Critical Conditions for Flame Acceleration and DDT for Hydrogen-Air Mixtures at Cryogenic Temperatures

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1 Introduction

Within the flammability limits, three principal combustion regimes can be distinguished for gaseous mixtures relatively the speed of sound: (1) slow subsonic deflagrations; (2) fast sonic and supersonic flames; (3) detonations. As suggested in [1-2], the critical expansion rate σ* and 7λ - criteria can be used as potentials for strong flame acceleration to speed of sound and to detonation onset. Mixtures with expansion rate σ above the critical value σ* can effectively accelerate to the speed of sound and then detonate, if the detonation criteria L > 7λ is satisfied (L is the characteristic size of the combustible domain; λ is the detonation cell size). The mixtures with σ < σ* cannot accelerate to the speed of sound and only subsonic combustion regimes may occur.

The critical expansion ratio σ* is a function of dimensionless integral scale as Peclet number Pe = L_T/δ (L_T - turbulent length scale, δ -laminar flame thickness) and Zeldovich number β (β = $E_a(T_b-T_u)/T_b^2$). The critical Peclet number Pe > 100 was experimentally found to be required for the strong flame acceleration and to exclude a local flame extinction due to heat losses [1]. The Peclet number lower than 100 may result in critical expansion ratio increase. Since adiabatic combustion temperature T_b is almost independent of the initial temperature, the critical expansion ratio is only a function of the energy activation E_a and temperature T_u [1]:

$$\sigma^* = 9.0\cdot10^{-6}x^3 - 0.0019x^2 + 0.1807x + .2314$$

where $x=E_a/RT_u$. Assuming a constant activation energy E_a=7500K for hydrogen-air mixtures in wide range of temperatures and concentrations, an extrapolation to cryogenic temperature T = 100K gives the values of the critical expansion ratio σ* = 6.9 which corresponds to 7-8%H2 in air. Direct extrapolation of experimental data on critical expansion ratio at elevated temperatures [1] to cryogenic temperature T = 100K without an effect of the energy activation gives the value σ* = 8.5 (9.6% H_2). Nevertheless, both correlations are far beyond the known experimental range of initial temperatures and it needs an additional research of flame acceleration conditions at cryogenic temperatures.

Independent of initial temperature, the detonations may only occur if the flame reaches the speed of sound. The dependence of run-up-distance to sonic deflagration or detonation can be calculated according to papers [1-4]. The dependence is based on papers [3-4] and uses the formula that takes into

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account the roughness or blockage of the channel and chemical reactivity of the mixture [4]. For instance, a simplified rough value for run-up distance to detonation in a smooth channel sounds as X_D=500λ [3]. Then, the critical condition for detonation onset when the characteristic size of the channel L > 7λ for an obstructed channel should be satisfied [2]. In particular, the condition L >7λ can be transformed to d > λ for BR=0.3 and d > 3λ for BR=0.6 [5-6]. The critical condition for detonation onset in a smooth channel is d > λ/π, where characteristic size d is the tube diameter. If one of the abovementioned detonation conditions is not satisfied, a sonic deflagration in an obstructed tube can be stabilized as a chocked flame that propagates with the speed of sound in combustion products [1-4].

Such conditions for detonation onset work well for different mixtures in wide range of initial temperatures. The only problem is the lack of experimental data on detonation cell size at cryogenic and reduced (lower than the ambient) temperatures in mixtures containing the hydrogen. The only one reference is known regarding the cryogenic temperature conditions [7] that gives detonation cell sizes for stoichiometric hydrogen oxygen mixture at T = 123K and different initial pressures. In general, in accordance with experimental data [8-10] the detonation cell size is increasing with temperature decrease. These referred data cover relatively narrow range of temperatures (278-373K) for hydrogen-air mixture with ϕ = 0.5.

A semi-empirical code CELL_H2 for accurate detonation cell size predictions at different temperatures and pressures can be used [11]. The code CELL_H2 uses detail chemical kinetics and takes into account multidimensional detonation cell structure. The code is verified in wide range of elevated pressures and temperatures and mixture compositions. For instance, the calculations with CELL_H2 fit well to experimental data [8-10] within the temperature range T = 278-373K. The problem is to apply the CELL_H2 code below 200 K due to the lack of available thermodynamic and kinetic data. Because of very far extrapolation beyond the verification range we strongly need additional experimental data on detonation cell sizes at cryogenic temperatures.

The objective of current work is to evaluate the critical conditions for flame acceleration (FA) and detonation transition (DT) for hydrogen-air mixtures at cryogenic temperatures. The data are required for safety analysis to evaluate the strongest possible combustion pressure and safety distances in case of liquid hydrogen (LH2) explosions.

2 Experimental Details

A series of experiments on flame acceleration and DDT at 1 bar of initial pressure and different temperatures from T =90K to ambient temperature T = 293 K has been conducted. The facility consists of a stainless steel tube of 5-m long with an outer diameter of 73 mm and an inner diameter of 54 mm. To provide the cryogenic temperatures, the tube was exposed in a metal basin filled with liquid nitrogen (LN2). The tube and the basin were supported by metal frame structure (Figure 1). A basin made of stainless steel insulated with Styrofoam providing the cooling. The cooling degree was controlled by varying amount of LN_2.

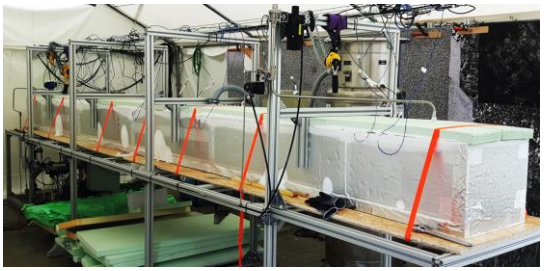

Figure 1. Cryo-shock tube inside a bath of LN2 with supporting structure.

The experimental procedure was different for ambient and cryogenic initial temperatures. Only the Cryo valves are exposed to LN_2 prior to the cryogenic experiments. All other valves and devices are at ambient temperature. All valves have pneumatic actuators. To extract water, the tube was first purged with dry compressed N_2. Then, the tube was evacuated down to < 1 mbar. The bath was filled with liquid N2. The temperature of the tube wall was controlled at 3 outside points along the tube with thermocouples clamped to the wall. A test mixture was prepared with 2 Mass Flow Controllers (MFC, Bronkhorst), one for H2 and another for synthetic air (N2+O2). The mixture was flowed through a pipeline loop below the LN2 level to cool the mixture down before entering the tube. Then, the mixture was kept flowing through the tube until the concentration at the outlet reached a required value. When the gas temperature inside were stabilized, all the valves were closed to be ready for the test. Finally, the mixture was ignited triggering the data acquisition. A standard automotive spark plug was used for ignition. The number of repetitions was limited, because the cooled tube acts as a cold trap. It was nearly impossible to remove the condensed combustion products by pumping them at temperatures below 183 K. Then, we needed to heat the tube up to ambient temperature to remove condensed water/ice.

The experiments on hydrogen flame propagation have been conducted in a tube geometry with 3 different blockage ratios BR = 0, 30 and 60%. 0% of blockage simply means a smooth tube without obstacles. The blockages 30 and 60% are provided by a set of metal rings fully filled the tube length and spaced by the tube diameter. The blockage ratio is defined as follows: $BR = 1 - d^2/D^2$, where d is the internal diameter of the obstacle ring; D is the inner tube diameter. All ports and sensors are placed midway in between the obstacle positions. Two types of dynamic pressure sensors suitable for cryo-temperatures with PCB 116B and PCB 112A05 were used. InGaAs photodiodes were chosen as the light sensors. Because the photo sensor material does not withstand the low temperature, the light signal was guided by a polymer optical fiber to the sensor outside of the LN_2 bath.

To monitor the cooling process, four thermocouples (type K) were placed at the outer tube surface, and two thermocouples were inside the tube, just at the inner surface. Their distances from the front flange were 22.5 cm, 102.5 cm, 103 cm, 227 cm, 378 cm and 472.5 cm respectively. In preliminary experiments, the thermocouples were exposed at ambient and LN2 boiling temperature of 77K. Then, a linear correlation is used to adjust the measured temperature to the real one. By the averaging, it yields the linear correction with an RMS = ± 0.18 K:

$$T_r\,[K] = 1.1013 * T_m\,[K] - 31.024$$

where T_r and T_m are the real and measured temperatures in Kelvin. An actual initial temperature for each test was assumed to be as an average for all six thermocouples.

3 Experimental Results and Discussion

Warm tests (T=293K). A series of reference tests at ambient pressure and temperature and different blockages of the tube 0, 30 and 60% was conducted to check the well known criteria for flame acceleration and DDT [1-2] for the same tube geometry as for the forthcoming cryogenic tests. The experiments with a smooth tube (BR=0) cover hydrogen-air mixtures in the range 8-60%. That was mainly relatively slow subsonic deflagration registered because of longer run-up-distance (RUD) to detonation than the length of the tube L=5 m. The only stoichiometric mixture was able to detonate at the shock wave reflection on the far end flange.

According to paper [3], the run-up distance to detonation in a smooth channel should be 500 times larger than the detonation cell size $x_D = 500\ \lambda$. The run-up-distance to detonation $x_D = 5000$ mm for stoichiometric hydrogen-air with detonation cell size λ=10 mm exactly fits to tube length L=5000 mm. *Vice versa*, for 45%H_2-mixture, the flame accelerates very slowly and, since the run-up distance to fast sonic flame was larger than the tube length, the detonation did not occur: $x_D = 8400$ mm which exceeds the tube length L=5000 mm. This happens independent of the high mixture reactivity and small enough detonation size λ = 16.8 mm sufficient for detonation propagation in a smooth tube ($\lambda < \pi D = 170$ mm).

With the obstructions, we can experimentally evaluate the critical expansion ratio σ* for an efficient flame acceleration to the speed of sound because obstacles reduce the run-up-distance almost three times compared to smooth tube. In presence of obstacles, the flame continuously accelerates until a steady-state velocity is established. For both obstacles (BR=0.3-0.6), for hydrogen concentration above 11%H2 (σ=3.77), characteristic flame velocity above the speed of sound (blue dotted line in Figure 2, right) and characteristic combustion pressure above the adiabatic combustion pressure ΔPicc (red dotted line in Figure 2, left) is established. For more reactive mixtures, the velocity approaches the detonation velocity D_CJ, when the detonability criteria are satisfied. The detonation cell size of test mixture should be larger than the orifice diameter, λ < d=45.2 mm for BR = 0.3 or λ < d/3=9.5 mm for BR = 0.6 according to papers [2,5-6,14]. In reality, it corresponds to more than 19.5%H2 for BR=0.3 or 30%H2 for BR=0.6. Figure 2 confirms well known critical expansion ratio σ*=3.75 for hydrogen-air mixtures at ambient conditions in a tube with BR=0.3 [1]. The same threshold was found for BR=0.6.

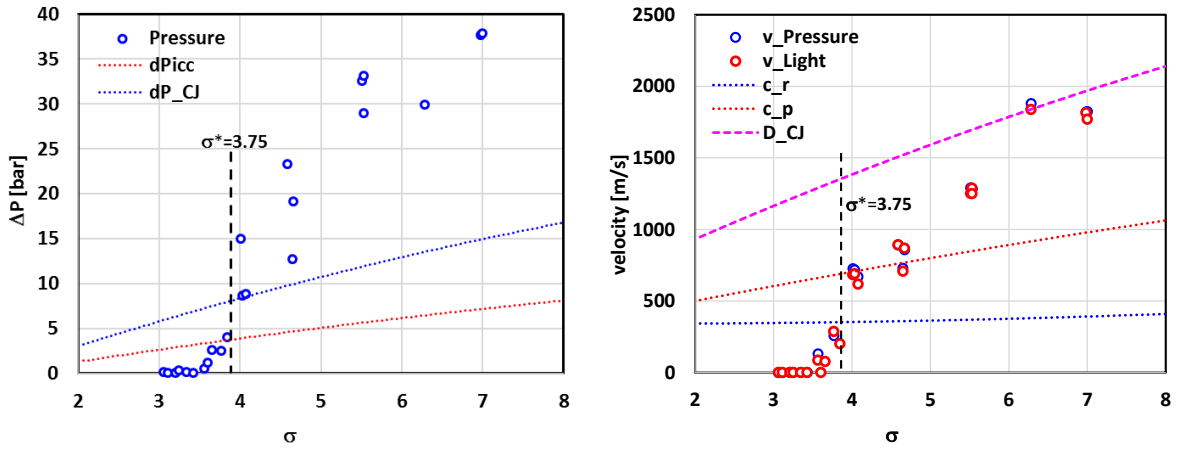

Figure 2. Characteristic pressure (left) and flame velocity (right) in obstructed tube (BR=0.3) as function of expansion ratio at ambient conditions: black dashed line is a cut-off line at σ*=3.75.

Cryogenic tests (T=90-130K). The tube is cooled down in the basin surrounded the tube with LN_2, and the experiments are conducted during the warm-up phase. It takes about 2 hours to cool the tube down from ambient to the test temperature 90-130 K. Temperature uniformity along the tube is monitored by six thermocouples. The temperature of test mixture is assumed as an average one before the test.

The analysis of x-t diagrams for cryogenic hydrogen combustion in a smooth tube (BR=0) shows that for the first time a stationary supersonic flame propagation in a channel without obstacles was discovered. For hydrogen-air mixtures of 16 - 20%H_2 a stationary flame front coupled with shock wave propagates with characteristic velocity of the order of speed of sound in combustion products Uf=600-800 m/s (Mach number M=3). It can be classified as a chocked flame supported by spatial problems and energy losses. If the detonability of tested mixture would be larger, then the detonation for mixtures above 20% could occur. Since the critical condition for detonation propagation in a smoot channel is d > λ/π, we can assume the detonation cell size λ < π d = 170 mm for mixtures of more than 20%H_2. In contrary, for non-detonable mixtures with 16 and 17%H2 the detonation cell size is λ > π d = 170 mm. Assuming that the run-up distance to detonation $x_D = 500 \cdot \lambda$, the detonation cell size for stoichiometric hydrogen-air at cryogenic temperature T=101.7K is estimated to be λ = 9 mm and for 45%H2 the detonation cell size λ = 5 mm. Since the quasi-detonation has occurred, the detonation cell size for 20 and 50%H2 shouldn't be larger than the tube diameter (λ_{max} = d = 54 mm)

A comparison of flame velocity for warm and cold experiments shows that cryogenic temperature promotes the sonic flame propagation or even quasi-detonation for lean (20%H2) and rich (50%H2) hydrogen-air mixtures in comparison with ambient temperature combustion with a velocity below 80

m/s. For more reactive mixtures with 29 and 45% H_2-air, cryogenic temperatures shorten the run-up distance to detonation compared to ambient temperatures. This might be due to more efficient flame acceleration in more viscous and dense gas and also due 2 times lower speed of sound at cryogenic temperatures because it leads to two times higher dynamic pressure for the same flow/flame velocity. The Reynolds number at cryogenic temperatures might be 5 times higher to reach the same threshold velocity for sonic deflagration. It promotes creation of turbulent flow ahead of the flame, which leads to faster flame acceleration to sonic deflagration.

Figure 3 shows that the critical expansion ratio σ*=12.5 is typical for hydrogen-air mixtures in obstructed tubes at cryogenic temperature T=100K. For hydrogen concentration above 16%H2 (σ=11.9) characteristic flame velocity is above the speed of sound in reactants c_r (blue dotted line in Figure 3, right) and characteristic combustion pressure is above the adiabatic combustion pressure ΔPicc (red dotted line in Figure 3, left). Similar to warm tests, for more reactive mixtures the velocity establishes at the level of the speed of sound in combustion products c_p typical for chocked flames in congested areas when the detonation transition is suppressed by the detonation cell size larger than the orifice diameter, λ > d=45.2 mm for BR = 0.3, according to papers [2,5-6]. The same flame acceleration threshold σ*=12.5 was found for BR=0.6 with the difference that the critical detonation cell size is λ < d/3=9.5 mm.

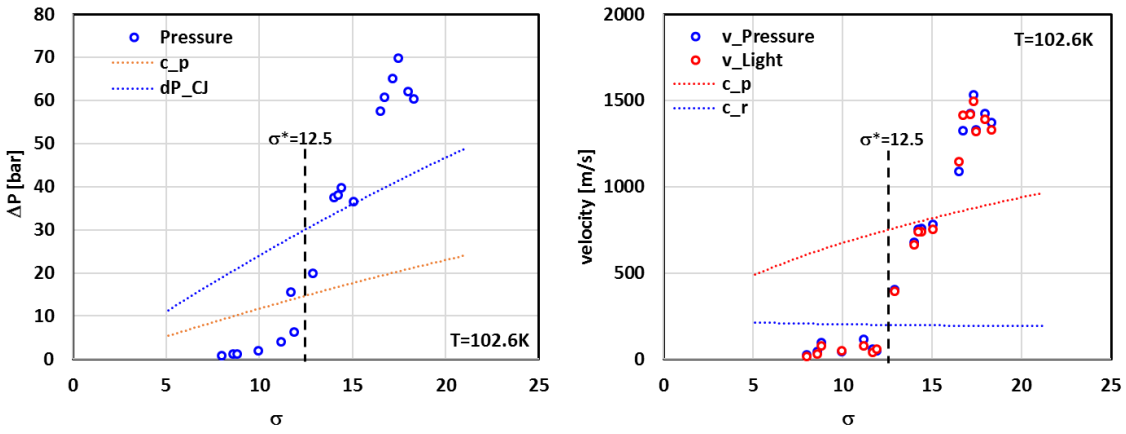

Figure 3. Experimental characteristic pressure (left) and flame velocity (right) as function of expansion ratio in obstructed tube (BR=0.3) at cryogenic temperature (T=102.6K): black dashed line is a cut-off line at σ*=12.5.

3 Conclusions

More than 200 experiments were made for hydrogen-air mixtures with the Cryogenic Shock Tube. About half of the experiments was made at cryogenic temperatures (from 80 to 130 K). It turned out to be impossible to ignite hydrogen-rich mixtures at 77 K. The photo sensors turned out to be too insensitive for slower combustion processes with less intensive radiation. However, all the problems were satisfactory solved and the flame propagations regimes at cryogenic temperatures were found.

The critical conditions for flame acceleration were evaluated as a function of initial temperature within the range 90 – 650K. It shows a much higher hydrogen concentration leading to sonic deflagration than it was predicted by advanced extrapolation of well known correlations [1] before the tests. The correlation based on current experiments is quite simple and useful:

$$\sigma^* = 2200 \cdot T^{-1.12}$$

The detonation cell sizes at cryogenic temperature T = 100K are evaluated on the basis of existing criteria for detonation onset in smooth and obstructed tubes and can be presented as a polynomial function of hydrogen concentration [H2]:

$$\lambda[\text{mm}] = 0.0006724[H_2]^4 - 0.1039[H_2]^3 + 6.0786[H_2]^2 - 159.74[H_2] + 1603.3$$

Based on evaluated detonation cell size the well known criteria can be used to assess the detonability of hydrogen –air mixtures at cryogenic temperatures in different geometries and scales.

The run-up distance to detonation at cryogenic temperatures was found to be two times shorter than at ambient temperature. For the first time in a smooth channel, a steady-state flame propagation with the speed of sound in combustion products was registered for a long distance.

It was found that the maximum combustion pressure at cryogenic temperatures is 2-3 times higher than that for ambient conditions. It demonstrates a high level of the danger under cryogenic hydrogen combustion. Theoretically, even adiabatic combustion pressure corresponding to sonic deflagration at cryogenic temperature is 1.5 times higher than the CJ-detonation pressure at ambient temperature.

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