

Shock-tube study of the ignition of fuel-rich CH₄/ozone/air and natural gas/ozone/air mixtures at high pressure

Jürgen Herzler, Mustapha Fikri, Christof Schulz
Institute for Combustion and Gas Dynamics – Reactive Fluids
University of Duisburg-Essen,
Duisburg, Germany

1 Introduction

Flexibility between conversion and storage of energy will be an important aspect in future energy systems due to the fluctuating availability of renewable energies. In times of low demand but high availability of energy, external mechanical (i.e., converted electrical) energy can be used in internal combustion engines (ICEs) to convert “inexpensive” chemicals (e.g., natural gas) into higher-value chemicals so that most of the exergy of the inexpensive fuels is stored [1]. This production of chemicals typically proceeds at very fuel-rich conditions, far away from the conventional operating regimes of ICEs. Fundamental understanding of the chemical kinetics and the availability of validated reaction mechanisms for these fuel-rich conditions are essential for the successful development and optimization of such processes. However, most of the reaction mechanisms were validated preferentially for lean and stoichiometric mixtures, because these conditions are typical for ICEs and gas turbines. Natural gas is relatively cheap and its composition strongly depends on its source. It can consist almost entirely of methane (e.g., 98.3 mol% methane, 0.52 mol% ethane, 0.21 mol% propane (Russia 2)) or contain large amounts of higher hydrocarbons (8.90 mol% ethane, 2.70 mol%, propane (San Joaquin, California)) [2]. We investigate pure methane to mimic natural gas with low content of higher hydrocarbons and a natural gas surrogate with 90 % methane, 9 % ethane, and 1 % propane as a model fuel for natural gas with a large content of higher hydrocarbons. Combustion Studies of methane or natural gas/additive/air mixtures at $\phi = 2$ showed synthesis gas as main product whereas only minor quantities of higher hydrocarbons were found [3, 4]. To shift the product formation from synthesis gas to higher hydrocarbons, more fuel-rich conditions must be used. Equivalence ratios up to $\phi = 10$ must be used to limit the reaction temperature and thus avoid soot formation. The heat release at $\phi = 10$ is so low, that the temperature increase after ignition is about 450 K. The final temperature is significantly below the low-temperature onset of soot formation [5]. Energy storage and production of higher-value chemicals in ICEs can be achieved by compressing methane/argon mixtures [6]. Methane concentrations of less than 20 % and an inert gas with low heat capacity such as argon must be used to achieve the high compression temperatures necessary to initiate the endothermic methane pyrolysis [6] that then leads to the formation of species with higher enthalpy of formation. This process has also been studied in shock tubes with time-resolved infrared-laser absorption measurements of the methane concentration and the

temperature, and GC/MS concentration measurements after fast sampling during/after the cooling phase at ~ 2 and ~ 30 bar [7].

The reactivity of neat methane is quite low so that high compression temperatures are required for ignition in homogeneous-charge compression ignition (HCCI) engines with conventional compression ratios so that a preheating of the reactants is necessary. Alternatively, more reactive additives such as n-heptane or ethers (dimethyl ether, DME; diethyl ether, DEE; dimethoxy methane, DMM) [8-10] can reduce the ignition temperature. The influence of all these additives on the low-temperature ignition of methane was studied in shock tubes at engine relevant conditions [8-10]. These studies [8-10] and measurements in an ICE [11] showed that relatively high additive concentrations of up to 10 vol% are necessary for a stable operation of the ICE in the HCCI mode. To avoid the high costs of these additives, adding ozone as ignition promotor provides a potential alternative. Ozone can be produced on-line at low costs with an ozone generator. First experiments in an ICE showed that half of the DME could be replaced by low amounts of ozone [12]. To further optimize the use of ozone as additive, a mechanistic understanding of its influence on the ignition of methane is required. Therefore, the ignition of methane/air mixtures with ozone as additive was studied at engine-relevant conditions and the experimental results were compared to simulations to validate a reaction mechanism. This reaction mechanism is an essential input for a model-based optimization of the use of ozone as additive in ICEs at fuel-rich conditions.

2 Experimental setup

A high-pressure shock tube with a constant inner diameter of 90 mm and lengths of the driver and driven sections of 6.4 and 6.1 m, respectively, was used for ignition delay time (IDT) measurements. The maximum test time is extended up to 15 ms by driver-gas tailoring with helium as the main driver gas and Ar addition to match the acoustic impedance of the driver gas and the test gas. The driver gas was mixed *in situ* by using two high-pressure mass flow controllers (Bronkhorst Hi-Tec flowmeter F-136AI-FZD-55-V and F-123MIFZD-55-V). The driver gas composition depends on the test gas mixture and the Mach number and was calculated prior to the experiment using formulas by Oertel [13] and Palmer and Knox [14]. Mixtures of the fuel with nitrogen were prepared manometrically in a mixing vessel and stirred for at least one hour. The experiment is described in more detail in Ref. [15]. The temperature T_5 and pressure p_5 behind the reflected shock waves were computed from the incident shock velocity using a one-dimensional shock-wave model. The shock-wave velocity was measured over three intervals using four piezoelectric pressure transducers (PCB 112-B05) and the related temperature uncertainty of ± 15 K was determined by the method of Petersen et al. [16] considering the uncertainty of the position of the pressure transducer, the time when the incident shock wave passes the pressure transducer, and the error caused by the interpolation of the incident shock-wave speed to the end flange. The determined error represents an average value for the temperature range of our measurements. Band-pass-filtered (308 ± 5 , 431 ± 5 nm) emission from OH* and CH* chemiluminescence was monitored through windows in the sidewall 15 mm from the end flange with Hamamatsu 1P28 photomultipliers. The pressure was recorded at the same position using a piezoelectric pressure transducer (PCB-112B05) that was shielded with a thin high-temperature silicone layer. Ignition delay times were defined as the interval between the rise in pressure due to the arrival of the reflected shock wave at the measurement port and the extrapolation of the steepest increase in emission to its zero level on the time axis. The uncertainty of the determination of ignition delay times from the chemiluminescence profiles is about ± 10 μ s for IDTs < 100 μ s, ± 30 μ s for IDTs of about 1000 μ s and ± 100 μ s for IDTs around 10 ms. These values were determined considering the uncertainties of the extrapolation of the steepest increase of the measured chemiluminescence intensity and the uncertainties of the blast-wave correction [17].

Fuel/oxygen/ozone/nitrogen mixtures could not be prepared and mixed in the high-pressure mixing vessel due to the fast decreasing ozone concentrations in these mixtures. Therefore, we prepared these mixtures *in situ* in the shock tube. We used a separate 3-l vessel to prepare O₃/O₂ mixtures. A 1-bar

O_3/O_2 mixture was produced with an ozone generator (Innotec OGuA-5000MG) and filled up with O_2 to 6 bar. After waiting for 30 min, the fuel/ N_2 mixture and the O_3/O_2 mixture were filled into the shock tube through a valve in the end flange (Parker Hannifin Pulse Valve Series 9 with IOTA ONE[®] driver) with two mass flow controller (MKS GE50 A (5 slm Ar) for fuel/ N_2 and Brooks SLA5850 (PTFE sealed, 2 slm N_2) for O_2/O_3). The ozone concentration in the shock tube was measured with a silicon hollow-cathode lamp, a 253.7 nm bandpass filter (FWHM = 10 nm) and a Hamamatsu 1P28 photomultiplier. The decrease of the ozone concentration was less than 0.3% / min. An absorption coefficient of $1.13 \times 10^{17} \text{ cm}^{-2}$ [18] was used for the determination of the ozone concentration. A value of 600 ± 50 ppm was found as ozone concentration in the different experiments. The scheme of the experimental setup is shown in Fig. 1.

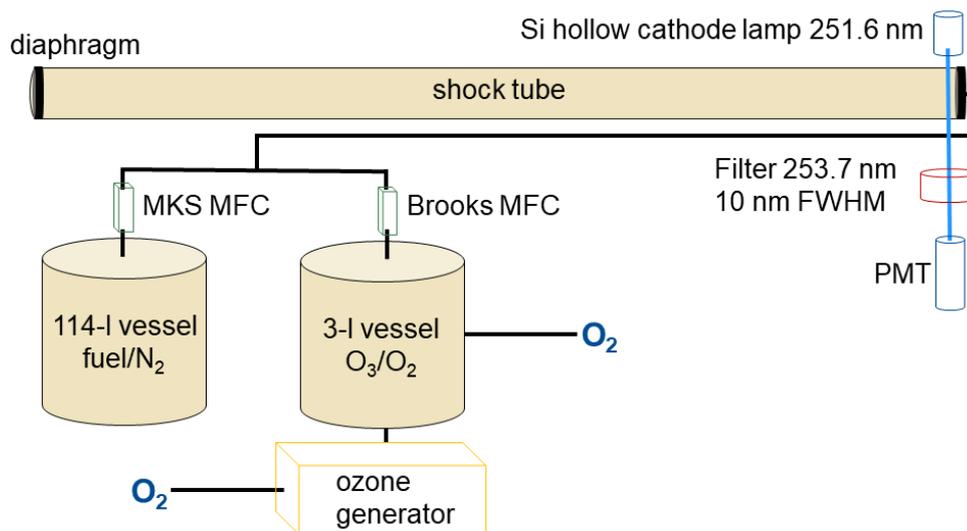


Figure 1: Scheme of the experimental setup.

3 Results and discussion

The ignition delay times of methane/ and natural gas surrogate/ozone/air were measured at fuel-rich conditions ($\phi = 2$) and pressures of about 30 bar in a high-pressure shock tube. The results were compared to simulations with the AramcoMech 3.0 [19] complemented by ozone reactions of Zhao et al. [20]. Ignition delay times were simulated with Chemical Workbench 4.1.18493[®] [21] using the conP approach (adiabatic isentropic compression or expansion) based on predefined pressure profiles that are derived from experiments with non-reactive test-gas mixtures. A profile with a pressure increase of 2 %/ms for the initial 2.8 ms followed by a constant pressure was used.

The measured ignition delay times for the methane mixture with 600 ppm ozone are shown in Fig. 2 in comparison with data of pure methane/air [9]. At temperatures below 1100 K, a significant decrease of the ignition delay times by the addition of ozone can be observed whereas the effect of ozone at higher temperatures is negligible. The influence of ozone at $T < 1100$ K is increasing with decreasing temperatures. The experimental values agree well with the simulations with and without ozone addition. The mechanism reproduces very well the influence of ozone addition.

Experimental results of the natural gas mixture with 600 ppm ozone in comparison with data of natural gas/air [4] are presented in Fig. 3. The influence of ozone is identical with the methane experiments. The mechanism predicts very well the measured ignition delay times and the influence of ozone.

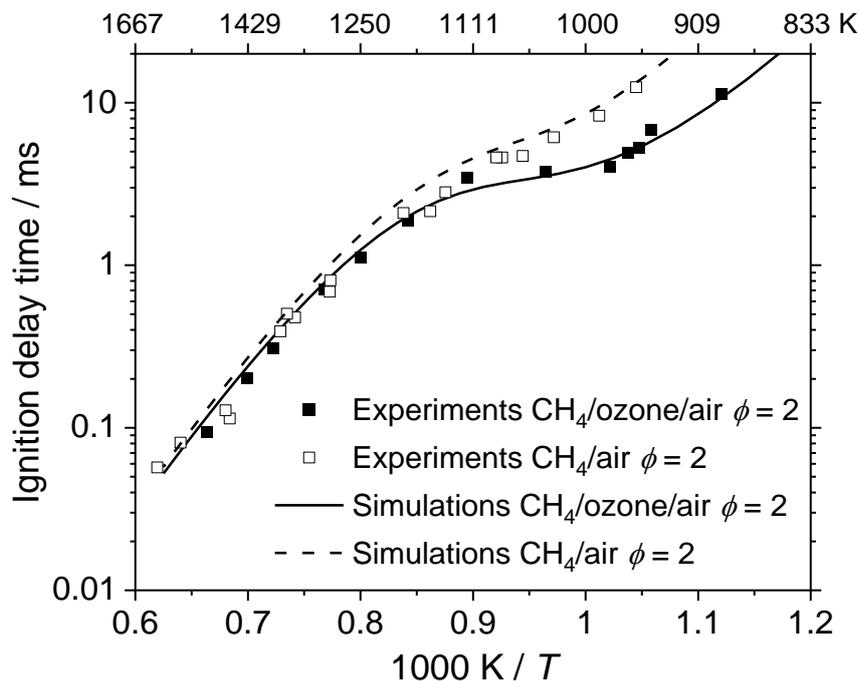


Figure 2: Measured and simulated ignition delay times of methane/(600 ppm ozone)/air mixtures at $\phi = 2$ and 30 bar. Data of methane are taken from an earlier study [9].

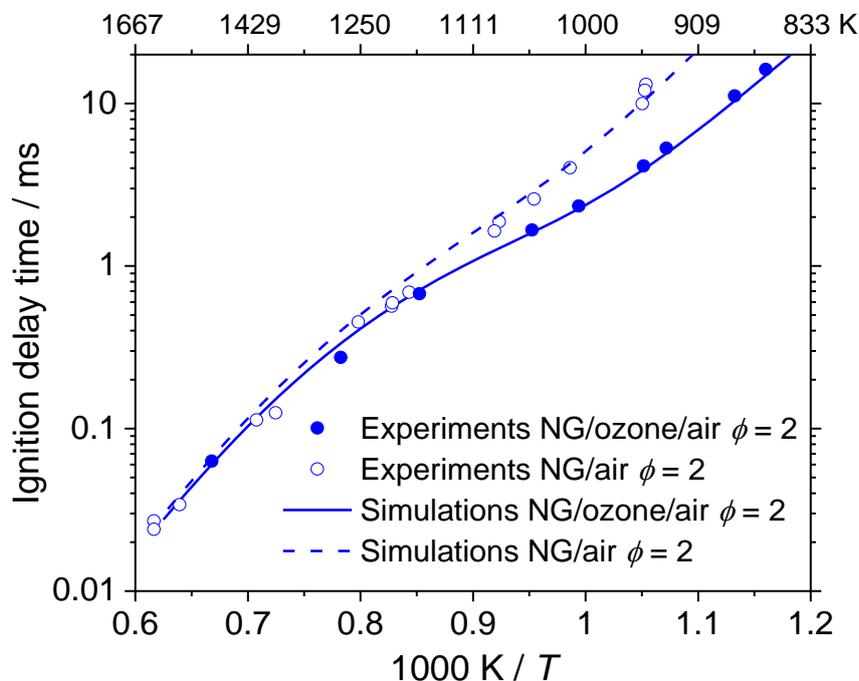


Figure 3: Measured and simulated ignition delay times of natural gas (NG, 90 vol% CH₄, 9 vol% C₂H₆, 1 vol% C₃H₈)/(600 ppm ozone)/air mixtures at $\phi = 2$ and 30 bar. Data of natural gas are taken from an earlier study [4].

4 Conclusions

The influence of ozone on the ignition delay times of methane and natural gas was determined in a high-pressure shock tube at fuel-rich conditions ($\phi = 2$) and pressures of about 30 bar. The measured ignition delay times agree very well with simulations using the AramcoMech 3.0 [19] complemented by ozone reactions of Zhao et al. [20]. A strong decrease of the ignition delay times was observed for temperatures below 1100 K. The influence of 600 ppm ozone was similar to the influence of 7000 ppm of other additives (n-heptane, dimethyl ether, diethyl ether, dimethoxymethane) [4, 8-10]. The results are important to develop and optimize polygeneration concepts in an ICE [1] and show that relative expensive additives like ethers can be replaced by on-line produced ozone at lower costs. Further ignition delay and product measurement studies at $\phi = 10$ with ozone as additive will be performed to investigate if ozone can also replace other additives at these fuel rich conditions which are important for the production of higher hydrocarbons whereas at $\phi = 2$ mostly synthesis gas (CO, H₂) is formed.

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