1988) using a homogeneous reactor model. HOMREA has been extended over years by its functions (Golda et al., 2019, Yu et al., 2019) and by its input algorithm for reading new reaction mechanisms and their functions.

Characterising the RCM and its specific heat losses, an effect volume is calculated and serves as an input for the simulations (described below in more detail). The initial temperature, pressure, and chemical composition of the mixture are defined by the corresponding experimental conditions.

Detailed reaction mechanisms from Sakai et al. (2017) (341 species and 1867 reactions) and from Eble et al. (2017) (133 species and 792 reactions) are used.

In RCM experiments, an adiabatic core is assumed in the center of the combustion chamber. However, the whole combustion chamber is affected by heat losses. Combining the idea of this adiabatic core and the heat losses of the surrounding gas layers, an effective volume model, as described by Goldsborough et al. (2017) and Sung and Curran (2014), can be used to perform IDT simulations taking the facility effects into account.

To obtain this effective volume, a RCM experiment with an inert mixture is used. Hereby, for each mixture in Table 1, the oxygen ( $O_2$ ) is substituted by the same molar amount of nitrogen ( $N_2$ ).  $N_2$  has a similar molar heat capacity as  $O_2$ ; however, in the range of conditions it is considered here, there is practically no reaction of the fuel as shown by (Vin et al., 2016). The unreactive experiments are performed with compression temperatures below 830 K to prevent thermal decomposition/pyrolysis of DEE (Vin et al., 2016). Further, gas chromatography analysis has shown that there was no thermal decomposition (pyrolysis) of the inert gas mixture. This means that the pressure trace is only affected by the volume change and the heat losses.

Thus, at isochoric conditions, a pressure drop is directly linked to heat losses and the corresponding drop in temperature caused by heat losses. The time-dependent effective volume  $V(\tau)$  is calculated from

$$\ln\left(\frac{p_0}{p(\tau)}\right) = \int_{V_0}^{V(\tau)} \frac{c_p(T)}{c_v(T)} \frac{1}{V^*} dV^*. \quad (1)$$

Here,  $p_0$  and  $V_0$  are the initial pressure and volume, respectively,  $p(\tau)$  is the pressure trace over time and  $V(\tau)$  the effective volume over time. Moreover  $c_p$  and  $c_v$  are the temperature-dependent heat capacities at isobaric and isochoric conditions.

As a result of the heat losses, the effective compression ratio used in the simulation is lower than the geometric one defined by the experimental apparatus. Furthermore, after reaching TDC, the effective volume expands slightly over time.

## 4 Results and discussion

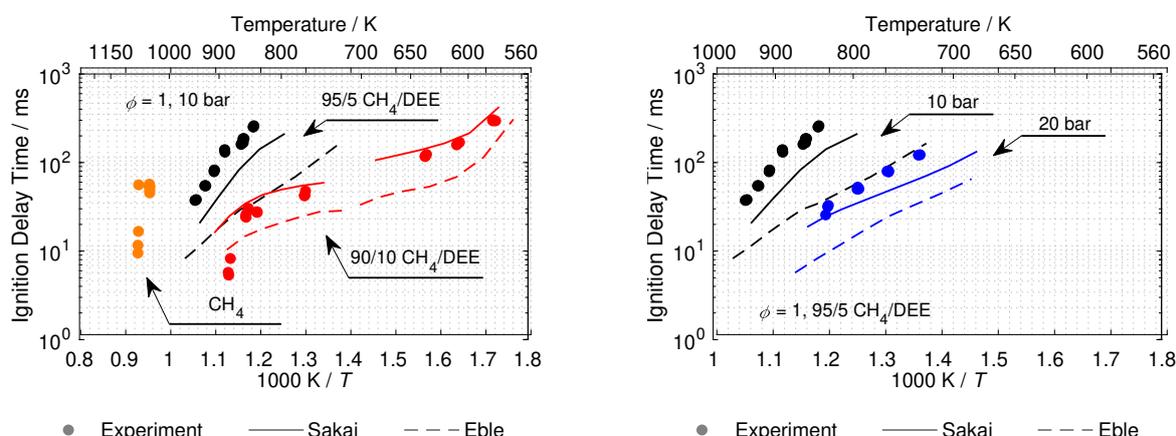
### 4.1 Ignition delay times of stoichiometric $CH_4/DEE$ mixtures

In this section, the IDT of the stoichiometric  $CH_4/DEE$  mixtures of Table 1 are presented (mixture #1 and #2). Figure 1a shows the behaviour of different  $CH_4/DEE$  mixtures vs.  $CH_4$ . Comparing the 95/5 vs. 90/10  $CH_4/DEE$  mixture, three effects are notable:

First, at a given temperature, the ignition of 90/10 CH<sub>4</sub>/DEE mixtures is about one order of magnitude faster than for the 95/5 mixture. Second, with the higher amount of DEE, the gas mixture can be ignited at lower temperatures. Here the DEE chemistry becomes more dominant. Third, comparing the 95/5 CH<sub>4</sub>/DEE mixture to CH<sub>4</sub> one observes that the small addition of DEE already has a significant effect.

Adding 5 mol-% DEE, there is ignition at lower temperatures, a lower apparent activation energy is observed and ignition delay times above  $\tau_I \approx 60$  ms can be measured. Comparing 95/5 CH<sub>4</sub>/DEE to CH<sub>4</sub> by the temperature with an IDT of  $\tau_I = 55$  ms, the required temperature is lowered from  $T_C \approx 1045$  K (CH<sub>4</sub>) to  $T_C \approx 925$  K (95/5 CH<sub>4</sub>/DEE).

Comparing the experimental results with the simulation in Figure 1a, the reaction mechanism of Sakai et al. (2017) agrees better with the experimental results than the reaction mechanism of Eble et al. (2017). Further, both reaction mechanisms show a better agreement with the 90/10 CH<sub>4</sub>/DEE mixture than with the 95/5 CH<sub>4</sub>/DEE mixture. A reasonable explanation at this point is, that both reaction mechanisms were developed for auto-ignition of DEE.



(a) Comparison of different CH<sub>4</sub>/DEE ratios and CH<sub>4</sub> at constant pressure (10 bar). (b) Comparison of two compression pressures at constant 95/5 CH<sub>4</sub>/DEE ratio.

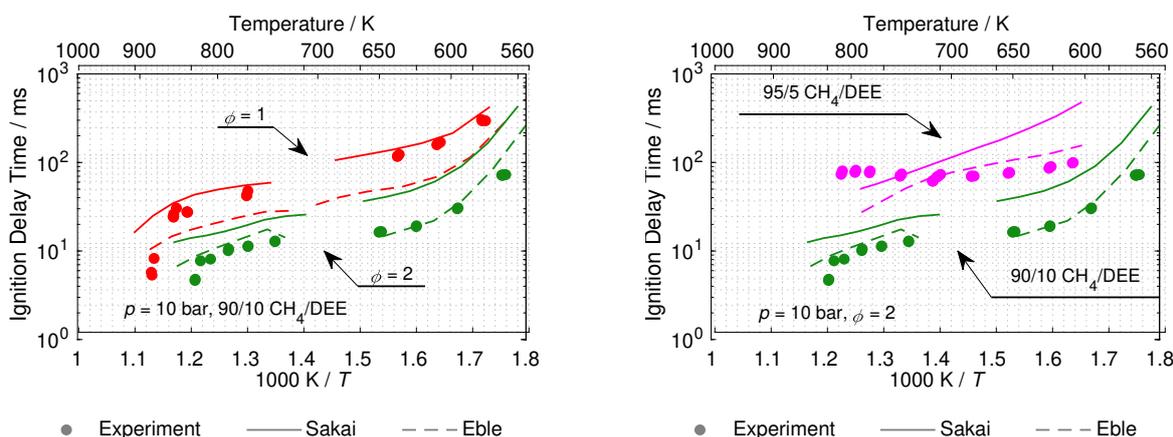
**Fig. 1:** Stoichiometric 95/5 CH<sub>4</sub>/DEE and 90/10 CH<sub>4</sub>/DEE mixtures at two different compression pressures. Simulations (lines) are performed with the reaction mechanism of Eble et al. (2017) and Sakai et al. (2017)

Figure 1b compares the stoichiometric 95/5 CH<sub>4</sub>/DEE mixture at two different compression pressures ( $p_C = 10$  vs. 20 bar). The increased compression pressure results in a shorter IDT. Furthermore, ignition is detected at lower compression temperatures. For the 95/5 CH<sub>4</sub>/DEE mixture, both reaction mechanisms predict a shorter IDT than the experiments, however, at higher pressure, the experiments and simulations agree better than for the 10 bar case.

The C0-C4 base-reaction mechanism of Sakai et al. (2017) is based on the reaction mechanism from Burke et al. (2014, 2015a) (Part of AramcoMech 2.0). Replacing this C0-C4 base-reaction mechanism with its newer C0-C4 base-reaction mechanism of the AramcoMech 3.0 (Zhou et al., 2018) resulted in almost the same IDTs (for this reason the result is not shown). However, one can argue, that the differences in IDTs cannot be attributed to the base-reaction mechanism of small alkanes such as CH<sub>4</sub>.

#### 4.2 Ignition delay times of fuel rich CH<sub>4</sub>/DEE mixtures

To investigate the behavior of fuel rich mixtures, the presented mixtures with the same CH<sub>4</sub>/DEE ratio are mixed with O<sub>2</sub>/inert species to reach an overall equivalence ratio of  $\phi = 2$  (Table 1 mixture #3 and #4). The results for these mixtures are shown in Fig. 2 with an end of compression pressure of 10 bar. In Fig. 2a, a comparison of the fuel rich 90/10 CH<sub>4</sub>/DEE to its stoichiometric mixture is shown. Overall, at low temperatures, the IDT of the  $\phi = 2$  fuel rich mixture is approximately one order of magnitude shorter than that of the stoichiometric ones.



(a) Comparison of 90/10 CH<sub>4</sub>/DEE mixtures at stoichiometric and fuel rich conditions, respectively. (b) Influence of DEE in CH<sub>4</sub> at fuel rich conditions (φ = 2).

**Fig. 2:** Effect of fuel rich mixtures at a compression pressure of 10 bar. Simulations (lines) are performed with the reaction mechanism of Eble et al. (2017) and Sakai et al. (2017).

Since DEE ignites faster than CH<sub>4</sub>, the ignition process is controlled by DEE. Further, stoichiometric mixtures ignite faster than (ultra) lean mixtures (Yasunaga et al., 2010). By comparing the equivalence ratio of only DEE in O<sub>2</sub> (by ignoring CH<sub>4</sub>), the overall stoichiometric mixture #2 has a DEE-equivalence ratio of φ<sub>DEE</sub> = 0.25 and the overall fuel rich mixture #4 has a DEE-equivalence ratio of φ<sub>DEE</sub> = 0.5. This is probably one reason for the ignition promoting effect of the fuel rich conditions. At this point, this behaviour is not investigated in this work. However, alkanes with an equivalence ratio of φ = 2 ignite fast than the stoichiometric ones (Healy et al., 2008).

Both reaction mechanisms show a similar trend in shortening the IDT for the transition from stoichiometric to fuel rich conditions. However, in the experiments, another trend is observed. At a given temperature, the IDT for a fuel mixture is reduced more by changing the equivalence ratio from φ = 1 to 2 than in the simulations.

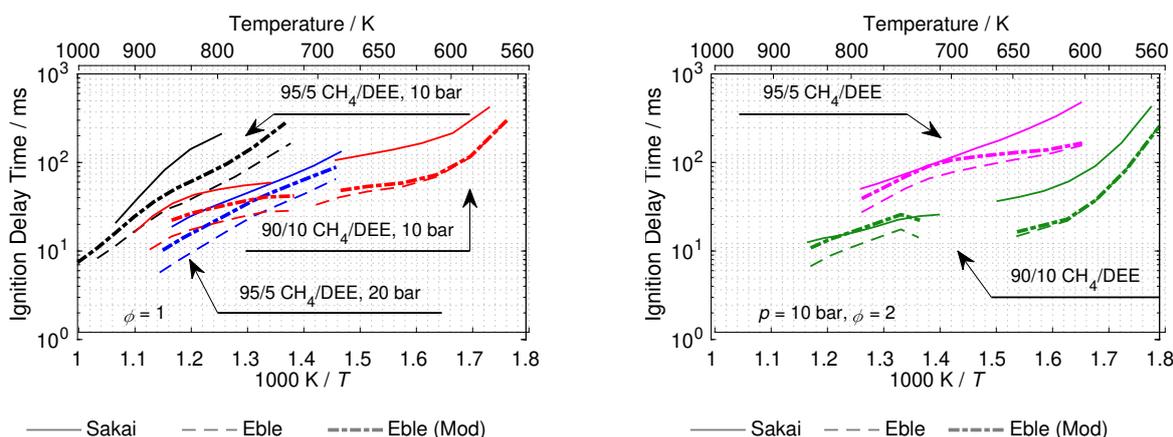
Figure 2b compares the different CH<sub>4</sub>/DEE mixtures at an equivalence ratio of φ = 2 and 10 bar. Again, the higher amount of DEE enhances auto-ignition. Both reaction mechanisms predict the trend of the fuel rich conditions. Here, the Eble et al. (2017) reaction mechanism results predict the results of the experiments better.

### 4.3 Difference of the reaction mechanisms

Comparing both reaction mechanisms and the experimental results, it is observed that especially at a low amount of DEE, the reaction mechanism of Eble et al. (2017) overestimates the IDT. Investigating this behavior in more detail, IDT simulations (homogeneous reactor, adiabatic and isochoric conditions) are performed for different initial temperatures and different amounts of DEE in the fuel. The first observation is that for the cases with CH<sub>4</sub>, both reaction mechanisms result in the same IDT. Starting from CH<sub>4</sub> and increasing the amount of DEE in the fuel, especially at low temperatures (besides 700 K), there is an increasing difference in the predicted IDT by both reaction mechanisms in the range between 5 to 10 mol-% DEE in the fuel.

Understanding the difference between both reaction mechanisms at low amounts of DEE more, sensitivity analysis according to the OH radical are performed for an adiabatic and homogeneous reactor, for both, the Eble et al. (2017) and the Sakai et al. (2017) reaction mechanisms. According to mentioned IDT simulations, an initial temperature of 800 K and an initial pressure of 10 bar is taken for a stoichiometric 95/5 (molar) CH<sub>4</sub>/DEE mixture. Under these conditions, for both reaction mechanisms, the reaction





(a) Stoichiometric conditions, different pressures and (b) Fuel rich conditions ( $\phi = 2$ ) and a constant pressure (10 bar).

**Fig. 3:** Comparison between simulations (experiments are not shown for better readability) with the reaction mechanism of Eble et al. (2017), Sakai et al. (2017) and the modified reaction mechanism of Eble et al. (2017).

is most sensitive at the time  $\tau = 0.9\tau_I$ . Analyzing this reaction, the parameters of the modified Arrhenius equation are summarized in Table 2.

**Table 2:** Coefficients from reaction (R1) for the Arrhenius equation  $k = AT^\beta \exp(-E/(RT))$ .

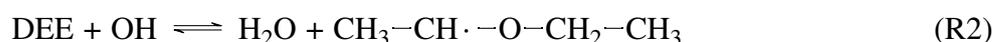
Reaction Mechanism	A	$\beta$	E / (cal/mol)
Eble et al. (2017)	$1.176 \cdot 10^{14}$	0	17700
Sakai et al. (2017)	$7.240 \cdot 10^{-01}$	3.980	9058.0

Updating the mentioned reaction (R1) in the reaction mechanism of Eble et al. (2017) by the values of Sakai et al. (2017), an improved IDT is found for higher temperatures (closer results to the experimental data and the predicted IDT of Sakai et al. (2017)) for the stoichiometric mixtures as shown in Fig. 3a.

Fig. 3b shows the comparison between the reaction mechanisms for fuel rich conditions. The IDTs at higher temperatures are too long with a similar result obtained with the reaction mechanism of Sakai et al. (2017). At lower temperatures, the result is similar to the original reaction mechanism of Eble et al. (2017).

The sensitivity analysis was performed for an initial temperature of 800 K, which refers to the upper limit of the investigated temperature regime. Furthermore, the mentioned modification has a higher impact at higher temperatures. On the other side, at lower temperatures the original reaction mechanism (thin dashed lines) and the modified one (thick dashed lines) show a similar result.

For this reason, a sensitivity analysis is performed at an initial temperature of 600 K as well. Both reaction mechanisms show reaction R2 (positive sensitivity) and reaction R3 (negative sensitivity) to be the most sensitive reactions.



However, R2 has similar Arrhenius parameters in both reaction mechanisms. For this reason, adapting the Arrhenius parameters shows just a minor change in IDT. Furthermore, reaction R3 has the same values of the Arrhenius equation.

The second most sensitive reactions (R4 and R5) include those DEE molecules for which the first O<sub>2</sub> addition already took place. The second O<sub>2</sub> addition, reaction R4, has a positive sensitivity. In contrast to this, the chain branching reaction R5 of this molecule has a negative sensitivity.



Reactions R4 and/or R5 in the reaction mechanism of Eble et al. (2017) can be adjusted by adapting the Arrhenius parameters from Sakai et al. (2017), as described above. However, by changing reaction R4 and/or R5, the IDTs predicted by the modified reaction mechanism are too long and the IDT is depending on both reactions (R4 and R5). Since there is a too strong effect by changing the Arrhenius parameters, this modification is not recommended.

For an initial temperature of 600 K, a further sensitive reaction is found in both reaction mechanisms, namely reaction R1. This reaction is found most sensitive for an initial temperature of 800 K for both reaction mechanisms and was already adjusted.

Further sensitive reactions related to DEE molecules, are not found in both reaction mechanisms. For example, in the reaction mechanism of Eble et al. (2017) a reaction of DEE and CH<sub>3</sub>O is the third most sensitive reaction, however, under the investigated conditions, this reaction has a minor sensitivity in the reaction mechanism of Sakai et al. (2017).

Other sensitive reactions are reactions of intermediates and radicals and are not directly linked to the fuel structure of DEE (C-C-O-C-C) or are reactions which are sensitive just in one reaction mechanism.

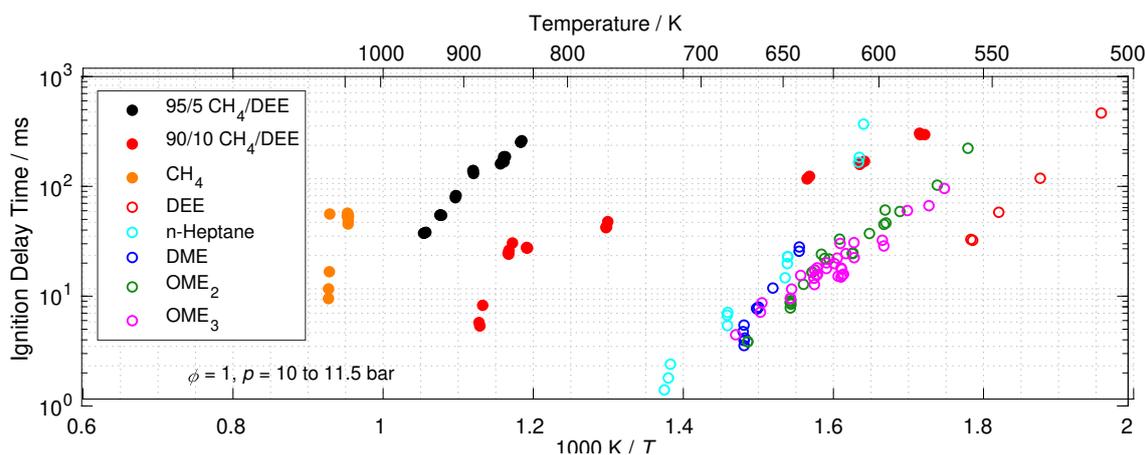
#### 4.4 Comparison of CH<sub>4</sub>/DEE mixtures with other fuels

Highlighting the effect of even small amounts of DEE in fuel, Fig. 4 compares the IDT of the present study against IDT of previous studies obtained in the same RCM. The selected fuels are known as reference fuel (n-Heptane, C<sub>7</sub>H<sub>16</sub>), potential bio fuels for CI engines (oxygenated fuels) or as a reference for this study (DEE). The fuels are summarized in Table 3. Fig. 4 shows, DEE auto-ignites at the lowest temperature and CH<sub>4</sub> at the highest temperatures. By adding already 10 mol-% DEE to CH<sub>4</sub>, at low temperature the IDT of this 90/10 CH<sub>4</sub>/DEE mixture is of the same order of magnitude as the IDT of C<sub>7</sub>H<sub>16</sub>.

**Table 3:** Mixture compositions in mol-% fractions

No.	Fuel	Chemical formula	Pressure / bar	Literature
E1	DEE	H <sub>3</sub> C-CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>3</sub>	$p_C = 10.5 - 11.5$ bar	Werler et al. (2015a)
E2	DME	H <sub>3</sub> C-O-CH <sub>3</sub>	$p_C = 10 - 11$ bar	Werler et al. (2015b)
E3	OME <sub>2</sub>	H <sub>3</sub> C-O-(CH <sub>2</sub> -O) <sub>2</sub> -CH <sub>3</sub>	$p_C \approx 10$ bar	Drost et al. (2019)
E4	OME <sub>3</sub>	H <sub>3</sub> C-O-(CH <sub>2</sub> -O) <sub>3</sub> -CH <sub>3</sub>	$p_C \approx 10$ bar	Drost et al. (2019)
E5	n-Heptane	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub>	$p_C \approx 10$ bar	Drost et al. (2019)

However, in the investigated pressure regime, the 90/10 CH<sub>4</sub>/DEE mixture shows a weaker temperature dependence (reduced IDT by increased temperature) than the other oxygenated fuels. For this reason, the IDT does not drop as fast as for example for OME<sub>3</sub> (slope in the Arrhenius diagram).



**Fig. 4:** Comparison of  $\text{CH}_4/\text{DEE}$  mixtures with other potentially bio fuels and  $\text{CH}_4$ . Full symbols represent data from this work, opened symbols represent data from literature with the references in Table 3.

One reason for this observation is the negative temperature coefficient (NTC) behaviour of DEE. Werler et al. (2015a) showed that DEE has a pronounced NTC behaviour. The IDT data of DEE in Fig. 4 does not show this NTC behaviour since the IDT at 10 bar and above 600 K is too short in relation to the compression time. Thus, the DEE data (red circles) show here only the IDT at low temperatures below the NTC behaviour. The IDT data of DEE show a steeper slope and a strong dependence on temperature change in comparison to 90/10  $\text{CH}_4/\text{DEE}$ . One can argue, that the 90/10  $\text{CH}_4/\text{DEE}$  mixture is affected by the NTC behaviour of DEE. In comparison to this, due to lower DEE concentration, the 95/5  $\text{CH}_4/\text{DEE}$  mixture is affected less.

## 5 Conclusions

Ignition delay times of  $\text{CH}_4/\text{DEE}/\text{air}$  mixture have been investigated in a Rapid Compression Machine. Two different  $\text{CH}_4/\text{DEE}$  ratios, both at stoichiometric and fuel-rich conditions ( $\phi = 2$ ) are investigated, in a temperature range of 515 to 925 K and a pressure range of 10 to 20 bar. The ignition delay times are compared to predictions from simulations based on detailed chemistry, using two reaction mechanisms. Further, the two reaction mechanisms are compared to each other, using a homogeneous reactor model and different fuel compositions as well as a sensitivity analysis. Experimental IDTs of the  $\text{DEE}/\text{CH}_4$  mixtures are also compared to other fuels. The main results are:

1. By adding 5 mol% of DEE to the fuel  $\text{CH}_4$ , the ignition delay is strongly decreased. For instance, to obtain an IDT shorter than 55 ms requires a temperature of at least about 1045 K for  $\text{CH}_4$ ; with 95/5  $\text{CH}_4/\text{DEE}$  (molar), the required temperature is reduced to about 925 K.
2. Throughout the investigated temperature and pressure-range, the ignition delay time decreases by a factor of about 10 by doubling the amount of DEE from 5 mol-% to 10 mol-%.
3. For the investigated conditions, the reaction mechanisms from Eble et al. (2017) and Sakai et al. (2017) predict the trend in IDT change over temperature well, except for the mixture 95/5  $\text{CH}_4/\text{DEE}$  at fuel rich conditions.
4. For a temperature of  $T = 600$  K and a stoichiometric 95/5 (molar)  $\text{CH}_4/\text{DEE}$  mixture, the reaction of DEE with OH and the reaction of  $\text{CH}_4$  and OH are most sensitive (positive and negative).
5. For temperature  $T = 800$  K and low amounts of DEE in  $\text{CH}_4$ , the reaction of  $\text{DEE} + \text{CH}_3\text{O}_2 \cdot \rightleftharpoons \text{C}_4\text{H}_9\text{O} \cdot + \text{CH}_3\text{O}_2\text{H}$  is most sensitive.
6. In the investigated conditions, updating the reaction  $\text{DEE} + \text{CH}_3\text{O}_2 \cdot \rightleftharpoons \text{C}_4\text{H}_9\text{O} \cdot + \text{CH}_3\text{O}_2\text{H}$  in the reaction mechanism of Eble et al. (2017) with the values of Sakai et al. (2017) results in IDTs closer to the experimental IDTs and closer to IDTs predicted by the reaction mechanism of Sakai et al. (2017).

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