Expanding the boundaries of the explosion risk assessment for H_2/O_2/N_2 mixtures in conditions relevant to radioactive materials transportation

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EXPANDING THE BOUNDARIES OF THE EXPLOSION RISK ASSESSMENT FOR $H_2/O_2/N_2$ MIXTURES IN CONDITIONS RELEVANT TO RADIOACTIVE MATERIALS TRANSPORTATION

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ABSTRACT

The aim of the paper is to present the major results of a three years study which goal was to assess the risk of explosion due to hydrogen accumulation in closed containments used for the transportation of radioactive materials. To do so, an experimental work on the flammability domain of multiple ternary $H_2/O_2/N_2$ mixtures has been conducted at the CNRS-ICARE laboratory in collaboration with the CEA.

The flammability limits of $H_2/O_2/N_2$ mixtures were assessed using two spherical bombs equipped with a central ignition system consisting of two tungsten electrodes linked to a controlled high voltage discharge device. The combustion is monitored using two different diagnostics: pressure measurements during the combustion test and the recording of the flame with a high-speed camera. A mixture is considered as flammable when both the imaging and the pressure indicate a successful ignition followed by a flame propagation.

The first part of the study has been focused on the precise determination of lower flammability limits of $H_2/O_2/N_2$ mixtures at a wide range of pressure (from 0.3 bar up to 4 bar) and for different initial temperatures ranging between 25°C and 100°C. The limit of the total inerting of a H_2/O_2 mixture by N_2 has also been determined. In addition, the lower flammability limits of $H_2/Air/H_2O_{vapor}$ mixtures has also been studied from 0.3 bar to 2 bar and from 25°C up to 200°C.

The study has then been extended to the flammable domain close to the lower flammability limit and up to hydrogen concentration of 13%. The visualization of the flame coupled with the pressure monitoring has allowed the observation and characterization of three sub-domains, each one with very specific behaviour in terms of combustion parameters (maximum overpressure, explosion index).

The first sub-domain close to the lower flammability limit allows the introduction of a new limit for the study of hydrogen risk in nuclear transport safety studies: the explosion severity low limit. Indeed, in this domain beginning after the low flammability limit, the overpressure stays very limited and opens a new way of considering safety studies related to hydrogen risk of explosion.

INTRODUCTION

Determining the risk caused by hydrogen combustion hazard is a very important topic for the nuclear safety analysis of transport packages. In closed containments used for the transportation of radioactive materials, hydrogen can be produced by the radiolysis of different materials, and also by the thermal decomposition of organic components of the content.
Usually in the transport package safety report, 2 parameters need to be determined for the H_2 risk assessment: the production rate of H_2 by the aforementioned mechanisms and the time to reach the Lower Flammability Limit (LFL) of H_2 within the containment; this sets whether the transport can be operated without H_2 risk or if others means have to be implemented to limit the risk of H_2 ignition.
The first parameter, the production rate of H_2 can vary depending on the containment type and on the state of the material/waste being transported; this will not be discussed in this paper.
The second parameter, the LFL of H_2, should be considered in conditions of pressure and temperature relevant to radioactive materials transportation, in air but also for different N_2/O_2 ratios and for different diluents such as water vapor. But so far, the experimental determination of H_2 Lower Flammability Limit was limited to atmospheric pression and 2.5 bar, the effect of pressure on LFL was limited to ambient temperature and the differences between both experimental set up and the methods used did not ease the comparisons. That's why, in order to cover a large pressure domain including sub-atmospheric values as well as a range of initial temperatures higher than the ambient one, an experimental work on the flammability domain of multiple ternary mixtures containing H_2, O_2, and N_2 has being conducted over a 3 years period at the CNRS-ICARE laboratory, within a collaboration with the CEA.
In the first part of this paper, the most important results are reported concerning the precise measurements of LFL for $H_2/O_2/N_2$ mixtures for a wide range of thermodynamics conditions. In a second part, the combustion parameters of these mixtures are studied in the flammable domain close to the LFL and up to hydrogen concentration of 13%, which leads in the end to a new way of processing hydrogen risk assessment by considering a more relevant limit than the LFL for transport safety analysis.

EXPERIMENTAL SETUP

The spherical bomb method has been chosen to study the flammability limits of $H_2/O_2/N_2$ mixtures. It consists of double-wall stainless steel spherical vessel (one 8 L bomb and one 56 L bomb) regulated at a given temperature using thermal fluid. The maximum operating pressure and temperature are respectively 50 bars and 150°C for the 8 L bomb and 50 bars and 250°C for the 56 L bomb. Two tungsten electrodes were located along a diameter of the sphere (Fig. 1). A more detailed presentation of the experimental setup is given in [1].

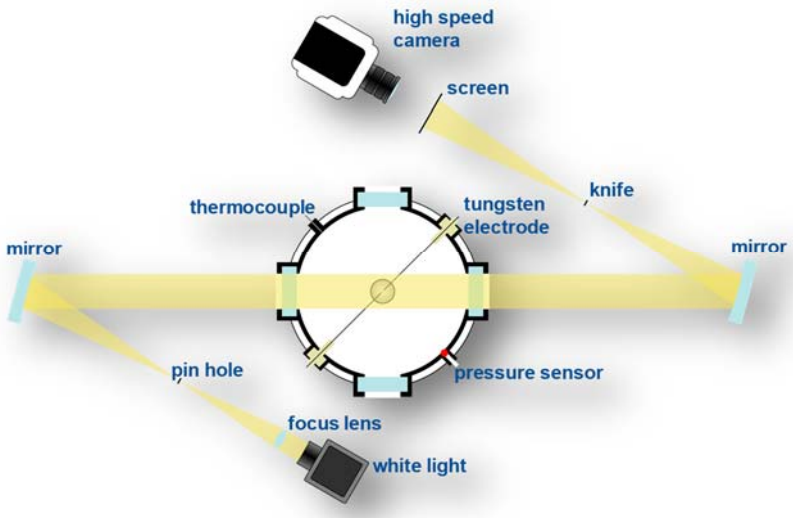

Figure. 1. Schematic diagram of the experimental setup for the Z-type Schlieren visualization.

The 2 electrodes are linked to a controlled high voltage discharge device (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. The estimation of the delivered energy to the spark is obtained from the temporal integration of the product of U*I.

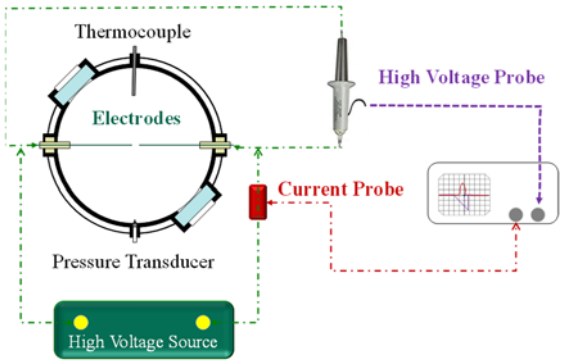

Figure. 2. Schematic of the ignition system coupled with the spherical vessel.

The ignition and the flame propagation are visualized through a classical Z-type Schlieren setup with a high-speed camera. The initial gas temperature inside the bomb is monitored via a thermocouple before each run.

The gases were prepared directly in the bomb using the partial pressure method to obtain the desired mixture. Hydrogen, air were supplied by Air Liquide with a purity better than 0.9999. 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 [6].

METHODOLOGY

Following our previous studies and according to the literature [3, 4, 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.

For each condition of initial temperature and pressure, a probability density function is plotted (Fig. 3) using a logistic function [7] from which the lower flammability limit is derived at the 50% threshold.

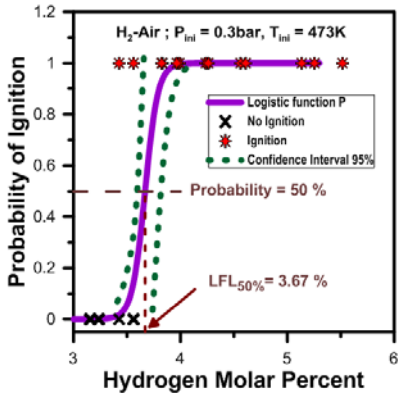

Figure. 3. Probability distribution for tests of H_2/O_2 mixtures initially at 2 bar and 297 K.

RESULTS

Lower Flammability limits in conditions relevant to radioactive materials transportation

Following the methodology described previously, thousands of tests have been performed with $H_2/O_2/N_2$ mixtures in the 8 L bomb in order to determine the H_2 LFL on a wide range of pressure, temperature and N_2 dilution (Table 1):

Table 1. Detail of the tests performed on $H_2/O_2/N_2$ mixtures for LFL determination depending on temperature, pressure and N_2 dilution.

T(K)	P_{ini} (bar)	N_2 dilution				
		0%N_2	20%N_2	40%N_2	60%N_2	80%N_2
294±2	0.3	140	88	80	84	82
	0.5	76	82	74	80	82
	0.8	98	90	88	102	96
	1	130	135	128	140	123
	2	76	74	68	64	75
	3	87	76	81	74	82
	4	62	74	68	82	60
333±1	0.3	135	-	-	-	131
	1	116	-	-	-	133
	2	128	-	-	-	114
373±1	0.3	118	-	-	-	143
	1	94	-	-	-	96
	2	113	-	-	-	91
Number of tests performed		**1373**	**619**	**587**	**626**	**1308**

Moreover, above a critical molar percentage of N_2, the inerting content is reached and suppress totally the combustion. For each couple of (P,T) mentioned in Table 1, the inerting molar percentage of N_2 has been determined and results are given in the following table:

Table 2. Inerting molar percentage of N_2 above which no combustion is possible in $H_2/O_2/N_2$ mixture

T_{ini}(K)	0.3 bar	0.5 bar	0.8 bar	1bar	2bar	3bar	4bar
294±2	82.7±0.1	87.2±0.1	87±0.1	88.8±0.1	88.8±0.1	88.6±0.1	88.6±0.1
333±1	86±0.1	-	-	89±0.1	88.8±0.1	-	-
373±1	87.75±0.1	-	-	89.75±0.1	90±0.1	-	-

The flammability limits of $H_2/O_2/N_2$ have been determined to understand the effect of initial temperature and pressure. Figure 4 (a and b) illustrates the variation of the LFL as we change the initial conditions on pressure and temperature:

- At low pressure (P<1 bar), an increase in pressure leads to a decrease in LFL and an increase in pressure at high pressure (P>1 bar) leads to an increase in LFL. For example, for a temperature of 294K (Figure 4a), the LFL decreases from 4.51%H_2 (0.5 bar) to 4.12%H_2 (1 bar). When the pressure is increased from 1bar to 4bar, the LFL increases from 4.12%H_2 to 4.75%H_2.This evolution of the LFL is also observed by Kumar [8] for H_2/O_2 at 0.5 bar (4.6%H_2) and 1 bar at (4%H_2) mixtures.
- contrary to pressure, an increase in temperature at any pressure induces a decrease in LFL (Figure 4b) as can be observed in the literature [9,10,11].

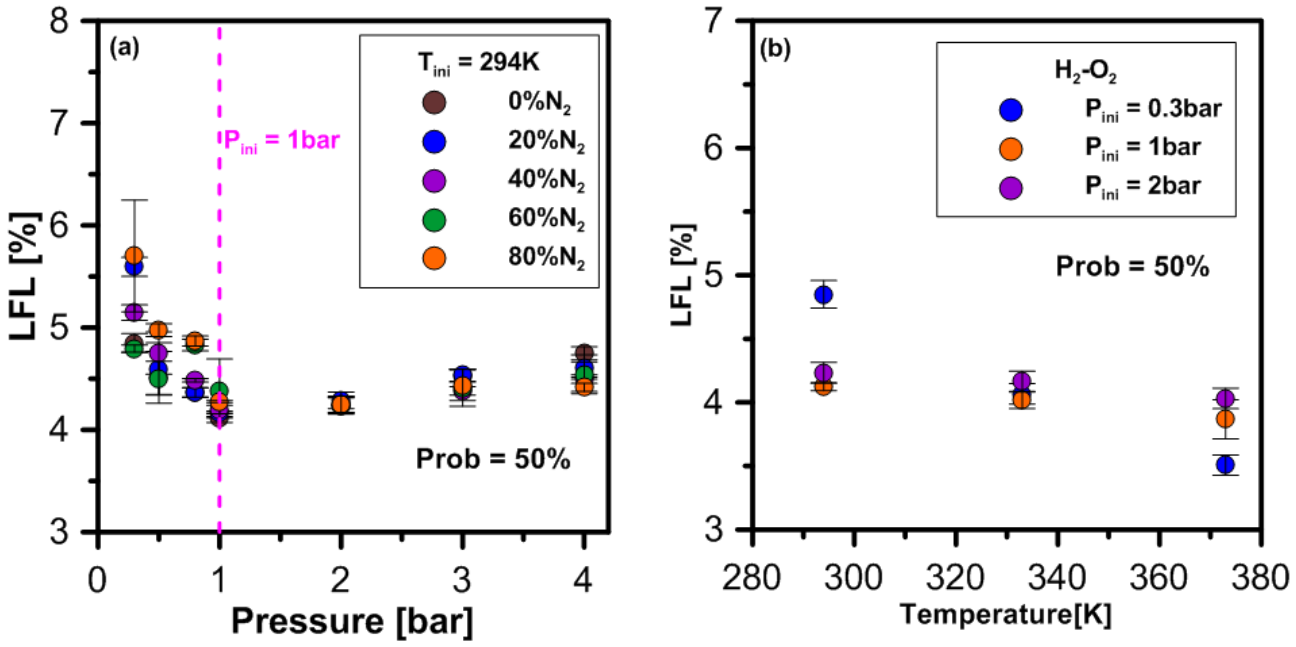

Figure 4. Evolution of the LFL as a function of pressure for 5 dilutions conditions in N_2 at 294K (a) and as a function of temperature for three pressure conditions (0.3, 1 and 2 bar) (b).

Another part of the work has focused on H_2/Air/H_2O_{vapor} mixtures in the 56 L bomb over the following range of pressure, temperature and water vapor dilution:

- 0.3, 1 and 2 bar
- 300, 373, 423 and 473 +/- 1 K
- H_2O_{vapor} of 0 and 40% (except at 300 K).

The main results of this study have already been presented in [2].

Study of combustion parameters in $H_2/O_2/N_2$ mixtures close to the lower flammability limit and up to hydrogen concentration of 13%.

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 5, 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 only 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.

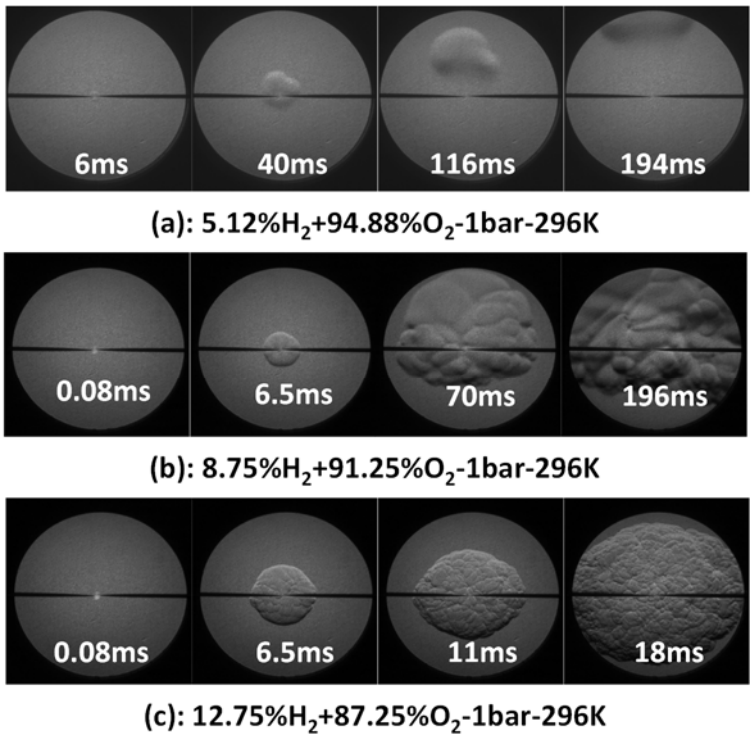

Figure 5. Type of lean flame propagation of H_2/O_2 mixture at 1bar and 296 K.

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}).
The evolution of the combustion overpressure and the comparison between P_{max} and P_{AICC} are plotted in figure 6.
As one can see, the maximum pressure depends strongly on the H_2 percent in the mixture and 3 main areas can be distinguished with strong differences in combustion behavior : in the first area from the LFL and up to ~8% of H_2, the partial combustion of the fresh combustible mixture only leads to an overpressure limited to ~40% of P_{AICC}. Then, in a second area, a change is observed as the combustion becomes more and more complete: the overpressure rapidly grows to reach up to 90% of P_{AICC}. In the third area, the combustion is complete and the overpressure observed nearly equals P_{AICC}.

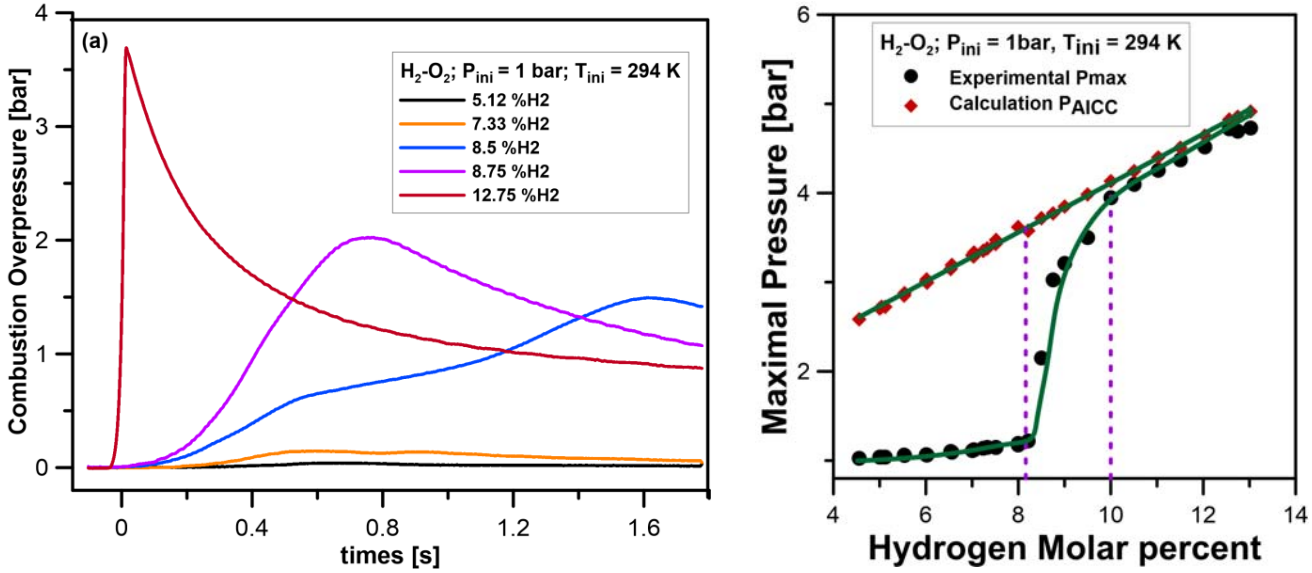

Figure 6. Evolution of the experimental combustion overpressure versus time (a) and theoretical (P_{AICC}) and experimental maximum pressure (P_{max}) versus H_2 molar percent (b). The mixtures were initially at 1 bar and 294 K.

The effect of N_2 dilution on the overpressure behavior is weak, as shown in figure 7.

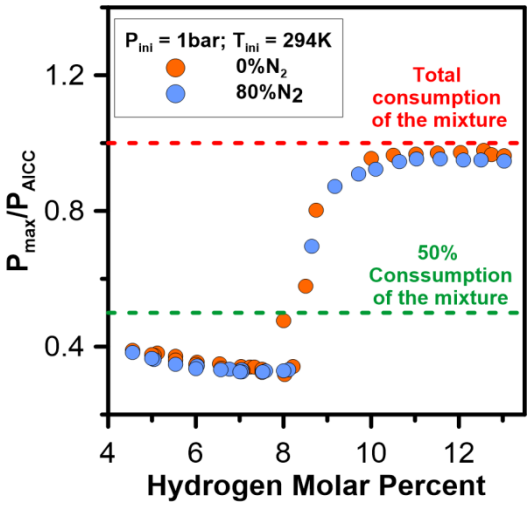

Figure 7. Evolution of the ratio of maximum pressures as a function of the molar fraction of hydrogen: effect of the addition in percentage of nitrogen.

Introducing a new limit to study H_2 explosion risk assessment for nuclear safety transportation.

Another key parameter to look after for the safety of the transport package is the speed of the overpressure; as shown in figure 8, 2 different areas can be easily distinguished: in the first area from the LFL and up to 8/10% of H_2 (depending on P, T and $H_2/O_2/N_2$ mixture), the speed pressure stays very weak and follows a linear behavior. On the contrary, in the second area, the speed pressure grows suddenly and follows roughly a linear behavior.
The limit between these 2 areas is called the **Lower Severity Explosion Limit (LSEL)**: indeed, below the LSEL (and above the LFL), even though a flame is created in the mixture, the combustion stays partial and this limits tremendously the impact this combustion can have on its close environment: the severity of the mixture is not significant. It is only above the LSEL that the impact of H_2 combustion has really to be taken into account as a potential damage to the transport package. The LSEL can be determined at the crossing of the 2 straight lines representing the evolution of the speed pressure in each area.

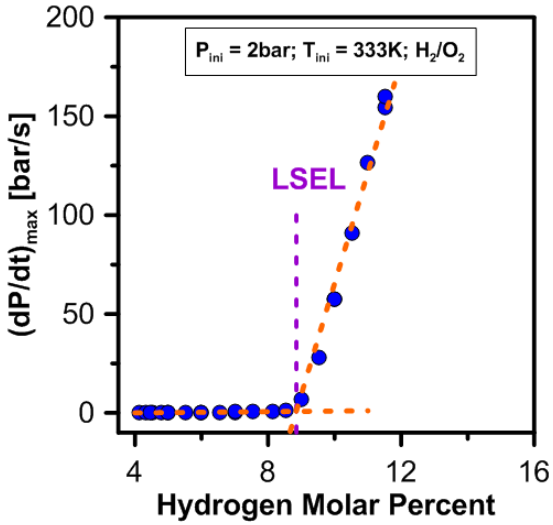

Figure 8. Evolution of the experimental combustion overpressure speed versus H_2 molar percent and determination of the LSEL. The mixtures were initially at 2 bar and 333 K.

In order to use the results independently from the volume of the bomb, the overpressure speed is usually multiplied by the cubic root of the volume of the bomb and this parameter is called the explosion index K_g.

The behavior of K_g is shown in the figure 9 where we can easily see that LSEL does not change significantly with P or T.

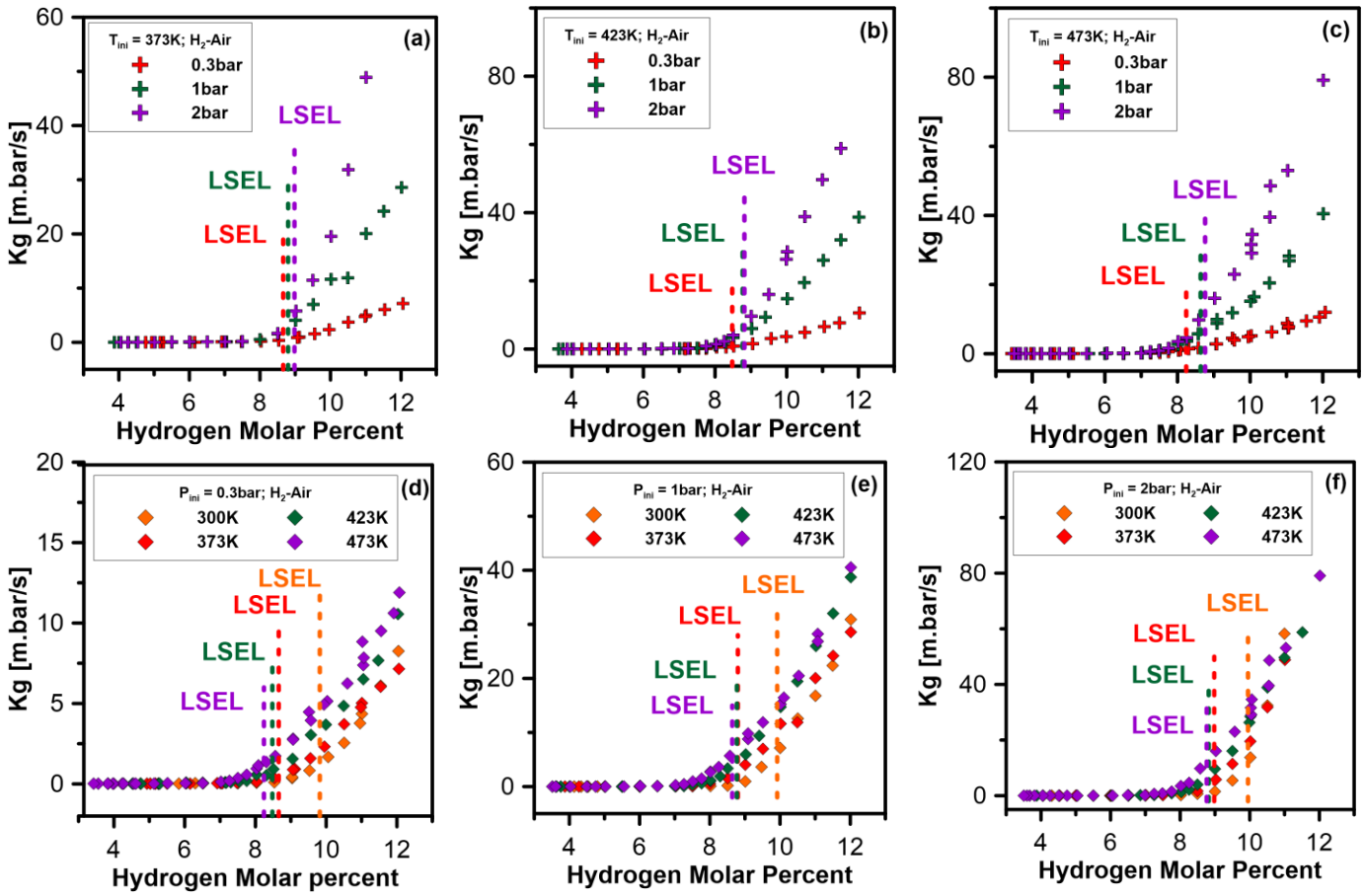

Figure 9. Evolution of the explosion index Kg versus H_2 molar percent and determination of the LSEL for different pressures, temperatures on H_2/Air mixtures.

CONCLUSIONS

The 3 years period experimental work presented on H_2 Lower Flammability Limit (LFL) covers a wide range of pressure, temperature and diluents relevant of radioactive materials transportation conditions. The results have been obtained following the same methodology that is sound and robust so the results have a good accuracy and can be directly compared.

Moreover, close to the LFL, the study of the flame propagation regimes and the data acquired have shown even more interesting results concerning the knowledge of the hydrogen combustion phenomena: above the LFL and up to a new limit called the Lower Severity Explosion Limit (LSEL), the severity of the H_2 mixture is not significant because of an incomplete combustion of H_2 which mechanical consequences can be easily absorbed by a transport package. It is only above the LSEL that the impact of H_2 combustion has really to be taken into account as a potential damage to the transport package. This new limit is set between 8 to 10 % of H_2 (depending on P, T and $H_2/O_2/N_2$ mixture). Correlations will be constructed and given to derive the severity limit based on the mixture (diluted or not) and for different thermodynamic conditions.

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REFERENCES

[1] K. N'Guessan, M. Idir, N. Chaumeix, J. Pavageau and T. Cuvillier, Evaluation of flammability limits of $H_2/O_2/N_2$ mixtures in conditions relevant to nuclear waste transportation, Proceedings #1053 of the 18th PATRAM, September 18-23, 2016, Kobe, Japan

[2] K. N'Guessan, N. Chaumeix, J. Pavageau and T. Cuvillier, Effects of pressure and temperature on the flammability limits of H_2 based mixtures relevant to nuclear transport conditions, Proceedings #18032 of the 2018 Waste Management Symposium, March 18-27, 2018, Phoenix, Arizona, USA

[3] H. Cheikhravat, N. Chaumeix, A. Bentaib, C.-E. Paillard, "Flammability Limits of Hydrogen-Air Mixtures", Nucl. Technol., 178 (1), pp. 5–16 (2012).

[4] C. J. Coronado, J. A. Jr Carvalho, J. C. Andrade, E. V. Cortez , F. S. Carvalho, J. C. Santos, A. Z. Mendiburu, "Flammability limits: a review with emphasis on ethanol for aeronautical applications and description of the experimental procedure", J. of Hazardous Materials, 241-242, 32-54 (2012).

[5] J. Biet, M. Ndem, M. Idir and N. Chaumeix, "Ignition by electric spark and by laser-induced spark of ultra-lean CH4/air and CH4/CO2/air mixtures at high pressure", Combustion Science and Technology, 186 (1), pp. 1-23, 2014

[6] COSILAB, The combustion simulation laboratory. (2017). Version 4.1.1. http://www.rotexo.com

[7] S.P.M. Bane, J.L. Ziegler, P.A. Boettcher, S.A. Coronel, J.E. Shepherd, "Experimental investigation of spark ignition energy in kerosene, hexane, and hydrogen", Journal of Loss Prevention in the Process Industries, 26 (2), 290-294 (2013).

[8] R.K. Kumar, J. Fire Sci., 3, 245-262 (1985).

[9] S.Kondo, K. Takizawa, A. Takahaki, K. Tokuhashi, On the temperature dependence of flammability limits of gases, Journal of Hazardous Materials, 187, 585-590, 2011.

[10] I. A. Zlochower, Experimental flammability limits and associated theoretical flame temperatures as a tool for preding the temperature dependence of these limits, Journal of Loss Prevention in the Process Industries, (25), 555-560, 2012.

[11] Schroeder V., Holtappels K., Explosion Characteristics of hydrogen-Air and Hydrogen-Oxygen Mixtures at elevated Pressures, 2005.