

# A RCM study on DME-methane-mixtures under stoichiometric to fuel-rich conditions

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## 1 Introduction

The awareness of the finite nature of oil based fuels leads to a search for more widespread alternatives. Methane as a main component in natural gas is an interesting alternative, because its resources last for longer times compared to oil. However, the poor auto-ignition behavior of methane can make the additivation with ignition enhancing substances necessary [1]. Dimethyl ether (DME) is a possible candidate for such an ignition enhancer due to its advantageous characteristics like for example a high cetane number, low soot emission and a good availability [2–4, 6]. Studies on the chemical kinetics of DME in several experimental setups exist, like burner-stabilized flame, flow reactor, stirred reactor, shock tube and rapid compression machine [3–13]. Furthermore, two reaction mechanisms for DME were developed by Fischer et al. [4–6] and by Zhao et al. [11].

Amano et al. investigated the ignition promoting effect of DME in methane-air-mixtures by adding small amounts of DME to methane-air-mixtures in a flow reactor [7]. They found that a little amount of DME additivation had a stimulating effect on autoignition of methane-air-mixtures [7]. The effect of DME addition on high temperature ignition and burning properties was studied by Chen et al. [14]. They also concluded that small amounts of DME lead to an acceleration of ignition delay time [14]. Using shock tube experiments Tang et al. studied ignition delay times of methane-air and DME-air mixtures as well as blends between 1% and 50% of DME additivation to methane-air-mixtures under stoichiometric conditions and high temperatures [15]. This study confirmed the promoting effect of small amounts of DME on the ignition delay time of methane-air mixtures. However, they showed that higher amounts of DME additivation still lead to shorter ignition delay times, but the promoting effect decreased [15]. A good agreement between the mechanism of Zhao et al. [11] and their measurements between 1 and 10 bar was observed [15]. In a recently published study of Burke et al., ignition delay times for DME-methane-air-mixtures were measured and a chemical kinetic model was developed [16]. Measurements under a wide range of conditions ( $T = 600 - 1000$  K,  $p = 7 - 41$  atm,  $\phi = 0.3 - 2$ ) were conducted [16].

In summary, there are various studies on the auto-ignition behavior of DME and Methane-DME mixtures. Most of these studies do not investigate extremely fuel rich conditions, since these are usually of less interest for combustion applications. However, fuel rich conditions can be of interest for other systems, e.g. polygeneration systems or chemical process engineering. Nowadays energy conversion in thermal engines and chemical production processes are separated. Whilst the yield in thermal engines is

power generation regardless of exergy destruction in the combustion process, chemical production processes pay attention on high conversion rates [19]. A combination of both processes by partial oxidation of the fuel could be more efficient than the single processes. Therefore in this study DME-methane-air mixtures were investigated from stoichiometric to fuel rich conditions. Ignition delay times were measured in a rapid compression machine (RCM) at pressures of 10 and 20 bar. Furthermore the exhaust gas was analyzed using micro gas chromatography to investigate the influence of the equivalence ratio on its composition.

## 2 Experiment

The rapid compression machine (RCM) used in this study was previously described by Werler et al. [17], therefore only a short account is given here.

The RCM consists of a temperature controlled cylinder-piston device where the piston is driven by a pneumatic actuator and stopped at top dead center (TDC) by a knee-lever system. The piston features a crevice which swallows the near-wall boundary layer, thus avoiding the formation of a roll-up vortex. This helps to create a more homogeneous post compression temperature field in the reaction chamber.

A relative pressure transducer (Kistler 6061B) mounted to the cylinder allows to record time-resolved in-cylinder pressure. Combined with the pre-compression pressure measured with an absolute pressure gauge (MKS Baratron 121A), the absolute pressure at each point in time of the experiment is known. A type K thermocouple is used to measure the pre-compression temperature of the cylinder load. A potentiometric position sensor (burst type 7812) is used to record the time-resolved piston position history during the compression event.

The RCM is equipped with an optical access to the reaction chamber. A photomultiplier tube with a dichroic shortpass filter (cutoff wavelength 450 nm) was used to detect chemiluminescence emissions during experiments. Along with the pressure signal, an ignition can be detected by this chemiluminescence signal.

In this study the ignition delay time was defined as the time between the moment where the piston reached TDC and the inflection point of an increase in pressure due to ignition. The ignition delay times are referenced to the pressure and temperature when the piston reaches TDC. At TDC the temperature,  $T_{TDC}$ , is calculated from the measured pre-compression pressure ( $p_0$ ), the pressure at TDC ( $p_{TDC}$ ) and the initial temperature  $T_0$  using the isentropic core assumption for an ideal gas. To adjust this temperature  $T_{TDC}$  in the experiments to the desired range, the initial temperature  $T_0$ , the compression ratio and the composition of the inert gases (nitrogen and argon) were chosen accordingly. The pressure at TDC was adjusted by varying the initial pressure.

Table 1: Test gas compositions / Mol%

Mix No.	DME Add.	$\phi$	DME	CH <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub> + Ar
1	0%	1	6.54	0	19.63	73.83
2	0%	2	12.28	0	18.42	69.3
3	10%	1	0.91	8.18	19.09	71.82
4	10%	2	1.67	15.01	17.5	65.82
5	20%	1	1.74	6.97	19.17	72.12
6	20%	2	3.21	12.82	17.63	66.34
7	5%	2	0.85	16.15	17.43	65.57

Gas samples can be taken from the RCMs cylinder at a freely selectable time after compression. In conjunction with a gas chromatograph, this allows studying, e.g., the partially reacted gas from the pre-ignition phase in detail. In this work, the reacted gas after ignition was studied.

Three blends of DME and methane, with 5, 10 and 20 mol% DME were studied for equivalence ratios ranging from  $\phi = 1$  to 2. The detailed compositions of the test-gas mixtures are shown in table 1.

### 3 Numerical Simulation

Numerical simulations of the RCM process were performed using a homogeneous reactor model. An experimental volume trace, describing the compression and expansion of the core gas, was used as input to take the compression phase and the heat loss into account. To derive the volume trace, non-reactive experiments were conducted under the same boundary conditions as the reactive measurements. For this purpose, oxygen in the cylinder load was replaced by nitrogen, yielding an inert gas mixture with similar isentropic exponents and thermal diffusivities [16]. The volume trace is calculated from the non-reactive cases using the assumption of an adiabatic core, which is described in detail by Mittal et al. [18].

### 4 Results

As described previously, ignition delay times were determined. Additionally, the chemical composition of the exhaust gas were measured in the RCM by a micro gas chromatograph. The results are presented below.

#### Ignition delay times (IDT)

Ignition delay times (IDT) were measured for the mixtures shown in table 1. The data were compared to the mechanism from [4–6] LLNL and Zhao [11], although both mechanisms were developed originally for pure DME-air-mixtures. Sharp bends in the simulated IDTs in figure 1 are caused by a change in the inert gas composition, which were adjusted in the simulation to match the experimental composition.

Figure 1 shows the main IDTs for the mixtures no. 3-6. As also described in literature [14, 15], an accelerating effect on the main IDTs can be observed for an increased additivation of DME to methane and apart from that unchanged conditions. Furthermore, mixtures with equivalence ratio  $\phi = 2$  leads to faster ignition than  $\phi = 1$ . For Mix no. 3, the Zhao mechanism shows a good agreement of IDT with experiments for temperatures below  $1000\text{K}/T = 1.09$ . For higher temperatures, the mechanism predicts longer IDTs. The simulation with the LLNL mechanism shows the same slope of IDT vs. temperature, but ignites slightly faster than the measurements. With 10% DME addition and an equivalence ratio of  $\phi = 2$ , a good agreement of the Zhao mechanism can be observed for the temperature range  $1000\text{K}/T = 1.22 - 1.35$ . A different slope of IDT is observed for higher and lower temperatures. The LLNL mechanism overpredicts the IDT for the investigated temperature range, but exhibits a good agreement in the slope with the temperature. In contrast to the mixtures 3 and 4, the LLNL mechanism describes the auto-ignition behaviour of mixtures with an additivation of 20% DME more precisely than the Zhao mechanism does. Both mechanism show a good agreement in the change of IDT with the temperature, but simulations with the Zhao mechanism result in little too short IDTs. In the simulations a first stage ignition took place for temperatures below  $1000\text{K}/T = 1.4$  within the compression time for this reason it was not possible to reference a pressure and temperature to the main IDT.

Figure 2 shows the main IDTs for the mixtures no. 1,2 and 7. For the pure DME-air mixtures (no. 1 and 2) both mechanisms show a very good agreement with the measured data at a pressure of  $p_{\text{TDC}}=10$

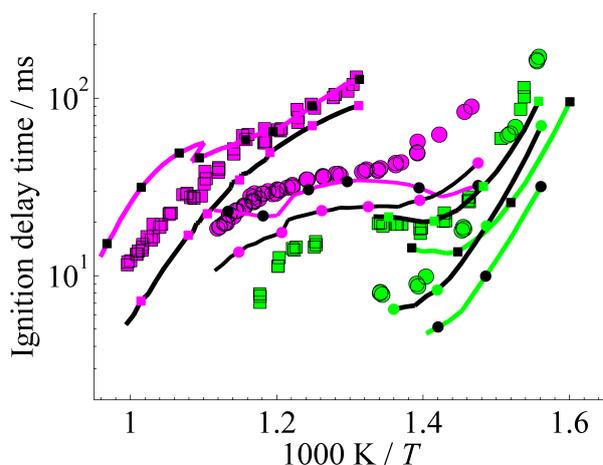


Figure 1: Comparison of measured and simulated main IDTs.

Magenta: 10% DME  $p_{TDC}=10$  bar;

Green: 20% DME  $p_{TDC}=10$  bar;

Squares:  $\phi = 1$ ;

Circles:  $\phi = 2$ ;

Black line colored symbols; LLNL mechanism [4–6];

Colored line black symbols: Zhao mechanism [11]

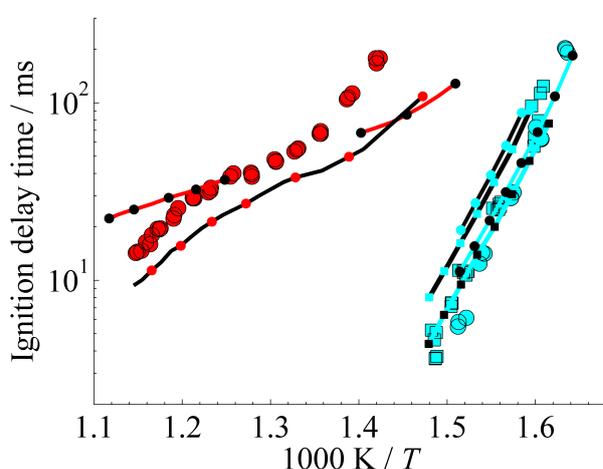


Figure 2: Comparison of measured and simulated main IDTs.

Cyan: 100% DME  $p_{TDC}=10$  bar;

Red: 5% DME  $p_{TDC}=20$  bar;

Squares:  $\phi = 1$ ;

Circles:  $\phi = 2$ ;

Black line colored symbols; LLNL mechanism [4–6];

Colored line black symbols: Zhao mechanism [11]

bar. In the investigated temperature range just a slight influence of the equivalence ratio  $\phi = 1 - 2$  was observed. The rich mixture (circles) has a slightly faster IDT than the stoichiometric mixture (squares), whereas both mechanisms predict a reverse influence.

Another comparison between measurements with a 5% DME additivated mixture (no. 7) at  $p_{TDC}=20$  bar and simulations is shown in figure 2. The Zhao mechanism shows a flatter slope and matches the measured IDT at around  $1000K/T = 1.22$ . Within the gap of  $1000K/T = 1.25 - 1.4$  the IDT of the Zhao mechanism are not shown due to a first stage ignition during compression. The slope of the LLNL mechanism is similar to the measured IDTs, but the mechanism predicts slightly too short IDTs.

In Figure 3, the first stage IDT of those measurements where a two stage ignition was observed are shown. For the mixtures with a low additivation of DME to methane (5 and 10%), both mechanisms predict too fast first stage IDTs. However, the slope of the IDT vs temperature is well predicted by both mechanisms. For the 5% DME-mixture the Zhao mechanism didnt show a clear first stage ignition. After compression, the pressure increased slightly therefore no IDT is shown in figure 3. At the higher additivation mixtures no. 5 and 6 the prediction of first stage ignition agrees better. The LLNL mechanism shows a better coincidence with the measurements than the Zhao mechanism which predicts a slightly too fast first stage IDT.

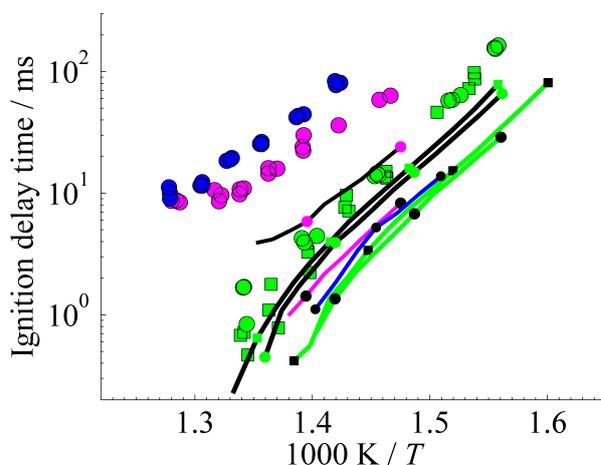


Figure 3: Comparison of measured and simulated first stage IDTs.

Blue: 5% DME  $p_{TDC}=20$  bar;  
 Magenta: 10% DME  $p_{TDC}=10$  bar;  
 Green: 20% DME  $p_{TDC}=10$  bar;  
 Squares:  $\phi = 1$ ;  
 Circles:  $\phi = 2$ ;  
 Black line colored symbols; LLNL mechanism [4–6];  
 Colored line black symbols: Zhao mechanism [11]

### Composition of the exhaust gas

For the mixtures no. 3-6, the composition of the post-ignition exhaust gases are shown in table 2. The water content is not taken into account for the Mol% values, since water is removed before the gas enters the micro-GC. Due to the minor influence of the investigated pre-ignition temperature, mean values over the investigated temperature range are shown. For both stoichiometric mixtures, an almost complete combustion is observed. In contrast to that the fuel rich mixtures contain a considerable amount of Syngas. There is just a minor influence of the DME additivation on the exhaust gas composition.

Table 2: Exhaustgas compositions / Mol%

Mix No.	$\phi$	DME	CH <sub>4</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO	H <sub>2</sub>
3	1	0.06	0.32	0.82	10.39	0.24	0.14
4	2	0.11	1.35	1.16	2.77	12.45	14.8
5	1	0.12	0.43	0.98	11.46	0.48	0.24
6	2	0.21	1.34	1.22	3.26	13.86	14.92

## 5 Conclusion

Measurements of ignition delay times and exhaust gas compositions were conducted for different DME and DME-methane-air mixtures, at two equivalence ratios ( $\phi = 1$  and 2) and pressures ( $p_{TDC}=10$  and 20 bar) in a RCM. Two mechanisms from [4–6] and [11] were used for a comparison of IDTs. Both mechanisms show a very good agreement with the pure DME-air-mixtures. Although both mechanisms were originally not designed for mixtures of DME and methane they also predict the main IDT for these mixtures well. The LLNL mechanism shows a very good agreement for the change with temperature, however for mixtures with a higher methane content the simulation results in slightly too fast IDTs. For the temperature range  $1000K/T = 1.2 - 1.4$ , the Zhao mechanism describes the main ignition well for all mixtures, but shows a slightly diverging slope for higher and lower temperatures. For first stage ignition, both mechanisms overpredict the IDT for the lower additivated mixture no. 3, 4 and 7. The LLNL mechanism predicts the first stage IDTs well for the 20% DME mixtures, while the Zhao mechanism overpredicts them slightly.

The main components of the exhaust gas composition were measured in a micro-GC for all measure-

ments with a DME-methane-mixture. As it could be expected, for the stoichiometric experiments an almost complete combustion to CO<sub>2</sub> and H<sub>2</sub>O could be observed. For the fuel rich mixtures the exhaust gas contains an appreciable amount of Syngas (CO and H<sub>2</sub>). This can be an interesting result for previously mentioned polygeneration processes as mentioned in the introduction. Further studies will focus on ignition and product gas analysis for very rich mixtures  $\phi > 4$ .

## 6 Acknowledgment

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## References

- [1] Morsy M. H. (2007). *Fuel*. 86:533-540
- [2] Semelsberger T. A., Borup R. L., Greene H. L. (2006). *J. Power Sources*. 156: 497-511
- [3] Dagaut P., Boettner J.-C., Cathonnet M. (1996). 26th Symp. Comb. 627-632
- [4] Fischer S. L., Dryer F. L., Curran H. J. (2000). *Int. J. Chem. Kinet.* 32: 713740
- [5] Curran, H. J., Fischer S. L., Dryer F. L. (2000). *Int. J. Chem. Kinet.* 32: 741759
- [6] Kaiser E. W., Wallington T. J., Hurley M. D., Platz J., Curran H. J., Pitz W. J., Westbrook C. K. (2000). *J. Phys. Chem.* 35: 8194-8206
- [7] Amano T., Dryer F. L. (1998). 27th Symp. Comb. 397-404
- [8] Wada T., Sudholt A., Pitsch H., Peters N. (2013). *Comb. Th. Mod.* 17:5
- [9] Mittal G., Chaos M., Sung C.-J., Dryer F. L. (2008). *Fuel Proc. Tech.* 89:1244-1254
- [10] Dagaut P., Daly C., Simmie J.M., Cathonnet M. (1998). 27th Symp. Comb. 3612-369
- [11] Zhao Z., Chaos M., Kazakov A., Dryer F. L. (2008). *Int. J. Chem. Kin.* 40:1-18
- [12] Cook R. D., Davidson D. F., Hanson R. K. (2009). *Proc. Comb. Inst.* 32:189-196
- [13] Oshibe H., Nakamura H., Tezuka T., Hasegawa S., Maruto K. (2010). *Comb. Flame* 157:1572-1580
- [14] Chen Z., Qin X., Ju Y., Zhao Z., Chaos M., Dryer F.L. (2007). *Proc. Comb. Inst.* 31:1215-1222
- [15] Tang C., Wei L., Zhang J., Man X. Huang Z. 2012. *Energy Fuels*. 26:6720-6728
- [16] Burke U., Somers K.P., O'Toole P., Zinner C.M., Marquet N., Bourque G., Petersen E.L., Metcalfe W.K., Serinyel Z., Curram H.J. 2014. *Comb. Flame*. in press
- [17] Werler M., Cancino L.R., Schiel R., Maas U., Schulz C. Fikri M. 2014. *Proc. Comb. Inst.* in press
- [18] Mittal G., Sung C.-J. 2007. *Comb. Sc. Tech.* 179:497530
- [19] Gao L., Li H., Chen B., Jin H., Lin R., Hong H. 2008. *Energy* 33:206-212