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Evaluation of flammability limits of $H_2/O_2/N_2$ mixtures in conditions relevant to nuclear waste transportation

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Abstract

The aim of the present work is to assess the risk of explosion in closed containments used for the transportation of nuclear materials or nuclear waste. Indeed, it is very well-known that hydrogen can be produced due to (i) the radiolysis of different materials within the containment, (ii) the thermal decomposition of mainly the organic part in the containment. Since hydrogen has a very low ignition energy and a very wide flammability domain, it is important to determine the risk of ignition of the subsequent mixture produced by the aforementioned mechanisms. The quantity of the hydrogen that can be produced can vary depending on the containment type and on the state of the material/waste being transported. It is then mandatory to have a very good knowledge not only of the flammability domain of hydrogen in air but also for different N_2/O_2 ratios. To do so, an experimental work on the flammability domain of multiple ternary mixtures containing $H_2/O_2/N_2$ is being conducted at the CNRS-ICARE laboratory within collaboration with the CEA.

The flammability limits of $H_2/O_2/N_2$ will be determined in a spherical bomb equipped with a central ignition at an initial pressure of 1 bar and for different initial temperatures between 60 and 200°C. Two tungsten electrodes are located along a diameter of the sphere. They are linked to a controlled high voltage discharge device. The voltage and intensity discharge are measured via a high voltage and a current probes. The adjustable gap between the electrodes is usually fixed around 1 mm and can be larger near the flammability limits. The combustion is monitored using 2 different diagnostics: pressure measurements during the combustion test using a piezo-electric pressure transducer (Kistler) and the recording of the flame. The visualization of the flame is obtained via a Schlieren diagnostic previously described [1]. A mixture will be considered as flammable when both the imaging and the pressure indicate a successful ignition followed by flame propagation. On the contrary, the mixture will be considered non-flammable when no flame propagation is observed and no increase of pressure inside the vessel is recorded.

Introduction

CNRS-ICARE

The CNRS is a state-funded science and technology establishment placed under the authority of the French Minister for Research. CNRS research units are located throughout France, and employ a large body of tenured researchers, engineers, and support staff.

CNRS-ICARE is an intramural lab, fully funded and managed by CNRS. It is specialized in combustion studies. It has a history of more than 40 years and is active in all areas of combustion studies from chemical kinetics to turbulent combustion. Presently ICARE is composed of about 100 scientists and support staff. Its main R&D activity area is Energy & Environment studies relating mainly to chemical conversion of energy. CNRS-ICARE has a large experience in the combustion studies of gaseous and heterogeneous systems. Particle combustion, droplet combustion, spray combustion, turbulent two-phase combustion are its main expertise areas together with the chemical kinetics of reactive systems. ICARE operates several large scale facilities including high pressure combustion chambers, high speed wind tunnel, shock tubes, flame acceleration systems and experimental platforms consisting of several advanced laser diagnostics systems. ICARE has also large expertise in the modelling and numerical simulation of complex reactive flows. The « Shock Wave » group of the ICARE laboratory at Orléans works on two aspects: the chemical kinetic of combustion and the dynamics of chemical explosion. The team has many additional experimental devices to determine the fundamental parameters of the combustion such as spherical bombs, shock and detonation tubes, fast flames rigs ….

The CEA

CEA is the French Alternative Energies and Atomic Energy Commission (Commissariat à l'énergie atomique et aux énergies alternatives). It is a public body established in October 1945 by General de Gaulle. A leader in research, development and innovation, CEA is active in four main areas: low-carbon energies, defense and security, information technologies and health technologies. In each of these fields, CEA maintains a cross-disciplinary culture of engineers and researchers, building on the synergies between fundamental and technological research.

The civil nuclear research is focused on two main fields: nuclear systems for the future and nuclear waste management.

The research studies are supported by demonstration resources and equipments using nuclear materials, which are spread all over the ten CEA research centers in France, each specialized in specific fields. Consequently, the transport of nuclear materials between its own nuclear facilities and also the waste produced by its activities, or the dismantling of old facilities, is a key issue for the good achievements of CEA programs and projects. CEA has therefore designed, licensed and manufactured a wide range of nuclear transport packages to cover its own varied needs over the last 70 years. The fleet of packages covers many kinds of nuclear materials that need to be transported:

- neutron sources and a large variety of fresh fuels,

- a wide variety of spent fuels from a large group of research reactors or laboratories, and conditioned in many forms (samples, rods, assemblies…),
- technological waste conditioned in various drums from 100l to 870l,
- liquid waste.

General context

It is very well-known that in closed containments used for the transportation of nuclear materials or nuclear waste, hydrogen can be produced due to (i) the radiolysis of different materials within the containment, (ii) the thermal decomposition of mainly the organic part in the containment. Since hydrogen has a very low ignition energy and a very wide flammability domain, it is very important during the safety demonstration process to determine the risk of ignition of the subsequent mixture produced by the aforementioned mechanisms. The quantity of the hydrogen that may be produced can vary depending on the containment type and on the state of the material/waste being transported. It is then mandatory to have a very good knowledge not only of the flammability domain of hydrogen in air but also for different N_2/O_2 ratios and in conditions of pressure and temperature relevant to nuclear waste transportation. To do so, an experimental work on the flammability domain of multiple ternary mixtures containing H_2, O_2, and N_2 is being conducted at the CNRS-ICARE laboratory within a collaboration with the CEA. Since this study is only at the early stages, the results will focus on the initial pressure of 1 and 2 bar. The work will be continued with the investigation of the effect of a larger domain of pressures (from 0.3 to 4 bar) and for different initial temperatures (from 60 to 200°).

Experimental Setup and Methodology

The spherical bomb method has been chosen to study the behavior of flame and to determine the flammability limits of $H_2/O_2/N_2$ mixtures. It consists of a spherical stainless steel vessel of 8-L (i.d. 25 cm) equipped with 2 quartz windows (70 mm optical diameter, 50 mm thickness). The maximum operating pressure and temperature are respectively 50 bars and 150°C (Figure 1).

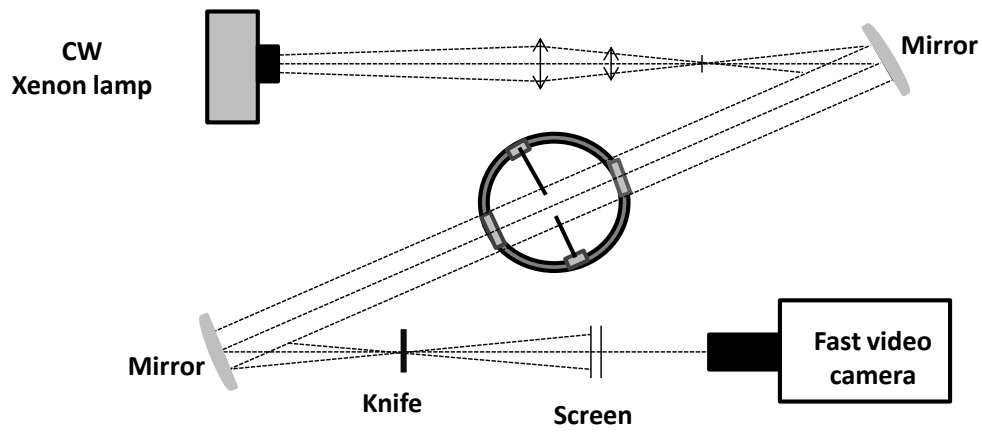


Figure 1 Schematic diagram of the experimental setup for the Z-type Schlieren visualization.

Two tungsten electrodes were located along a diameter of the sphere. They are linked to a controlled high voltage discharge device consisting of a capacity of 1.55 µF capacitor and a voltage of 1.3 kV able to store 1.31 J. The voltage and intensity discharge were measured via a high voltage (Tektronix, P6015A) and a current (Bergoz, CT-D1.0) probes (Figure 2). The adjustable gap between the electrodes was usually between 1 mm and 5 mm depending on the molar fraction of H_2 in the mixtures, it is fixed to the largest gap near the flammability limits. Indeed, as shown by Kumamoto et al., [1], a variation of the distance between the electrodes will induce an increase or decrease of the energy delivered by the spark.

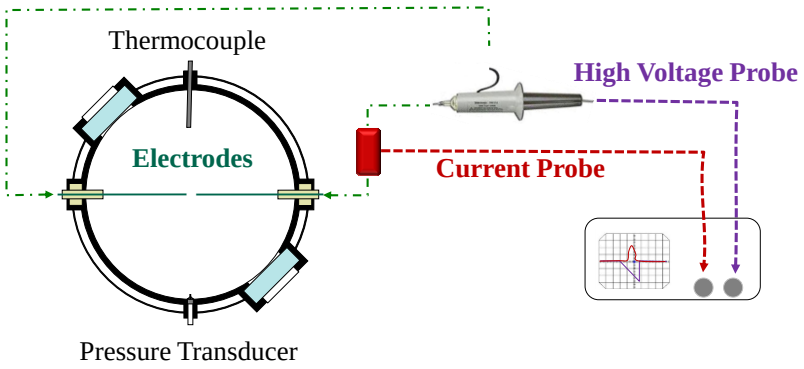


Figure 2 Schematic of the Ignition system coupled with the spherical vessel.

The current (I) and voltage (U) are acquired by a digital oscilloscope (Agilent DSO-100MHz, 2Gsa/s).The estimation of the delivered energy to the spark is from the temporal integration of the product of U*I. It depends of many factors such as the mixture composition, the initial pressure, the nature and surface quality of the electrodes, and the electrodes gap.

The ignition and the flame propagation are visualized through a classical Z-type Schlieren setup with a high-speed camera (Phantom V5 or V1610). These cameras are been used respectively at 500 frames/s and 25000 frames/s. The light source was a DC 150 Watts Xenon lamp (Lot Oriel, Compact 150W Xe model). The temporal behavior of the induced overpressure following the ignition is measured with a fast piezoelectric pressure transducer (Kistler 601A). The overpressure signal is recorded on a second oscilloscope (Agilent DSO-100MHz, 2Gsa/s).A digital delay generator (BNC, 575 model) is used to trigger the electric spark and the acquisition of the two oscilloscopes. The initial gas temperature inside the bomb is monitored via a thermocouple before each run.

The gases were introduced in a magnetically fan-stirred reservoir using the partial pressure method to obtain the desired mixture. Hydrogen, oxygen and nitrogen were supplied by Air Liquide with a purity better than 0.9999. The partial pressure was measured using capacitive manometers (MKS) of different full scales according to the desired pressure (10^3 Torrs and 10^4 Torrs). Based on the

precision of the capacitive manometers, the mixtures were obtained with an accuracy of 0.2 %.
Before each test, the chamber was vacuumed and the residual pressure was lower than 3 Pa, the premixed mixture is fed into the spherical bomb at the desired initial pressure. The mixture inside the bomb is let to rest for 5 mn before a spark is created at the center of the vessel. The camera and the oscilloscopes are subsequently triggered by the digital delay generator. The experimental maximum pressure observed for each test is compared to the theoretical value that is estimated based on the assumptions of: (i) adiabatic, (ii) isochoric, (iii) complete combustion. This theoretical maximum pressure is calculated using Cosilab code [2].

Results

Following our previous studies and according to the literature [3-5], a mixture is considered as combustible when following the flame kernel formation due to the spark plasma, a visible flame propagates away from the ignition location in the vessel. It may or may not induce a visible pressure increase inside the spherical bomb. Once the mixture is introduced inside the vessel, a spark is created: (i) if the ignition is obtained, the mixture will be labelled as flammable and a value of 1 is attributed to the test; (ii) if no ignition is observed, the mixture will be labelled as non-flammable and a value of 0 is attributed to the test. In the case where no ignition is obtained, the test is repeated 10 times before emptying the chamber and filling again with the same mixture. This cycle is repeated 3 to 4 times.

Definition of the flammability limit

Concerning the flammability limit, one can distinguish between the lower flammability limit (LFL) which is the minimum molar percent of the fuel in the mixture below which no flame propagation can be achieved and the upper flammability limit (UFL) which corresponds to the highest molar percent of the fuel above which no sustainable flame is observed. An example of the probability distribution between ignition / no ignition tests is given in figure 3. From this distribution, the lower flammability limit is derived: for H_2/O_2 mixtures initially at 1 bar and 297 K, the LFL is equal to 4.1 % of H_2 which is in very good agreement with the literature [6].

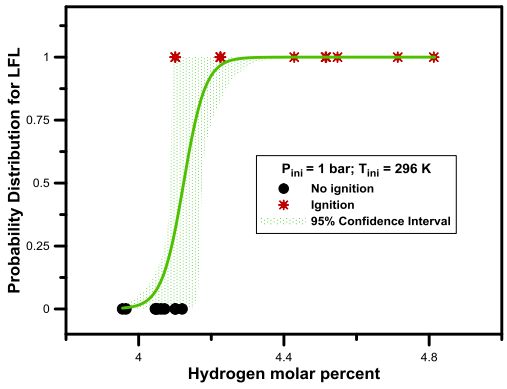


Figure 3 Probability distribution for tests of H_2/O_2 mixtures initially at 1 bar and 296 K.

Different flame regimes near the flammability limits

When the H_2 molar percent is higher than the LFL, the flame propagation and the subsequent pressure increase inside the spherical bomb depends strongly on the molar percent of H_2 in the binary mixture H_2/O_2. As it is shown in Figure 4, when the mixture is constituted of {5.12 %H_2 + 94.88 % O_2}, the spark leads to the formation of a flame that propagates in the upward direction and will be responsible of a partial combustion of the fresh combustible mixture. For a mixture constituted of {8.75 %H_2 + 91.25 % O_2}, the flame kernel grows faster: initially as a spherical flame, but then later we can still observe a preferential propagation in the upward direction. Increasing the H_2 molar percent to 12.75 %, the flame grows at a much larger speed and propagates in all directions. In this last case, the combustion will consume the total amount of the combustible mixture.

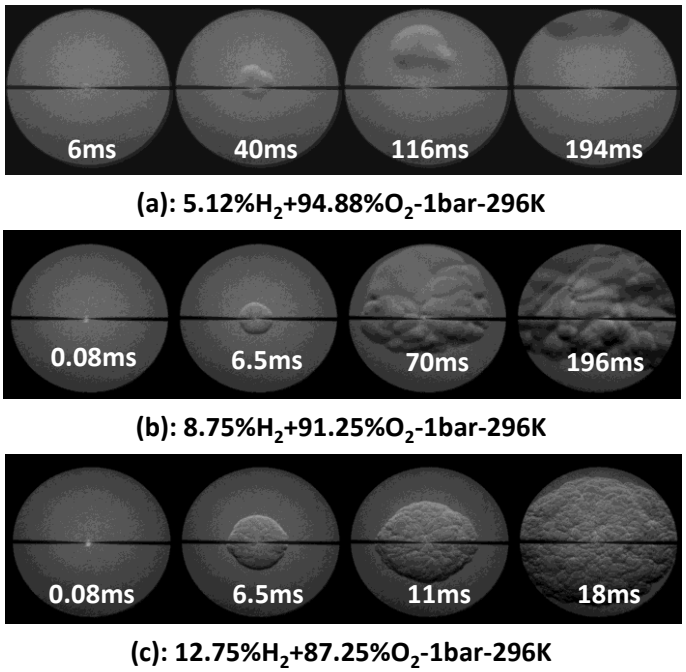


Figure 4 Type of lean flame propagation of H_2/O_2 mixture at 1bar and 296 K.

The evolution of the pressure inside the spherical bomb was also recorded for these 3 cases (Figure 5-a). In the case of {12.75 %H_2 + 87.25 % O_2}, the pressure inside the bomb increases as the flame propagates from the ignition center towards the walls of the vessel. When the pressure reaches the maximum value, the combustible mixture has been completely burnt. Indeed, this is verified by comparing the experimental maximum pressure (P_{max}) to the theoretical value calculated by assuming an adiabatic isochoric complete combustion (P_{AICC}). As one can see in figure 5-b, P_{max} and P_{AICC} are almost equal in this case which validate the assumption of a complete combustion. As the H_2 is lowered from 12.75 % down to 5.12 %, one can see that the pressure profile versus time is less

steep. Indeed it takes more time to combust the fresh gases and P_{max} drops drastically. One can see from figure 5-b that below 9 % of H_2 in the binary mixture, P_{max} becomes much lower than P_{AICC} which confirms that for these mixtures, the combustion is not complete since the flame does not propagates in all directions. The pressure history versus time and the comparison with the theoretical maximum pressure agree very well with the imaging observations.

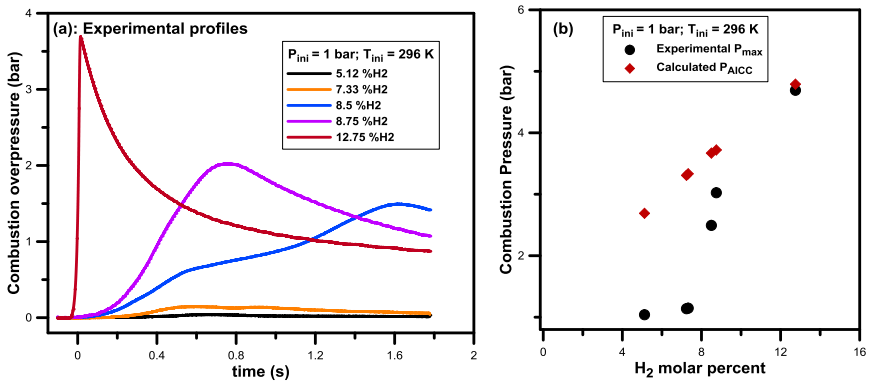


Figure 5 Evolution of the experimental combustion overpressure versus time (a) and theoretical (P_{AICC}) and experimental maximum pressure (P_{max}) versus the hydrogen molar percent (b). The mixtures were initially at 1bar and 296 K.

Impact of the initial Pressure on the flammability limits of H_2/O_2 mixtures

As the initial pressure is increased to 2bar, the probability function for the determination of the flammability limit is larger than the case of 1 bar. The LFL was found to be 4.3 % of H_2 (Figure 6). This value is nearly identical to the LFL obtained at 1 bar.

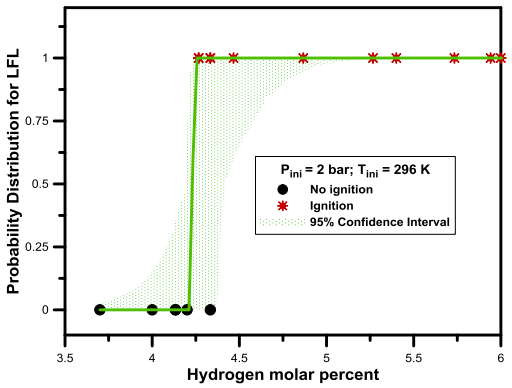
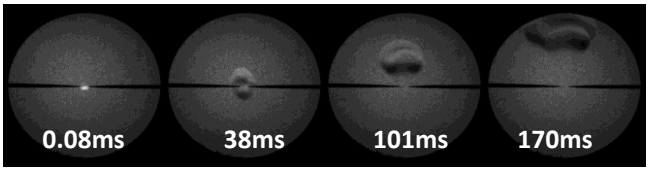
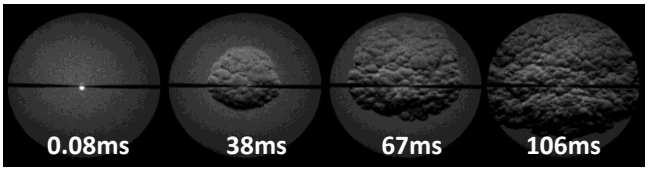


Figure 6 Probability distribution for tests of H_2/O_2 mixtures initially at 2 bar and 297 K.

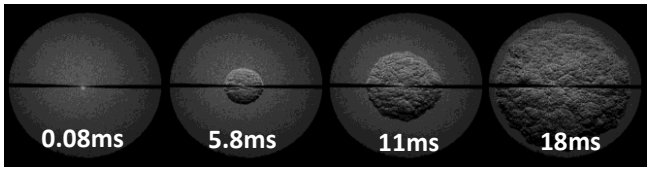
As for the different regimes observed at 2 bar, they are also very similar to the results obtained at an initial pressure of 1 bar (Figure 7). For very low H_2 molar percent (5.4 % of H_2), the flame propagate in the upward direction only while for the mixtures containing respectively 9.5 and 12.5 % of H_2, the flame propagates to the entire volume of the spherical bomb. The main difference between 1 and 2 bar cases is the wrinkling of the flame which is more pronounced for the 2 bar case.



(a): 5.4%H_2+94.6%O_2-2bar-296K



(b): 9.5%H_2+90.5%O_2-2bar-296K



(c): 12.5%H_2+87.5%O_2-2bar-296K

Figure 7 Type of lean flame propagation of H_2/O_2 mixture at 2 bar and 296 K.

The evolution of the combustion overpressure and the comparison between P_{max} and P_{AICC} are plotted in figure 8. As one can see, the maximum pressure depends strongly on the H_2 percent in the mixture, it increases strongly when the H_2 content is increased. Moreover, the time of combustion decreases as well when the H_2 percent increases. When comparing P_{max} to P_{AICC}, one can identify the conditions for which only a partial combustion is achieved due to the fact that flame could propagate only in the upward direction for H_2 percent lower than 9.5 %.

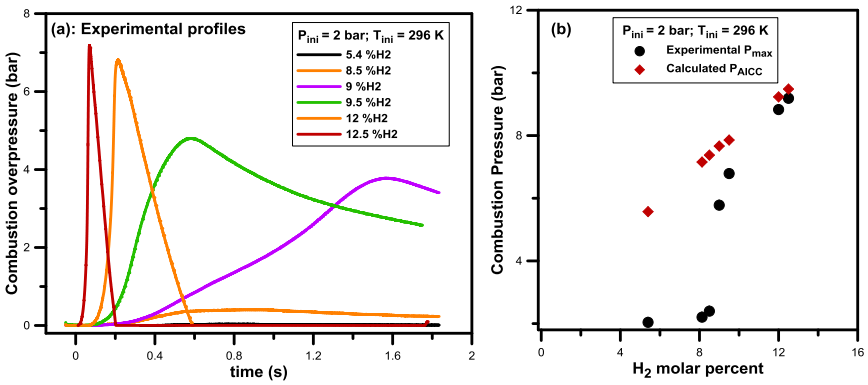


Figure 8 Evolution of the experimental combustion overpressure versus time (a) and theoretical (P_{AICC}) and experimental maximum pressure (P_{max}) versus H_2 molar percent (b). The mixtures were initially at 2 bar and 296 K.

Flammability limits of $H_2/O_2/N_2$ mixtures

The variation of the LFL of H_2/O_2 mixtures when N_2 is added to the mixtures has been studied by applying the same methodology as previously. Nitrogen was added to the binary mixtures gradually from 20 to 90%. At an initial pressure of 1 bar (Figure 9-a), when the N_2 content is between 20 and 80 % the LFL is hardly effected. A strong change in the flammability limit is obtained when the percentage of N_2 is higher than 80 % where the LFL increases from 4.3 % to 5.15 %. Above 90% of N_2 no ignition was obtained no matter what the H_2 molar percent was. This result is in very good agreement with the study of Kumar [6].

At an initial pressure of 2 bar, the same behavior is obtained, however it is only above 80 % of N_2 that the LFL varies strongly. As one can see from figure 9-b, the LFL remains at 4.3 % when the N_2 percent varies from 0 to 80 %. Above 80 % of N_2, the LFL increases rapidly when the diluent is increased. Finally, above 90% of N_2 no ignition was obtained no matter what the H_2 molar percent was.

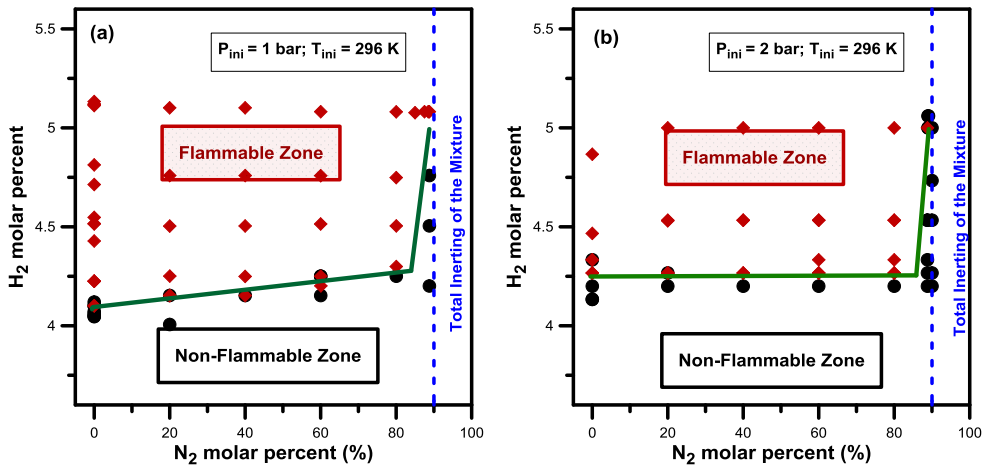


Figure 9 Evolution of the flammability limit with the N_2 dilution. (a): 1 bar and 296 K; (b): 2 bar and 296 K.

Close to the flammability limit, the flame propagation is limited since it propagates only in the upward direction and hence is responsible for a limited increase of pressure (Figure 10)

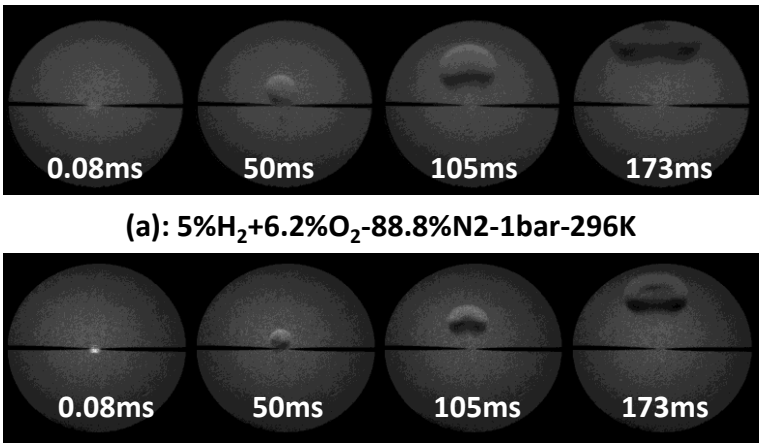


Figure 10 Typical flame propagation regimes for $H_2/O_2/N_2$ mixtures close to the flammability limit. (a): 1 bar and 296 K; (b): 2 bar and 296 K

The different flammability limits measured in this study are reported in table 1.

Table 1 Experimental lower flammability limits for $H_2/O_2/N_2$ mixtures at 296 K

N_2 (%mol)	P_{ini} = 1 bar	P_{ini} = 2 bar
0	4.1±0.1	4.3±0.2
20	4.3±0.1	4.3±0.2
40	4.4±0.1	4.3±0.2
60	4.4±0.1	4.3±0.2
80	4.5±0.1	4.3±0.2
88.8	5.0±0.3	5.0±0.2

Conclusions

During this work, the lower flammability limit (LFL) of $H_2/O_2/N_2$ mixtures have been investigated through the analysis of the flame propagation using the expanding flame in a closed spherical using both high speed imaging and pressure measurements at 1 and 2 bar initial pressure at room temperature. The lower flammability limit of H_2/O_2 mixtures agrees very well with the literature both at 1 and 2 bar. It was shown that close to the flammability limit, the flame propagation is limited to the upward direction and hence the combustion overpressure is very small compared to the theoretical value corresponding to complete isochoric combustion. This behavior is very important in the risk analysis of the containment of nuclear waste. It was shown that in order to modify substantially the LFL, large amount of N_2 needs to be added to the binary H_2/O_2 mixtures: at least 80 % of N_2 is needed for both initial pressures. The minimum of diluent in order to suppress any

combustion over the whole range of H_2/O_2 composition was found to be 90 %.
This work, which is still an ongoing investigation, will be extended to higher pressures (up to 4 bar) and to lower pressures (down to 0.3 bar). The effect of the initial temperature will also be investigated from 60 to 200°C.

Acknowledgments

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