EFFECTS OF OXIDANTS ON HYDROGEN SPONTANEOUS IGNITION: EXPERIMENTS AND MODELLING

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ABSTRACT

Experiments were performed on the influence of oxidants (air, pure oxygen O_2 and pure nitrous oxide N_2O at atmospheric pressure) in the straight expansion tube after the burst disk on the hydrogen spontaneous ignition. The lowest pressure at which the spontaneous ignition is observed has been researched for a 4 mm diameter tube with a length of 10 cm for the two oxidant gases. The ignition phenomenon is observed with a high speed camera and the external overpressures are measured. Numerical simulations have also been conducted with the high resolution CFD approach detailed chemistry formerly developed by Wen and co-workers. Comparison is made between the predictions and the experimental data.

1.0 INTRODUCTION

Literature reports the existence of multiple spontaneous ignitions of hydrogen leaks without any apparent reason [1]. In 2007, Dryer et al. [2] for the first time experimentally demonstrated that a hydrogen spontaneous ignition could be obtained by a high pressure hydrogen release in a straight tube filled with air.

From 2007 up to nowadays, the spontaneous ignition of hydrogen was extensively investigated experimentally [3-9]. The experimental studies were mainly aimed at the understanding of an ignition of hydrogen released through extension tubes of different lengths and diameters for different initial pressures. Some authors also studied the influence of alternative designs of a classical cylindrical extension tube: tube with varying cross sections, local enlargement, perforated channel, two dimensional ducts, T shaped channel, diaphragm rupturing conditions [10-16]. The influence of the addition to the hydrogen of different gases (methane and nitrogen) was also recently investigated [17-19]. Generally, the higher initial pressure, the longer tube length and the smaller its diameter the easier is the ignition of hydrogen. On the contrary, hydrogen dilution makes the ignition more difficult [17-18].

In numerical investigations [20-30], researchers mainly focussed on the modelling of the available experiments with codes coupling chemical kinetics of ignition and fluid dynamics of compressed flows.

However, none of the referred papers tried to investigate the influence of the composition of different gas in the atmospheric straight tube after the disk burst prior to the release. Different gases as oxidizers (air, oxygen O_2, nitrous oxide N_2O), inert (nitrogen, helium) or even fuels (C_2H_4, C_2H_2) can be considered as an ambient gas at atmospheric conditions to fill the pipeline just after the burst disk rupture. The choice of nitrous oxide and acetylene is caused by their thermodynamically unstable nature.

They have positive free enthalpy and then they can decompose exothermically following the reactions:

$N_2O \rightarrow N_2 + \frac{1}{2} O_2$ ($\Delta H = +82$ kJ/mole), (1)

$C_2H_2 \rightarrow H_2 + 2C$ ($\Delta H = +226$ kJ/mole) (2)

The advantage to use N_2O and C_2H_2 as an ambient atmosphere is their exothermicity with the difference that N_2O is strong oxidizer and C_2H_2 is a fuel.

The purpose of this paper is to investigate the spontaneous ignition process of high-pressure hydrogen release to modified atmosphere composed of oxygen, nitrous oxide and acetylene.

2.0 EXPERIMENTAL SETUP

Experiments are performed using an experimental setup designed and previously used for studying of hydrogen spontaneous ignitions in air [5].

The setup (Fig. 1 A, B) consists of a release tube of 4 mm internal diameter connected via a rupture disk to a cylindrical storage vessel of 0.37 L volume filled with hydrogen at a high pressure. A compressed air or helium driven valve (DN 4 mm) with a valve opening time lower than 2 ms works as a leak opening tool in all experiments. The thickness of the aluminium membrane used as a burst disk is adjusted to required hydrogen release pressure (see Fig. 2).

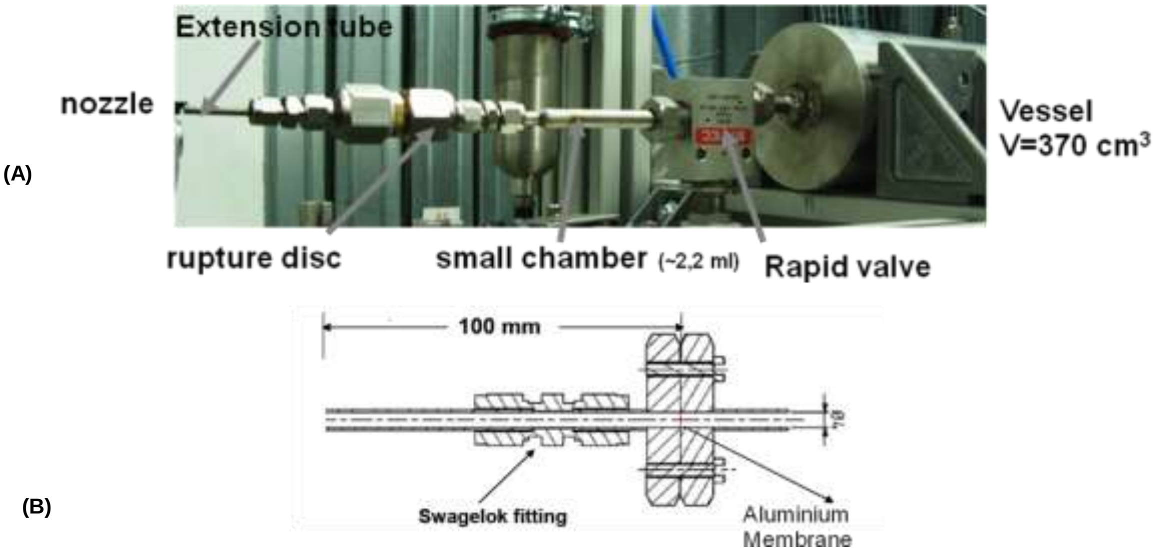


Figure 1. Scheme of the experimental setup (A - general view; B - burst disk details)

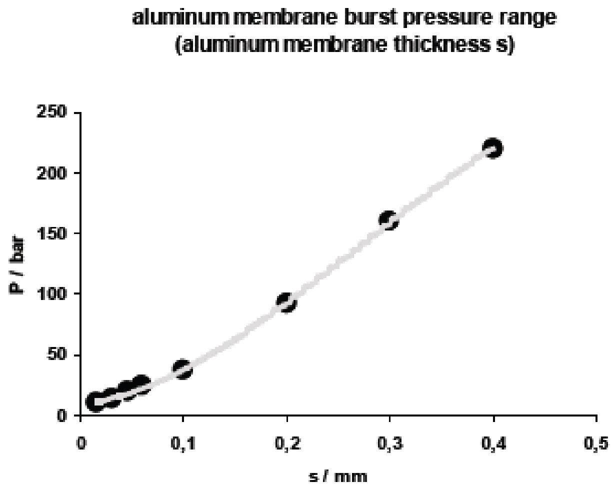


Figure 2. Dependence of burst pressure on thickness of the burst membrane.

For experiments, the vessel is pressurised up to the working pressure and then the rapid valve is opened. Hence the pressure increases above the disk rupture pressure leading to a disk burst and then to a release of hydrogen into the extension tube connected to ambient atmosphere. Depending on the pressure and on the nature of the gas in the extension tube, a spontaneous ignition of the high pressure hydrogen release can occur.

For experiments with a reactive test-gas (O_2, N_2O and C_2H_2) in the extension tube, a small vessel (0.3 L) filled by this test-gas at the initial pressure of 2.5 bar is connected via a capillary to the extension tube [A] (see Figure 3). To avoid perturbations of the experiment, the capillary is extracted by a horizontal movement from the extension tube [B] at the end of the filling. Finally, the test-gas vessel is rotated to remove the capillary from the nozzle exit [C]. A side view of three stages of a test preparation are shown in Fig. 3, bottom.

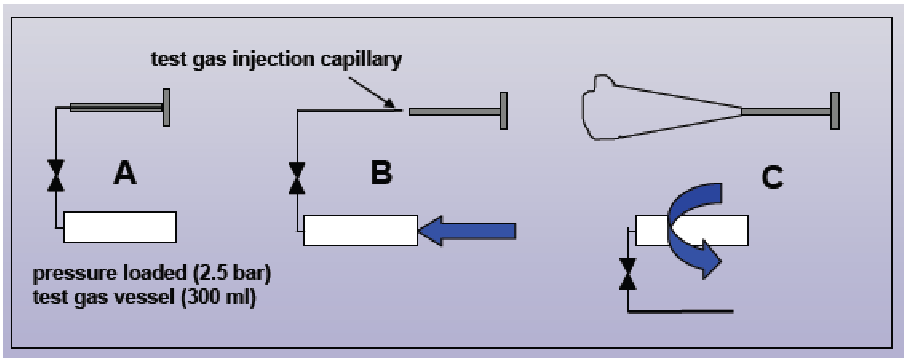


Figure 3. Realization of the injection of the test-gas in the extension tube (top - general scheme; bottom - an example of a capillary extraction at 49 bar H_2 in N_2O).

A high speed pressure gauge inside the 0.37 L storage measure the pressure decay after membrane burst. A high speed camera and a focalized photo sensor record the ignition.

3.0 EXPERIMENTAL RESULTS

An example of experimental results is given on Fig. 4 for pressure of 12 bar within the extension tube filled with O_2. Figure 4, left shows a sequence of high speed images of ignited hydrogen release at the frame rate of 20000 fps. High intensity light signal confirms the ignition of high pressure hydrogen released through extension tube filled with oxygen (Fig. 4, right). The combustion process in Fig. 4, left corresponds to afterburning of ignited hydrogen jet in ambient air.

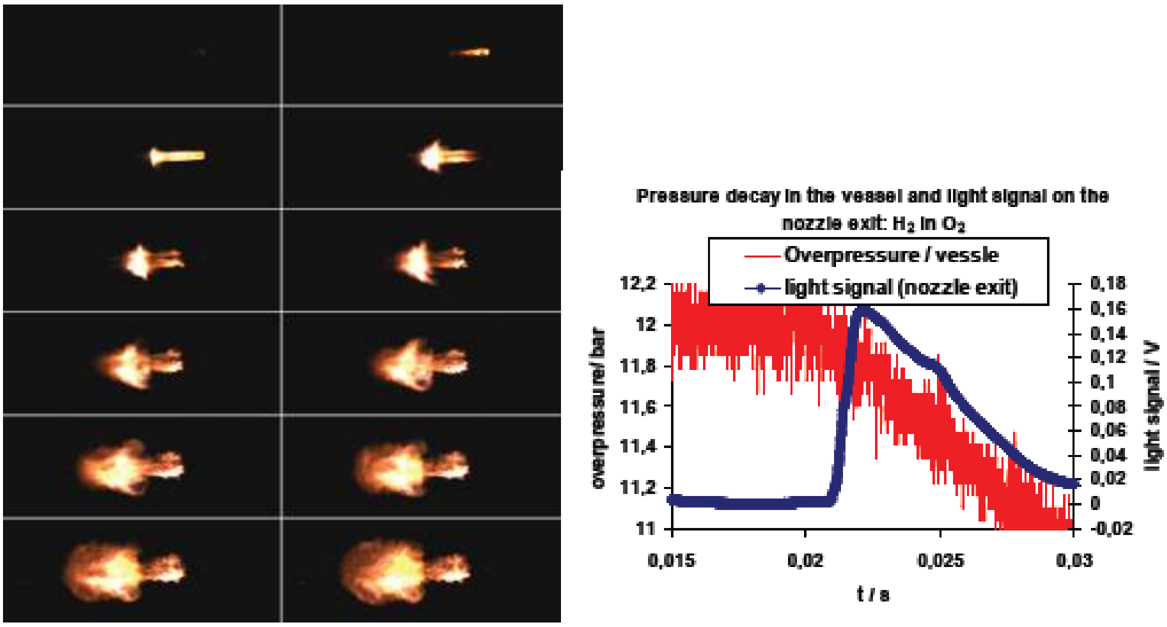


Figure 4. Experimental results for pressure of 12 bar within the extension tube filled with O_2.

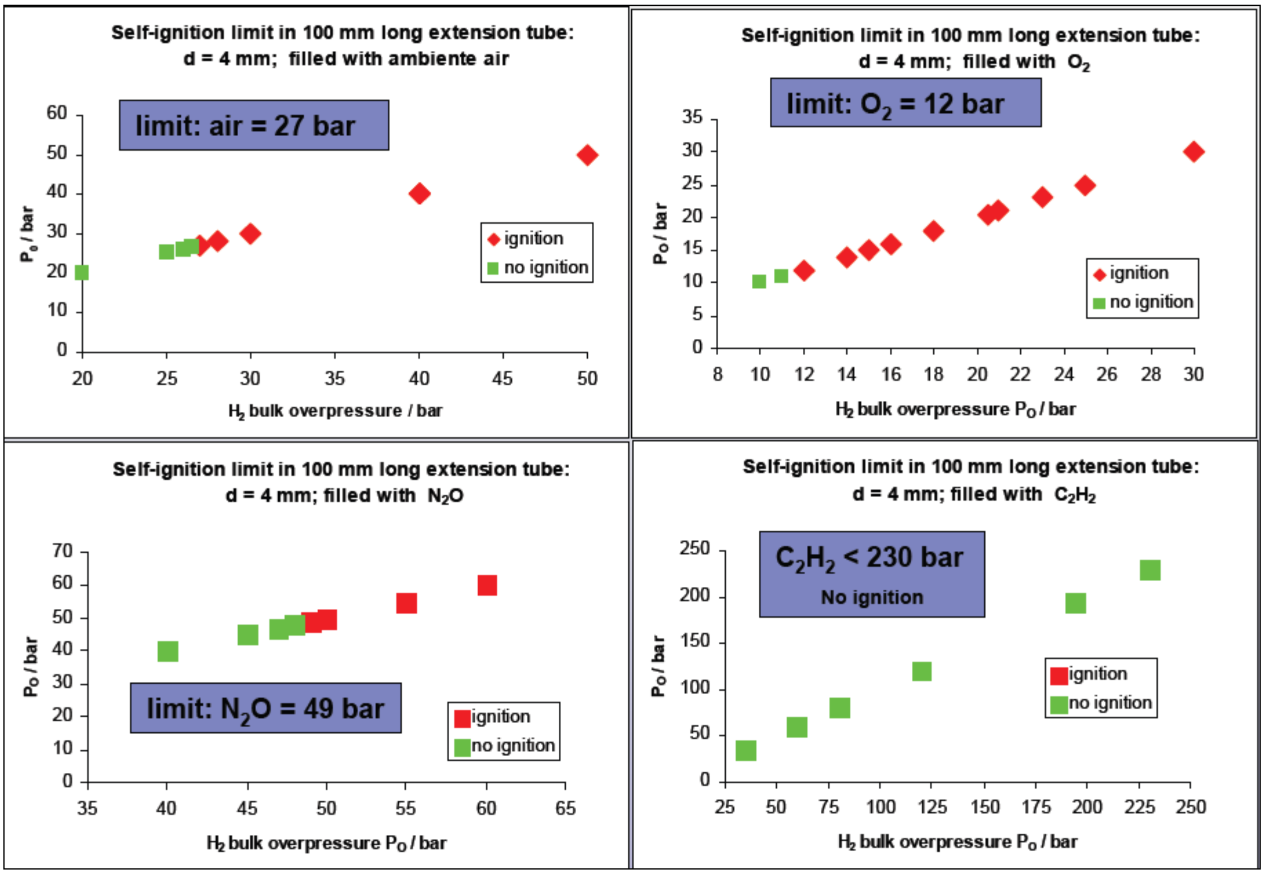


Figure 5. The lowest experimental pressures for spontaneous ignition

As shown on Fig. 5, experimentally is found that for a 4 mm tube diameter with a 100 mm length filled with different gases the lowest hydrogen pressure leading to spontaneous ignition is :

- 27 bars in air
- 12 bars in pure oxygen
- 49 bars in nitrous oxide
- No ignition is observed up to 230 bars for acetylene.

The pressure of 27 bars obtained for air is in good agreement with the previous published studies [2, 5, 7]. When there is oxygen is the extension tube, the minimum successful pressure is reduced to 12 bars showing the acceleration effect of the partial pressure of oxygen on the chemical kinetic of the ignition. When there is nitrous oxide in the extension tube, this pressure increases to 49 bars. Then even if nitrous oxide could be considered to O_2 enriched air (with 33% O_2), it shows that an important part of the shock energy is consumed to initiate the decomposition of the nitrous oxide. With acetylene in the extension tube, the energy generated by decomposition of acetylene in the shock wave is not sufficient to heat hydrogen up to a sufficiently high temperature to generate auto-ignition in air outside the extension tube.

All observed successful ignition events lead to an attached jet fire.

Experiments without burst disk are also performed. In this case, the hydrogen release is generated by the opening of the high speed valve. No ignition is observed for hydrogen pressure up to 250 bar with air in the extension tube. This result is in good agreement with the observations of [15] and [16] on the diaphragm rupture rate. The same configuration is used with O_2 and N_2O in the extension tube and it is impossible to produce an ignition in this conditions.

4.0 NUMERICAL RESULTS

Numerical simulations are conducted using the modified version of KIVA-3V developed by Wen and co-workers [20, 21]. The code uses the high-order weighted essentially non-oscillatory (WENO) shock-capturing schemes [31]. Exploiting the symmetric nature of the problem and the limitation of current computing resources, two-dimensional simulations are performed. The numerical schemes are based on an arbitrary Lagrangian and Eulerian (ALE) method [32] in which convective terms are solved separately from the other terms. Each time cycle is divided into two phases: a Lagrangian phase and a rezone phase. Considering the substantial scale difference between diffusion and advection, different numerical schemes are adopted in the two phases. In the Lagrangian phase, a second-order Crank-Nicolson scheme is used for the diffusion terms and the terms associated with pressure wave propagation, a 3^{rd}-order TVD Runge-Kutta method [33] is used in the rezone phase to solve the convective terms. The coupled semi-implicit equations in the Lagrangian phase are solved by a SIMPLE type algorithm with individual equations solved by a conjugate residual method [34]. For spatial differencing, a 5^{th}-order upwind WENO scheme [31] is used for the convection terms and the second-order central differencing scheme is used for all the other terms.

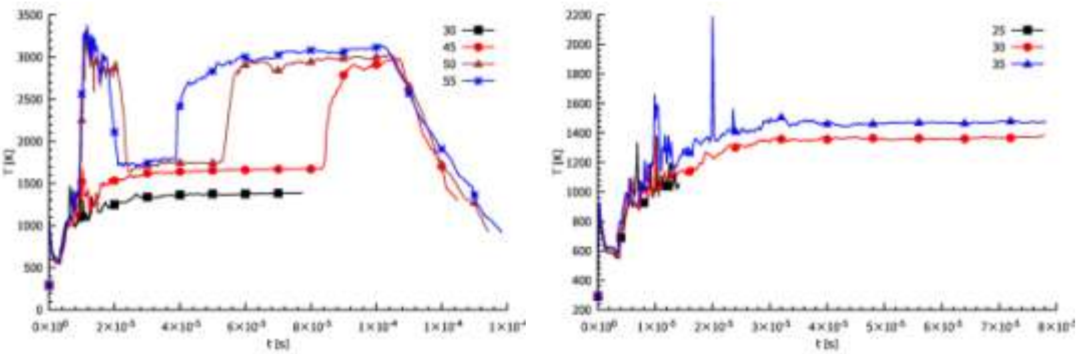
A mixture-averaged multi-component approach [35] is used for the calculation of molecular transport with consideration of thermal diffusion which is important for non-premixed hydrogen combustion. For auto-ignition chemistry, Saxena and Williams' detailed chemistry scheme [36] which involves 21 elementary steps among 8 reactive chemical species is applied. The scheme was previously validated against a wide range of pressures up to 33 bar. It also gave due consideration to third body reactions and the reaction-rate pressure dependent "falloff" behavior. Since high-pressure hydrogen release undergoes strong under-expansion after discharging into an open space, a detailed chemistry allowing for the pressure dependant reaction rate is essential to accurately predict chemical reaction rates. To deal with the stiffness problem of the chemistry, the chemical kinetics equations are solved by a variable-coefficient ODE solver [37].

Since spontaneous ignition first occurs inside release tubes, the present study is limited to the flow inside the release tube. The computational domain is composed of a cylindrical high-pressure vessel of large diameter and a release tube. The pressurized cylinder is set up to be sufficiently large to ensure that pressure drop during simulations does not exceed 3% of the initial pressure. The release tube has a diameter of 4 mm and a length L of 10 cm. An Iris model [20] is used to simulate the rupture process of the pressure boundary. It assumes that the pressure boundary, which is mimicked by a thin diaphragm with a thickness of 0.1mm, ruptures linearly from the centre at a finite pre-determined rate as simulations start. All the solid surfaces (e.g. walls) are assumed to be non-slip and adiabatic. Non-uniform grids are applied to the regions of pressurized cylinder and uniform grids to the tube region. Since ignition is first initiated at the thin contact region or inside the thin boundary layer, a very fine grid resolution is required there to resolve the species profiles in the ignited flame. In this study, a uniform10 micron grid size is used inside the release tube and the total grid points are approximately 4 millions. The key parameters of the computed release scenarios are summarized in Table 1.

Table 1 Computational details

Parameters	**Values**
Rupture time (μs)	5
Release pressure (bar)	Air: 30, 45, 50; Oxygen:25, 30, 35
Initial temperature (K)	293
Initial diameter of tube (mm)	4
Length of tube (mm)	100
Thickness of film(mm)	0.1
Minimum grid spacing (μm)	10

Numerical simulations are conducted for three cases involving releases into air and three cases for releases into pure oxygen. The predictions for the six simulated cases are listed in Fig. 6.



Release into air

Release into oxygen

Figure 6. Modelling of spontaneous ignition in different atmospheres

The experimental ignition limits are respectively 27 bar and 12 bar for air and oxygen. Current predictions are much higher than the measured values. The discrepancies are thought to be caused by the limitation in the wall treatment in the current code, i.e. it does not resolve the wall boundary layer and predict the heat production resulting from the wall friction. It is likely that the ignition should first occur inside the wall boundary layer and the roughness of tube wall might also play an important role in the propensity to ignition.

5.0 CONCLUSIONS

Experiments are performed to investigate the influence of oxidants (air, pure oxygen O_2 and pure nitrous oxide N_2O at atmospheric pressure) in the extension tube after the burst disk on the hydrogen spontaneous ignition. For the tube of 4 mm diameter and of 10cm length, the lowest pressures at which the spontaneous ignition is observed are 27, 12 and 49 bars respectively for air, pure oxygen and nitrous oxide in the extension tube. Experiments without a high speed valve instead of a diaphragm fail to produce ignition whatever the oxidant is (air, pure oxygen and nitrous oxide). Numerical simulations are also performed using a high resolution CFD approach. Simulations are in reasonable with the experiments, however predictions are higher than the measured values, due to the fact the boundary layer is not resolved in simulations.

6.0 ACKNOWLEDGMENTS

The authors thank Air Liquide for sponsoring this work and for permission to publish this paper.

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