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Ignition studies of undiluted diethyl ether in a high-pressure shock tube

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ABSTRACT

The high ignitability of diethyl ether (DEE) reflected by a high cetane number of ~125 leads often to unintentional far-endwall ignitions in shock tubes. This is the main reason why exclusively diluted DEE experiments with attenuated reactivity can be found in the literature. The current work deals with the ignition behavior of undiluted DEE/air mixtures at engine relevant conditions. The experiments are conducted in a high-pressure shock tube (HPST) under stoichiometric conditions comprising pressures of 18 and 40 bar and temperatures from 646 – to 1058 K and 622 – to 1100 K, respectively. A recently published detailed kinetic mechanism is employed for kinetic analyses and evaluation purposes. Comprehensive kinetic studies have shown that the oxidation process of DEE behind incident shock waves can proceed significantly leading even to weak and strong far-endwall ignitions. With the aid of *x*-*t*-diagrams, each influenced experiment by far-endwall ignitions could be identified and excluded from the dataset. The valid sets of data capture the ignition trend from low to high temperatures including the negative temperature coefficient region (NTC). A new oblique scaling method is introduced together with derived formulae, which enable the scaling of experimental data in the NTC region. The experimental ignition trend at both pressures and the overall ignition delay times at 18 bar are well described by the mechanism, whereas shorter ignition delays are predicted at 40 bar.

1. Introduction

The interest in novel biofuels is motivated by the shortage of fossil resources, rising fuel prices and the growing desire for reduction of pollutants. Comprehensive experimental and kinetic studies on biofuels are crucial for the identification of their application fields and their impacts on the environment. The list of potential candidates for spark ignition engines, diesel engines and HCCI engines is long [1–10]. Although deeper insights in the oxidation chemistry of some groups have been achieved over the past years, there is still a lack of knowledge for several oxygenated fuels, which should not be regarded only as additives to fossil fuels, moreover as sustainable fuels with the capability to replace fossil fuels in future. Furthermore, oxygenated hydrocarbons play a big role in the oxidation process of almost each fuel.

Regarding diesel surrogate fuels, a high promising group is represented by the ethers with prominent physical and physicochemical features such as their high ignitability expressed by high cetane numbers, Dimethylether (DME) ~55, Diethylether (DEE) ~125 [5] and Dibutylether (DBE) ~115 [9] or rather ~100 [4] and less pollution compared to conventional diesel fuels due to its oxygenated structure [4,9,11]. While DME reveals a volumetric energy density of ~21 MJ/L [12], which is less compared to conventional diesel (~33 MJ/L [12]), the energy density of DEE with 26.9 MJ/L [7] is an additional factor making DEE more attractive as a candidate for diesel surrogate. DEE can be won by the dehydration process of alcohols [13] which in turn can be produced by lignocellulosic biomass.

DEE was used in the past as a cold start enhancer in diesel and spark ignition engines. In spite of the fact that the addition of DEE to conventional diesel fuel inhibits the ignition due to cross reactions and hence decreases the cetane number [14], a volumetric addition up to 24% does not cause any unstable operation in engines [15]. Experimental and kinetic studies for DEE oxidation were done by several researchers. Salooja [16] was interested in finding the reason of the high reactivity of DEE and concluded that during the oxidation of DEE acetaldehyde formation leads to the high reactivity, while on the contrary, the oxidation with longer chained ethers produces higher aldehydes with less reactivity. Tommaso et al. [17] was engaged in the exploration of hazardous intermediates during DEE autoxidation employing density function theory calculations and linked the industrial hazards with hydroperoxide formation during the chain propagation step. Orlando [18] examined the formation of 1-ethoxyethoxy radical by C1 (next to the oxygen)

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atom-initiated oxidation of DEE. Griffiths and Inomata [19] examined the cool flames of DEE in a jet stirred flow reactor in order to understand the low temperature oxidation of DEE. Yasunaga et al. [20] studied along with kinetic modeling the pyrolysis and oxidation of DEE in a shock tube at 1–4 atm between 900 and 1900 K. Recently, Werler et al. [21] conducted high pressure shock tube experiments with highly diluted DEE/O_2/Ar mixtures at 10, 20 and 40 bar in a temperature range of 900 to 1300 K at an equivalence ratio of 1. In the same work, a rapid compression machine came into operation in the range of 2.5 to 13 bar for different DEE mixtures: DEE/O_2/N_2/CO_2 at 13 bar for temperatures between 500 and 590 K ($\phi = 1$), DEE/air at 2.5–5.5 bar for temperatures between 590 and 850 K ($\phi = 0.5$, 1 and 2), DEE/O2/Ar at 10 bar for temperatures between 850 and 1060 K ($\phi = 1$). Summarizing the work of Werler et al. [21], their DEE experiments are diluted in the pressure and temperature range of engine relevance.

For the first time, this work deals with undiluted DEE/air mixtures at high pressures and low to high temperatures comprising ranges of 646–1058 K (18 bar) and 622–1100 K (40 bar). These conditions including the negative temperature coefficient (NTC) region are ideal for describing the fuel behavior in real engines. This work also demonstrates that even high cetane number fuels without dilution can be measured in conventional shock tubes. Kinetic analyses including the oxidation behind incident shock waves clarify the near-endwall and far-endwall oxidation of highly reactive fuels. The experimental results of DEE/air mixtures are compared to the predictions of the detailed kinetic mechanism of Sakai et al [22], which is based on quantum mechanical predicted reaction rates including both, the high and low temperature oxidation pathways.

2. Experimental facility

The measurements of ignition delay times for undiluted DEE/air mixtures were performed behind reflected shock waves generated in a high-pressure shock tube (HPST). As the HPST is described in detail in [23], the following section will give only a brief description of the facility and the measuring techniques.

With an inner diameter of 140 mm, a total length of 15.5 m and the capability to withstand pressures of about 950 bar at initially heated conditions of 200 °C, the HPST is optimally suited for chemical ignition delay time measurements of undiluted fuels as well as low vapour pressure fuels. A double diaphragm chamber divides the high-pressure driver section from the 11 m low-pressure driven section by two aluminium diaphragms. The diaphragms used for the investigations in this work were of either 4 mm or 6 mm thickness, depending on the desired reflected shock conditions, and are scored to aid breaking as well as to define the predetermined breaking point. The long sections along with the large inner diameter allow test times more than 6 ms for non-tailored experiments and exhibit less physical influence on the ignition process compared to shock tubes with smaller diameters [23,24]. In real shock tube processes, the pressure and temperature behind reflected shock waves increase with time due to shock attenuation of the incident shock wave, which in turn is caused by boundary layer effects and non-ideal bursting of diaphragms [25–30]. The shock attenuation is inversely related to the initial filling pressure p_1 of the shock tube. The filling pressure p_1 increases generally when higher pressures behind the reflected shock wave p_5 are desired. Therefore, high pressure experiments (high p_5) exhibit less shock attenuation and hence less pressure-increase behind the reflected shock wave compared to low pressure experiments. The resulting pressure-increase behind the reflected shock wave is specified for each experiment in the units of $[dp^*/dt] = \%/\text{ms}$ (* related to the post-reflected shock pressure p_5 at time-zero).

The preparation of the stoichiometric fuel/air mixtures was realized directly in the evacuated ($< 2 \times 10^{-5}$ bar) low pressure section of the shock tube. The partial pressures were monitored and checked during and after the filling process. The experiments were conducted at least one hour after filling to ensure the homogenization of the mixture. In order to capture the pressure histories, the shock velocities as well as the beginning of the ignitions, seven piezoelectric sensors (Kistler 603B) and a photomultiplier (Hamamatsu, RR212UH) were utilized in the low-pressure section. A layer of high temperature silicone was shielded on each pressure sensor to protect them from heat loads of the shock heated gas. The amount of the pressure sensors and their positions relative to the endwall (EW) were as follows: 1 × 0 mm (EW), 2 × 10 mm, 1 × 260 mm, 1 × 510 mm, 1 × 760 mm and 1 × 1010 mm. The photomultiplier was equipped with a narrow band pass filter (LOT 430FS10, FWHM 10 ± 2 nm) to capture the CH* emission at the 10 mm location. The gas temperature behind the reflected shock is calculated with the in-house code KASIMIR [31] taking the initial conditions and the shock velocity as input. The ignition delay times were determined from pressure signals acquired either from the EW-sensor or the 10 mm-sensor, depending on the ignition location. The comparison to the largest slopes of the emission signals has shown a deviation of less than 2.5% between both detection methods. The uncertainties in the experimental temperatures are in the range of ±0.9% regarding the measurement uncertainties.

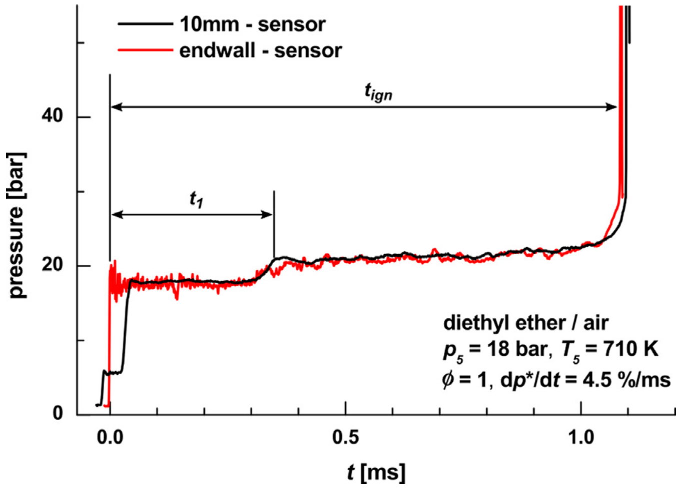

Fig. 1. Definition of ignition delay times in case of a 2-stage ignition. The first rise of the endwall-signal (red line at 0.0 ms) is declared here as the start time as the ignition takes place nearer to the endwall sensor. The first and final stage of ignition are represented by t_1 and t_{ign}, respectively. The pressure increase due to shock attenuation is given in the units of %/ms (see text for more information). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results

DEE from Carl Roth with a purity of ≥ 99.5% and synthetic air of Westfalen (20.5% O_2, 79.5% N_2) with a purity of 99.99% have been used for investigations of ignition delay times at post-reflected shock conditions of 18 and 40 bar in a temperature range of 646–1058 K and 622–1100 K, respectively. The measurements were taken at an equivalence ratio of 1 in the initially heated shock tube ($T_1 = 313 - 323$ K). The ignition delay times illustrated in this work are defined as t_{ign}. As each valid experiment at 18 and 40 bar was detected by the endwall sensor first, t_{ign} is the time difference between the arrival of the incident shock wave at the endwall and the steepest rise of the endwall signal. Figure 1 illustrates the ignition of DEE/air in the intermediate temperature region. The pressure traces of the endwall- and 10 mm sensor indicate a 2-stage ignition. In such cases, the first stage of ignition is defined as t_1