Evaluation of flammability limits of H_2/O_2 mixtures in conditions relevant to nuclear waste transportation: pressure and nitrogen addition effects.

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1 Introduction

Determining the risk caused by hydrogen combustion hazard is a very important topic for industries and nuclear safety. 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 [1,2], 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 collaboration with the CEA. Since this study is only at the early stages, the results will focus on the initial pressure of 0.3, 0.5, 0.8, 1, 2, 3 and 4 bar at room temperature. The work will be continued with the investigation of the effect of a larger domain of different initial temperatures (from 60 to 200°)

2 Experimental setup and Methodology

The spherical bomb method has been chosen to study 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. 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 1.5 µF capacitor and a voltage of

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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. 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.
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.
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 10000 frames/s. The light source is 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 prepared 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 adiabatic, isochoric, complete combustion Cosilab code [3].

3 Results

Following our previous studies [4,5] and according to the literature [6,7], 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 labeled as flammable and a value of 1 is attributed to the test; (ii) if no ignition is observed, the mixture will be labeled 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 limits

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 flammability determination with logistic function [8] between ignition / no ignition tests is given in figure 1. From this distribution, the lower flammability limit is derived: for H_2/O_2 mixtures initially at 1 bar and 296 K, the LFL is equal to 4.1 % of H_2 which is in very good agreement with the literature [7].

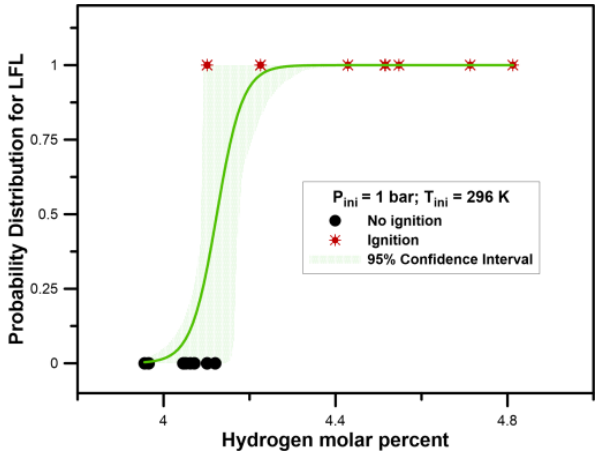

Figure 1. Probability distribution for tests of H_2/O_2 mixtures initially at 1 bar and 296 K

Pressure effect and regimes near the flammability limits

The initial pressure plays a very important role in flammability limits values. A variation of the pressure is able to increase or decrease the lower flammability limit. Table 1 show the hydrogen molar percent versus the initial pressure. Below 1 bar, a decrease in pressure results in a decrease of the flammability range and an increase in the pressure above 1 bar also contribute to reduce the flammability range of the mixture.

Table 1: Lean flammability limit versus pressure

Pressure (bar)	Hydrogen molar fraction
0.3	4.60±0.3
0.5	4.36±0.15
0.8	4.30±0.29
1	4.11±0.02
2	4.26±0.3
3	4.34±0.08
4	4.49±0.09

When the ignition takes place, the flame propagates and the subsequent pressure increase inside the spherical bomb depends strongly on the molar percent of hydrogen in the binary mixture H_2/O_2. As it is shown for example in Figure 2 for 0.8 and 1 bar, when the mixture is constituted of {5.12 %H_2 + 94.88 % O_2} and {5.5 %H_2 + 94.5 % 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} and {9 %H_2 + 91 % 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 11% for 0.8 bar and 12.75 % for 1 bar, 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.

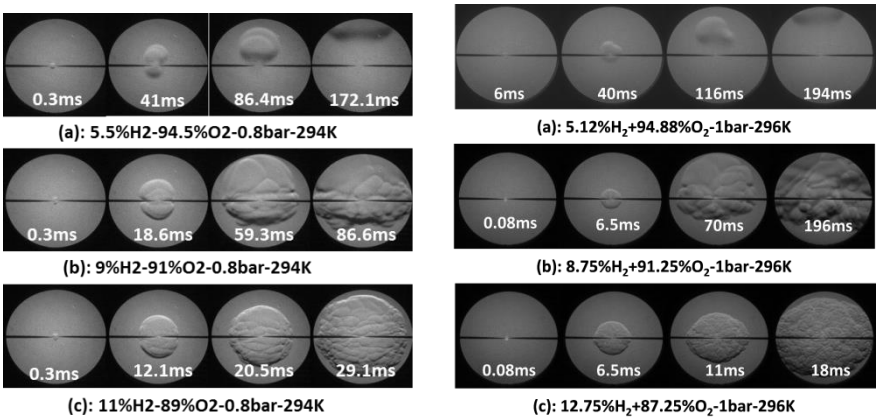

Figure 2. Type of lean flame propagation of H_2/O_2 mixture at 1bar and 296 K**.**

The evolution of the pressure inside the spherical bomb was also recorded for these 3 cases (Figure 3 and 4 left). In the case of {12.75 %H_2 + 87.25 % O_2} and {5.5 %H_2 + 94.5 % 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 3 right, 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 11% down to 5.5% for 0.8 bar and 12.75 % down to 5.12 % for 1 bar, 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 3 and 4 (left) 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.

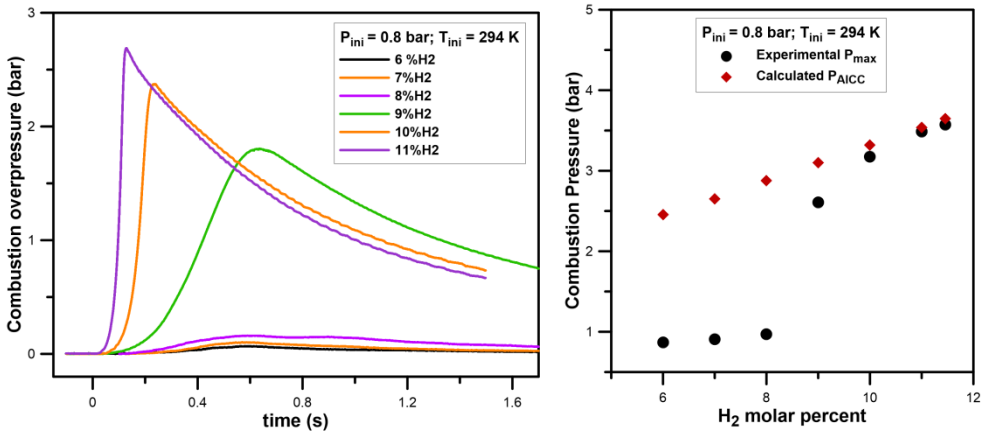

Figure 3. Evolution of the experimental combustion overpressure versus time (left) and theoretical (P_{AICC}) and experimental maximum pressure (P_{max}) versus the hydrogen molar percent (right) at 0.8 bar and 294K.

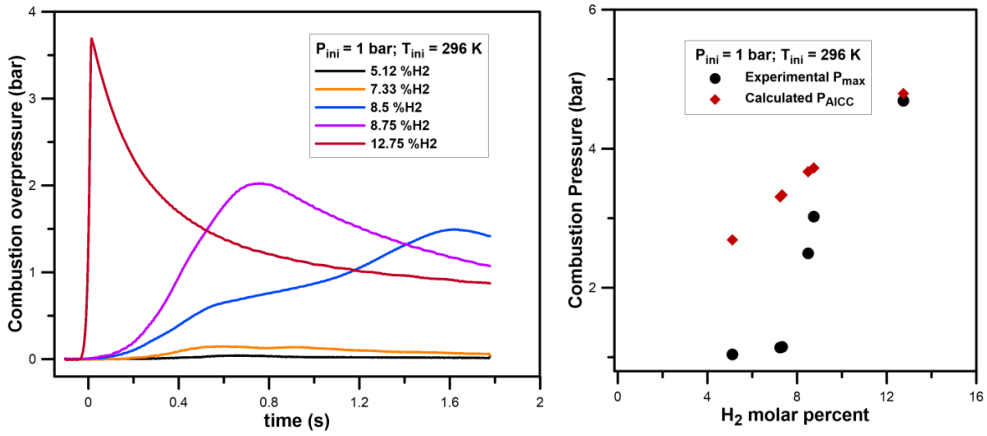

Figure 4. Evolution of the experimental combustion overpressure versus time (left) and theoretical (P_{AICC}) and experimental maximum pressure (P_{max}) versus the hydrogen molar percent (right) at 1 bar and 296K.

Effect of Nitrogen addition

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 at seven pressure conditions (0.3, 0.5, 0.8, 1, 2, 3, and 4). Nitrogen was added to the binary mixtures gradually from 20 to 90% for each initial pressure at 296K. Figure 5 shows an example of results obtained with 1 and 2 bar. At initial pressure of 1 bar (Figure 5 left), when the N_2 content is between 20 and 80 % the LFL is hardly affected. 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 [7]. 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 5 right, 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.

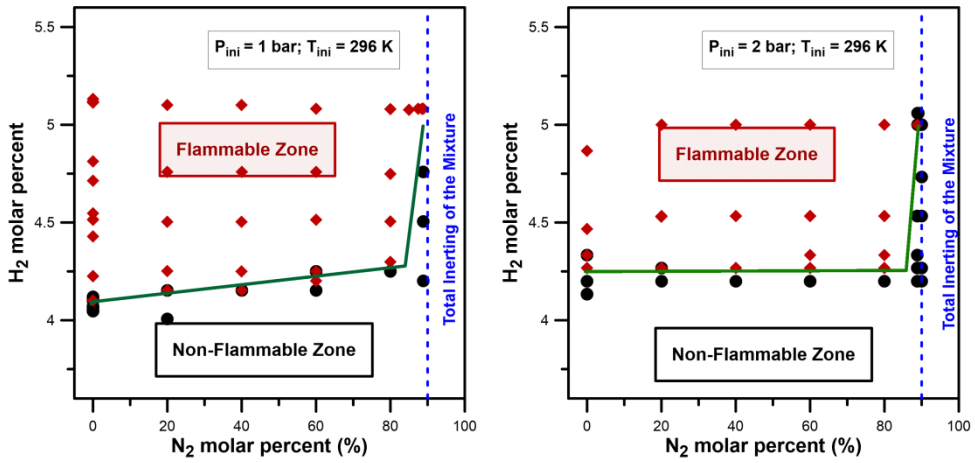

Figure 5. Evolution of the flammability limit with the N_2 dilution. (Left): 1 bar and 296 K; (Right): 2 bar at 296 K.

4 Conclusions

This work summarizes experimental investigations on the lower flammability limits (LFL) of $H_2/O_2/N_2$ mixture at seven pressure conditions and room temperature in a closed spherical using both high speed imaging and pressure measurement. New data were acquired (at 0.3, 0.5, 0.8, 2, 3 and 4 bar) and completed the existing ones (1 bar). The lower flammability limit of H_2/O_2 and $H_2/O_2/N_2$ mixture agree very well with the literature at 1 bar [7]. 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. This work, which is still an ongoing investigation, will be extended to higher temperatures (up to 200°C). A full analytical study will be carried out to demonstrate correlation with the effect of pressure and temperature.

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