# Influence of Methane Additions on Self-Ignition of Pulsed Jet of Hydrogen

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## 1 Introduction

One of type of self-ignition of gases is a spontaneous self-ignition of compressed hydrogen or another combustible gas at a pulse discharge from a vessel under high pressure into air. At this release a shock wave is formed in air which heats air to a temperature more than one thousand degrees . The experimental and numerical minimum values of the pressures and temperatures which cause the ignition of hydrogen are presented in [1-3]. The actions of obstacles, channel cross-section and channel length are presented in [4]. The kinetic mechanisms of the ignition of hydrogen with different boundary conditions are given by [5]. The ignition delays for the non-premixed mixtures were measured experimentally in [6], and numerically in [7].

The fact that the ignition delay of hydrogen can reach values of 23 [10] μs certainly suggests that the storage and operation of compressed hydrogen can be highly explosive, even when there are no external ignition sources. One method to increase the ignition delay of hydrogen is by using an admixture of other combustible gases. Wherein, the ignition delay of a binary mixture is several times higher than the delay of ignition of pure hydrogen. In the paper methane was used as the admixture. The values of the ignition delays for preliminary premixed hydrogen-methane mixtures behind the shock wave can be found in [8,9].

The aim of the present paper is the experimental determination of the ignition delays of the pulse jet of a binary mixture of hydrogen with methane for the different initial pressures of the hydrogen-methane mixture.

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## 2 Experimental technique. Mixture

For producing of the spontaneous discharge of hydrogen into the channel, rupture of the diaphragm between the chamber and channel was used. Figure 1 shows the schematic of the experimental set-up, organized according to the principle of a shock tube. The methodology is described in detail in [10]. The length of the channel was 185 mm, the distance from the diaphragm to the pressure gauge in the channel was 135 mm, and the internal diameter of the channel was 5 mm.

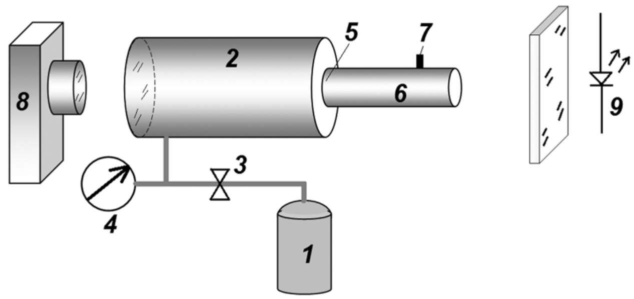


Figure 1. Schematic of experimental set-up. 1: compressed binary mixture; 2: high pressure chamber (initial pressure $P_4$); 3: regulating vent; 4: manometer; 5: diaphragm; 6: open channel (initial pressure $P_1$); 7: piezoelectric pressure transducers; 8: photomultiplier tube; 9: light diode

A photomultiplier tube 18A (PMT) (8) and light diode (LED) (9) arranged along the axis of the channel were used to register the initial moment of rupture of the diaphragm and to register the moment of ignition. The light diode created a light, directed along the axis of the channel. At the closed end of the chamber a transparent window and photomultiplier tube were installed. The moment of opening the diaphragm was registered by the intensity of light passing through the diaphragm. After the disclosure of the diaphragm the PMT registers the hydrogen self-ignition in any location along the channel. PMT registers the fact of the self-ignition and ignition delay relative to the rupture.

The diaphragms were made of aluminium of different thicknesses and depths of incision to provide a wide range of initial pressures. The thicknesses of the diaphragms were changed from 0.10 to 1.00 mm. The error of the determination of the initial pressure of hydrogen was 0.05 MPa. For registration of the shock waves, piezoelectric pressure transducers PCB 113A (7) were used, located in the channel. Additionally, the pressure transducer was used for triggering of the digital oscilloscope 100 MHz Tektronix TDS3014B. The hydrogen-methane mixture was prepared by partial pressures in a 40 litre vessel. The total pressure did not exceed 15 MPa. Molar fraction of methane in hydrogen-methane binary mixture was varied from 0 to 18%.

## 3 Experimental results. Ignition delay

Figure 2 (*left*) shows readings of pressure transducer and photomultiplier tube with light diode backlight relative to a laboratory time. Data are given for the mixture of hydrogen with 14% (mol.) of methane at an initial pressure of 10–11 MPa. The oscilloscope was triggered by the pressure transducer at the moment $t_{Tr}$. Prior to the rupture of the diaphragm (time interval *I*), the voltage at the output of the photomultiplier tube is zero. Immediately after the rupture of the diaphragm, the photomultiplier tube detects a light flow along the axis of the channel and high-pressure chamber (time interval *II*). The sequence of discrete signals is caused by the excessively high sensitivity of the photomultiplier tube. After the ignition the emission intensity is sufficient for the signal to be “smooth” (time interval *III*). In this paper, the ignition delay is determined relative to the initial moment of the rupture of the diaphragm $t_R$. After a certain duration $\tau$ after the rupture, the photomultiplier tube detects a more intense glow of the hydrogen-methane mixture inside the channel, caused by the ignition of the mixture (time interval *III*). Presented ignition delay $\tau$ for this case is 130 μs.

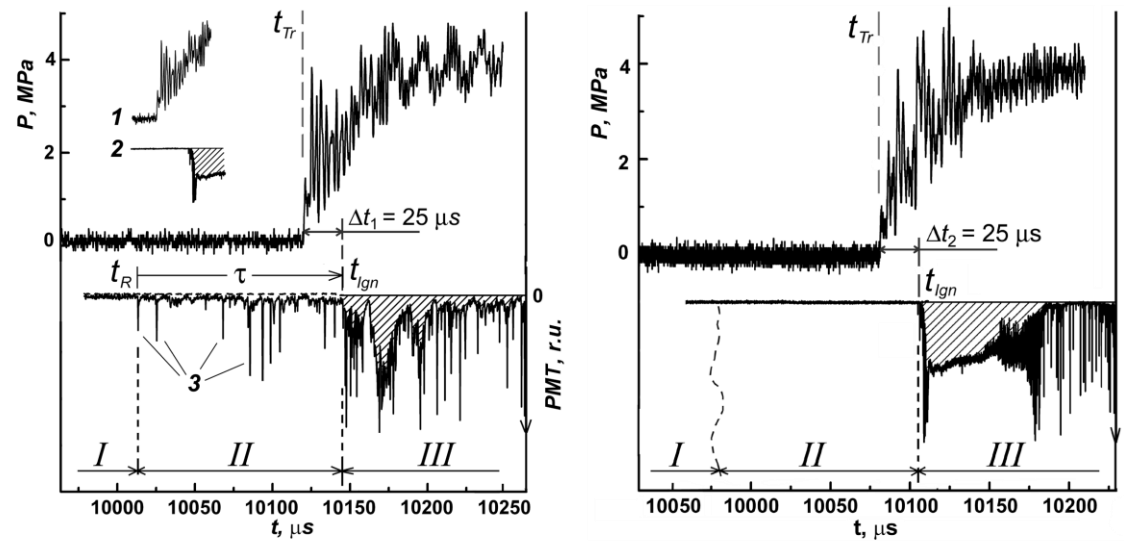


Figure 2. Readings of pressure transducer (1), and photomultiplier tube (2) with (left) and without (right) light diode. 3: non-linear photomultiplier responses caused by a large nominal voltages; $t_{Tr}$: trigger moment; $t_R$: rupture moment; $t_{Ign}$: ignition moment; $\tau$: ignition delay; $\Delta t_1 = \Delta t_2$: test phase difference. Time intervals: *I*: before rupture of the diaphragm; *II*: just after the rupture of the diaphragm; *III*: after the self-ignition in the channel

Figure 2 (*right*) shows readings of pressure transducer, photodiode and photomultiplier tube without light diode backlight. Data are given for the same binary mixture and initial pressure. The oscilloscope was triggered by the pressure transducer (time moment $t_{Tr}$). In the absence of the diode lighting the photomultiplier tube is not able to register the moment of breaking of the diaphragm. Therefore, during the time interval *I-II* photomultiplier detects no light emission. However, starting from the time moment $t_{Ign}$ the photomultiplier tube detects the ignition of the binary mixture inside the channel (time interval *III*). The experiments without external light diode were carried out solely to confirm the reliability of the ignition of the pulse jet and the phase difference $\Delta t$ between the registration of the shock wave (by PCB113) and the moment of ignition (by photomultiplier tube). As shown in the Figure 2, these phases are equal to each other: $\Delta t_1 = \Delta t_2 = 25$ μs. The ignition delays were determined only with using the external light diode.

## 4 Summary of graphs and discussion

Ignition delays were determined for the different initial pressure of the hydrogen- methane mixture. Figure 3 shows the experimental data obtained. As can be seen from the figure, the addition of methane increases the ignition delay of the binary mixture. Adding 18% (mol.) of methane leads to a 6-fold increase of ignition delays.

Figure 4 shows the dependence of the ignition delay on the methane concentration in the range of initial pressures of 8.2-8.5 MPa. This range was chosen because it covers the measured and interpolated values for all five concentrations of methane (see Figure 3, vertical line *II*). Error displays statistical dispersion values.

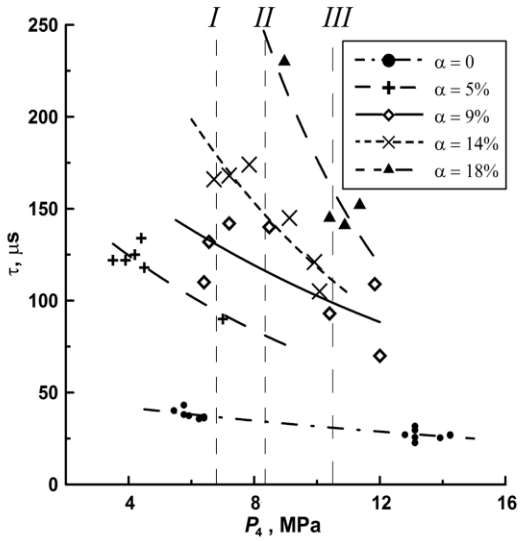


Figure 3. Dependences of ignition delays $\tau$ of binary hydrogen-methane mixture on initial pressure $P_4$ for different molar fraction of methane $\alpha$. *I,II,III*: markers for initial pressure 6.8, 8.35 and 10.5 MPa.

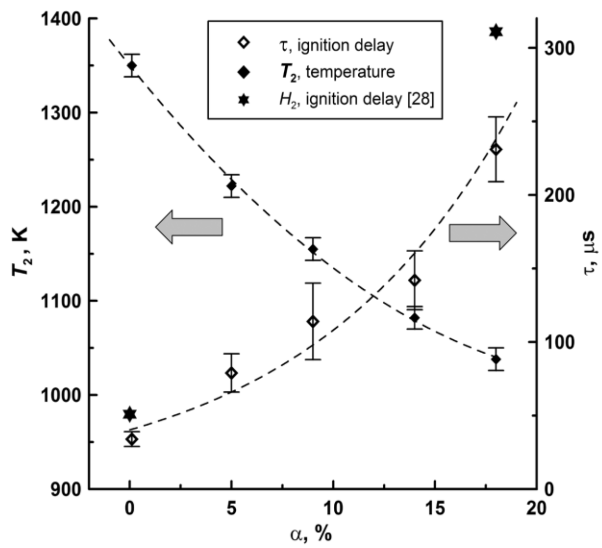


Figure 4. Dependences of ignition delay $\tau$ (experiment) and temperature $T_2$ behind the shock wave (evaluation) on molar fraction of methane $\alpha$ for initial pressure 8.2-8.5 MPa

Increasing the ignition delay of the binary mixture with the concentration of methane is caused by a change in the kinetic mechanism and thermodynamics. Addition of methane results in increase in the density of the pushing binary gas. It leads to decrease the Mach number of the generated shock wave and to decrease the temperature behind the shock wave. For each binary mixture, i.e. for each value of the methane concentration, it is possible to estimate the temperature $T_2$ behind the shock front. It can be easily evaluated by using equations of gas-dynamics for the one-dimensional moving shock wave. Within the range of initial pressures 8.2-8.6 MPa the average calculated Mach numbers was equaled to: 4.26-4.30 (0%, mol., methane concentrations); 4.00-4.03 (5%); 3.85-3.89 (9%); 3.69-3.72 (14%); 3.59-3.62 (18%). For pointed Mach numbers the temperature behind the shock front was determined and shown in Figure 4.

Figure 5 shows the dependence of the ignition delay on the temperature behind the shock front. Within experimental error data can be interpolated by a straight line by least squares in the temperature range $8*10^4$-$10*10^4$ $K^{-1}$. Figure 5 shows as well the results for initial pressure ranges 6.4-7.2 MPa and 10.1-10.9 MPa. The pressure ranges are presented on Figure 4 by vertical lines *I*, *III*. Within experimental error data can be interpolated by a straight line by least squares in the temperature ranges $8*10^4$-$10*10^4$ $K^{-1}$ (6.4-7.2 MPa) and $8.5*10^4$-$10.5*10^4$ $K^{-1}$ (10.1-10.9 MPa). The discontinuity in linear relationship in Figure 5 can be caused by a change in temperature regime, as was also shown in [8].

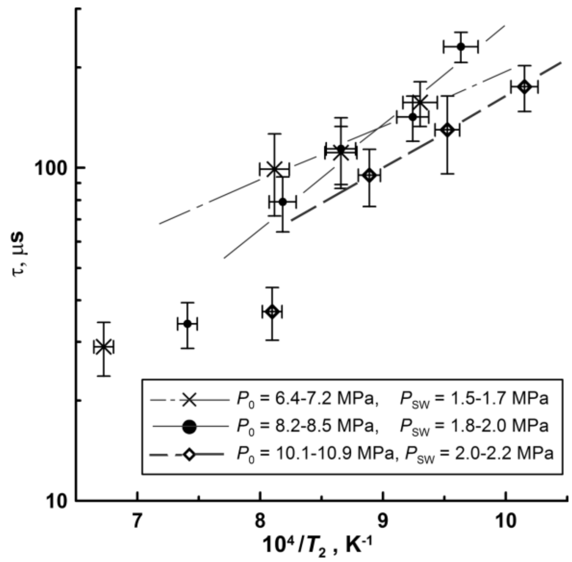


Figure 5. Dependences of ignition delays $\tau$ in the binary mixture on the temperature $T_2$ behind the shock wave. $P_4$: initial pressure; $P_{SW}$: shock wave pressure

As shown in the figure 5, the discontinuity was registered in the inverse temperature range $8.0*10^4$-$8.5*10^4$ $K^{-1}$. In some degree, this corresponds to "combined chemistry of methane and hydrogen dominant ignition" [8]. However, characteristic values of the ignition delays are in the range of 30-300 μs, which is several times smaller than presented in [8].

Despite the fact that under the same thermodynamic conditions and concentrations of oxygen (air) the ignition delays separately of hydrogen or methane may vary by three orders [8] (0.1-0.3 MPa), the combustion of the binary mixture should be considered taking into account the kinetics of both components simultaneously. As has been shown in [8] the main inhibition channels by methane $CH_4$ can be the interaction with the radicals OH, O and H, as well as the interaction of radicals $CH_3$ with each other and with $HO_2$. At the same time, the promotion channels are the interaction of $CH_3$ with O, $HO_2$, OH and $H_2O_2$.

## 5 Conclusion

Storage and using of the compressed hydrogen is very dangerous due to the high possibility of the ignition of the pulse jet formed during the rupture of the vessel or the valve action. However, the addition of methane may increase the ignition delay for the binary mixture of hydrogen and methane, and may reduce the risk of the ignition. Ignition delays of self-ignition of the binary mixture of hydrogen and methane were determined experimentally for the initial pressure range 3-15 MPa and concentration of methane range 0-18% (mol.). It was shown, that the adding of 18% (mol.) of methane leads to a 6-fold increase of ignition delays. Estimation with using the quasi-one dimensional equations of gas-dynamics showed that the addition of methane reduces the temperature behind the incident shock wave. For 18% (mol.) of methane the decrease was about 300 K. However, the change in the ignition delay can be caused not only by reducing the temperature, but also the participation of methane in the combustion chemical mechanism.

## 6 Acknowledgements

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