DETONABILITY OF BINARY H2 / CH4 -AIR MIXTURES

O. Bozier, R. Sorin, F. Virot, R. Zitoun, D. Desbordes

Laboratoire de Combustion et de Détonique UPR 9028 CNRS, Poitiers, (France),
florent.virot@lcd.ensma.fr

ABSTRACT

Abatement of greenhouse gas emissions and diversification of energy sources will probably lead to an economy based on hydrogen. In order to evaluate safety conditions during transport and distribution, experimental data is needed on the detonation of Hydrogen/Natural gas blend mixtures. The aim of this study is to constitute detonation and deflagration to detonation transition (DDT) database of H_2/CH_4-air mixtures. More precisely, the detonability of such mixtures is evaluated by the detonation cell size and the DDT run up distance measurements. Large experimental conditions are investigated, (i) various equivalence ratios Φ from 0.6 to 3, (ii) various H_2 molar fraction x ($x = H_2/(H_2 + CH_4)$) from 0.5 to 1, (iii) different initial pressure P_0 from 0.2 to 2 bar at fixed ambient temperature T_0=293 K. Detonation pressures P, velocities D and cell sizes λ were measured in two smooth tubes with different i.d. d (52 and 106 mm). For DDT data, minimum DDT run up distances L_{DDT} were determined in the d=52 mm tube containing a 2.8 m long Schelkin spiral with a blockage ratio BR = 0.5 and a pitch equal to the diameter. Measured detonation velocities D are very close to the Chapman Jouguet values (D_{CJ}). Concerning the effect of Φ, detonation cell size λ follows a classical U shaped-curve with a minimum close to Φ=1 and concerning the effect of x, λ decreases when x increases. The ratio $k = \lambda/L_i$ obtained from different chemical kinetics (L_i being the ZND induction length) is well approximated by the value 40 in the range $0.5 < x < 0.9$ and 50 for $x \geq 0.9$. Minimum DDT run up distance L_{DDT} varies from 0.36 to 1.1m when x varies from 1 to 0.8. The results show that L_{DDT} obeys the linear law $L_{DDT} \sim 30\text{-}40\lambda$, previously validated in H_2/Air mixtures. Adding Hydrogen in Natural Gas promotes the detonability of the mixtures and for $x \geq 0.65$ these mixtures are considered more sensitive than common heavy Alkane-Air mixtures.

NOMENCLATURE

BR	Blockage ratio
D	Detonation velocity
d	Diameter
E	Energy
k	Ratio λ/L_i
L	Length
P	Detonation pressure
T	Temperature
x	Molar fraction of H_2 in H_2/CH_4
λ	Detonation cell size

Subscripts

0	Initial value
c	Critical value
CJ	Chapman Jouguet value

DDT	Deflagration to detonation transition value
front	extrapolated value at the detonation front
i	ZND induction
spiral	Value inside the spiral

A&A

3D	3 Dimension
CJ	Chapman Jouguet
ZND	Zel'dovich, Von Newman, Döring
DDT	Deflagration to Detonation Transition

INTRODUCTION

The future candidate envisaged for classical fuel replacement to reduce greenhouse effects is a H_2/CH_4 blend. The transport and distribution by pipelines of this new fuel may use the existing natural gas network. From explosion safety point of view, difficulties arise concerning the use of H_2 fuel alone because of its extreme detonability with air. Fortunately and at the opposite, natural gas and more precisely pure CH_4, presenting the best hydrogen/carbon ratio among classical hydrocarbons, is by far the lowest detonable fuel with air. The blend of these two gases with a maximum volume ratio of H_2 may constitute a safe fuel from the explosion hazard point of view. So, the knowledge of combustion and detonation characteristics of hydrogen/methane - Air mixtures (with a volume ratio of H_2 in the fuel higher than 0.5) is needed to define a maximum value of x for safety and to permit correct sizing of distribution devices. Moreover, safe applications need data on the possibility of self explosion with air in the case of high pressure fuel release or in the case of low energy initiation (electric spark) of accidental hazardous mixtures and the occurrence of deflagration to detonation transition (DDT).

In a general way, fuel - Air mixtures detonability can be quantified on the basis of the so-called detonation dynamic parameters, namely: (i) the limiting tube diameter d_l corresponding to the detonation propagation limit mode in a tube (spinning detonation), (ii) the critical diameter d_c of successful self sustained detonation transmission from a tube to open space, (iii) the critical point energy E_c for direct initiation of detonation and (iv) the deflagration to detonation transition length L_{DDT}. These parameters can currently be evaluated by using a length scale corresponding to the detonation cell size λ. Thus, the limiting diameter for detonation propagation limit mode is given by the $\pi d = \lambda$ relationship. This limit becomes $d \approx \lambda$, for obstacle-laden tube with perforated plates, d being the diameter of the open orifice of obstacles. The critical diameter d_c required for a self sustained detonation successful transmission from a tube to a larger volume was determined first by Mitrofanov and Soloukhin [1], and can be written as $d_c = 13\lambda$ for $C_nH_m/O_2 - H_2/O_2$ mixtures. This parameter becomes larger, $d_c \approx 24\lambda$, for mixtures close to the stoichiometry with air as oxidizer (Schultz et al [2], Ciccarelli [3], Desbordes [4]). According to the criterion of Zeldovich et al. [5], the critical initiation energy is proportional to a minimum volume scaled by λ^3, i.e. $E_c \propto \lambda^3$. In the laden obstacle tubes, the DDT length can also be used as a criterion for the detonability of a reactive mixture. It has been shown recently [6] that, for a given d/λ, the ratio L_{DDT}/λ remains roughly constant for various mixtures with different reduced activation energy but of the same cell size. Results yielded an estimation of the necessary length for the onset of detonation, $L_{DDT} \approx 30\lambda$ for $d/\lambda = 2$. In this case, DDT is mainly governed by compressibility effects and poorly by transport effects. Consequently, the cell size is considered as the main detonability scaling parameter. If λ is known for H_2/Air and stoichiometric CH_4/Air mixtures, there is a lack of experimental data on detonation characteristics especially on cell sizes for binary H_2/CH_4 fuel - Air mixtures.

In the literature, the works devoted to detonation or to DDT characteristics of binary fuel - Air mixtures remain still rare. Takita et al. [7] were interested in detonation characteristics of H_2/CH_4 - Air, H_2/C_3H_8 - Air and CH_4/C_4H_{10} - O_2 mixtures. They measured detonation velocities and detonation limits in a small tube (10 mm i.d.), i.e. around cell size of stoichiometric H_2 - Air mixture. In their case, the cellular structure was larger than the tube diameter. Consequently, the detonation propagation was strongly influenced by the wall. In connection with safety of some industrial chemical processes involving no pure commercial fuels, Matignon et al. [8] studied detonation in a tube (52 mm i.d. and 7 m long) of two fuels blend with O_2 and diluted by N_2 (up to the air) of very different detonability (H_2/CH_4 and H_2/C_2H_6). Particularly, they noticed the great influence of CH_4 volume proportion in H_2/CH_4 on cell size λ especially if N_2 dilution is large. For instance, for stoichiometric H_2/CH_4 – O_2 mixtures at ambient temperature and pressure conditions, λ varies from 1.4 to 3 mm while for Air mixtures it varies from 8-10 to 280-300 mm. This study shows that the detonability of binary fuel – Air mixtures is rather influenced by the heavier fuel. Besides, detonation properties measurements of stoichiometric CH_4/H_2 - Air, C_3H_8/H_2 - Air and CH_4/C_3H_8 - Air mixtures were undertaken by Komori et al. [9] in a 100 mm i.d. and 2 m long tube. Their results show, for CH_4/H_2 - Air mixtures, an increase of cell size λ as the mole fraction of CH_4 in the fuel increases, and follow in outline the conclusion of Matignon et al. [8]. λ varies from 8-10 to 75 mm for CH_4 ratio ranging from 0% to 40%. Moreover for CH_4 mole fractions higher than 50%, it becomes increasingly difficult to obtain detonation. They compare λ with induction length calculated by using GRI-MECH 3.0 mechanism [10] and estimate that the λ/L_i ratio remains constant and is about 46 ± 10 for CH_4 mole fraction below 40%. Moreover, Sorin et al. [6] present data on DDT of H_2 - Air mixture at ambient condition in a 26 mm i.d. tube containing a spiral of blockage ratio (BR) of 0.5. They found that run up distance for detonation onset L_{DDT} is approximately equal to 37 cm. In addition Kuznetsov et al. [11] show that for stoichiometric CH_4 - Air mixtures at ambient conditions, the run up distance is equal to 12 m, that is 32 times higher than H_2 - Air L_{DDT}. This length was obtained in a tube of 520 mm i.d. and with orifice plate obstacles of BR = 0.3. Despite the difference of tube diameter, close to limit value of diameter related to criterion of existence of detonation in a tube [12], we can observe that H_2 is more sensitive than CH_4 to detonation in air. No data concerning detonability of binary mixture of H_2/CH_4 with air are up to now available.

OBJECTIVES.

In this work the detonation cell size λ and the run up distance L_{DDT} are measured at ambient temperature (T_0 = 293 K) in order to evaluate the detonability of the binary mixtures H_2/CH_4 – Air. The composition of the studied mixtures follows the formula:

$$\Phi\left[xH_2+(1-x)CH_4\right]+(2-1.5x)(O_2+3.76N_2), \tag{1}$$

where the equivalence ratio Φ ranges from 0.6 to 3 and the molar fraction x of H_2 in fuel varies from 0.5 to 1. x is given by:

$$x=\frac{H_2}{H_2+CH_4}, \tag{2}$$

The initial pressure P_0 of the mixture can be varied from 0.2 to 2 bar.

For detonation, to ensure that the cell size corresponds to the self-sustained detonation regime, the velocity D and pressure P are measured and compared to the calculated CJ values. A correlation between λ and L_i and between L_{DDT} and cell size λ are provided. L_i is the ZND induction length calculated using seven different detailed chemical kinetic schemes

EXPERIMENTAL DEVICES.

To measure detonation characteristics of binary fuel H_2/CH_4 with air, experiments were carried out in two stainless steel cylindrical tubes of different i.d d : d = 52 mm and 106 mm and of 9 m length. Each tube has a driver section (cf. Fig. 1) of 50 cm (or 1 m) long separated from the main tube by a thin Mylar foil (thickness 80 µm) in order to facilitate detonation initiation and to obtain self-sustained regime in the main tube. Pressure transducers (1µs rise time Kistler 603B) and a smoked foil are installed at the end of the tube.

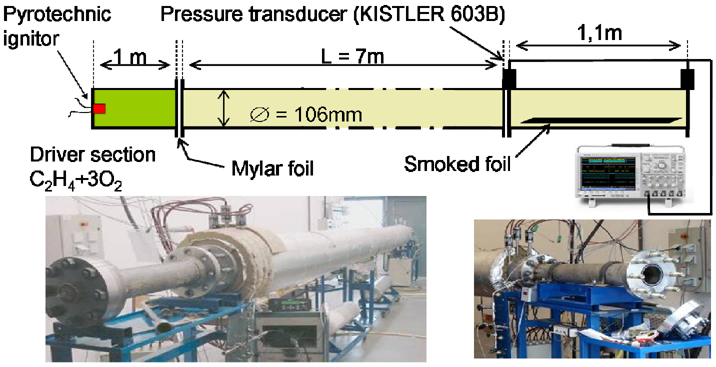

Figure 1: One of the experimental devices. i.d. 106 mm.

The self-sustained detonation velocity *D* and pressure *P* are obtained from pressure signals (cf. Fig. 2) and the cell size λ from smoked plate records (cf. Fig. 3). An example of pressure records is displayed in Fig. 2.The level of the first pressure peak in the detonation reaction zone has no meaning because, in our study, λ is at least two times larger than the pressure transducer sensitive surface size (diameter = 5 mm). Thus according to the position of the sensor compared to the cellular structure, the signal of pressure will differ and the peak of pressure cannot be compared with the CJ pressure. Nevertheless the pressure history behind the detonation front in the expansion of detonation products is reproducible. The determination of detonation front pressure can be obtained from the extrapolated value of the back pressure pseudo-plateau to the detonation front. This extrapolated value P_{front} corresponds to approximately 70 – 80% of the detonation pressure *P* for the tubes used (see ref. [13]).

The determination of the cell size λ in the mixtures involving H_2 and CH_4 is not easy due to the irregularity of the detonation structure and also to the presence of substructure inside the main cell. The values of λ are scattered. The results performing here are given with a 20% accuracy.

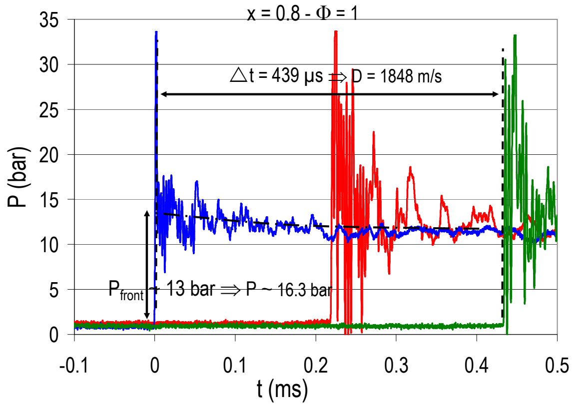

Figure 2: example of pressure signal.

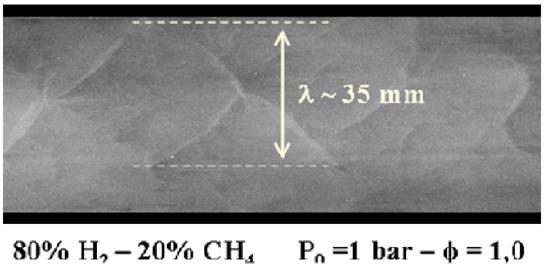

Figure 3: example of record on smoked plate.

The DDT data were obtained into a 6 m long stainless steel tube divided into a 2 m long section using 19 pressure transducers, separated by 100 mm, and a 4 m long tube with a pressure transducer located at the end of the tube (cf. Fig. 4). The ignition is obtained using an automotive spark plug with energy deposition of around 15 mJ. In order to enhance the detonation transition, a 2.8 m long Schelkin spiral, with a blockage ratio BR = $1-(d_S/d)^2 = 0.5$ and a pitch equal to the diameter d = 52 mm (d_S being the spiral i.d), is installed in the tube. For each experimental condition, at least 7 shots were done. The L_{DDT} corresponds to the average length measured.

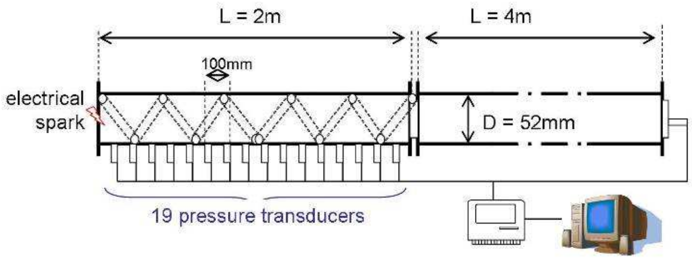

Figure 4: Experimental device for L_{DDT} measurement.

During the DDT process, the propagation of the flame in the tube induces a shock ahead whose time of arrival at different positions is determined from the pressure signal (cf Fig 5). The L-t (distance-time) diagram can be drawn and the local velocity of the wave (i.e, between two transducers) can be deduced.

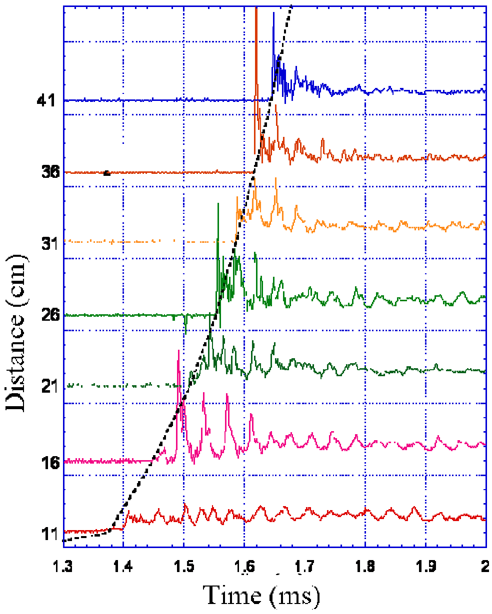

Figure 5: Typical DDT pressure records in distance versus time diagram for $x = 1$. Detonation starts at $L = 36$ cm.

The Fig. 6 shows an example of the evolution of the wave velocity as function of distance along the tube for $x = 0.9$ mixture (D-L diagram). Points indicated in the figure are the local velocity of each shot, the grey and "dash point" line are the average experimental self sustained detonation velocity (D_{spiral}) and the Chapman-Jouguet detonation velocity (D_{CJ}) respectively. We can notice, first, a strong increase of shock velocity up to $L \sim 0.35$ m and, after a peak, a plateau. Then, after a new acceleration up to a velocity higher or of the same order of D_{CJ}, DDT occurs. $L = L_{DDT} \sim 0.85$ m corresponds to the location where $D = D_{spiral}$ is first reached in the D-L diagram.

The evolution seen on Fig. 6 is typical of DDT in spiral section as observed in [3] for $d = 26$ mm i.d. tube. This evolution can be detailed in three phases: (i) a low velocity flame propagation (due to laminar flame after the ignition), (ii) a rapid acceleration to fast deflagration (around 1100 - 1200 m/s called chocking regime) and (iii) a transition to detonation identified by a resulting overdriven detonation peak. As noticed in [1], the detonation velocity in the spiral section is lower than D_{CJ} (D_{spiral} around $0.87*D_{CJ}$ for $d/\lambda \sim 2$), due to the spiral momentum losses on the detonation propagation regime.

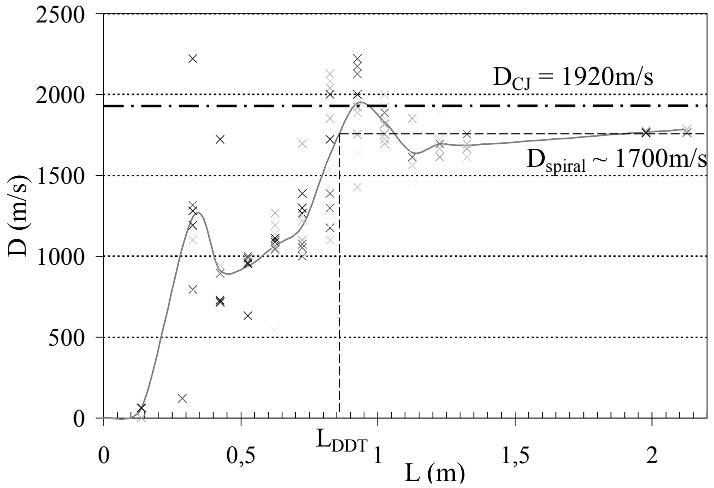

Figure 6: D-L diagram in the 2 m long transducer section with spiral for H_2/CH_4 - Air mixture with $x = 0.9$.

RESULTS AND INTERPRETATION

For each mixture, a calculation of detonation thermo chemical parameters is performed using the CHEMKIN code [14]. The ZND reaction zone and chemical induction time are calculated using seven detailed chemical kinetic schemes (Djebaili et al. [15], Li et al. [16], GRIMECH 3.0 [10], Konnov [17], Hughes et al. [18], Juchmann et al. [19] and Petrova and Williams [20]). The induction length L_i is determined by the delay between the leading shock wave and the maximum of heat release rate ($\left(dT/dt\right)_{\max}$) of the reaction zone.

Fig. 7 shows the evolution of D according to x (0.5 to 1) in the two different devices used. The dash lines represent D_{CJ}. Measured velocities are close to the CJ values within few percents. As expected, for fixed Φ, the velocity increases when x increases because the substitution of CH_4 by H_2 lowers the density of the mixture. For given x, the velocity presents a maximum at rich mixture. This value moves to rich side when x increases.

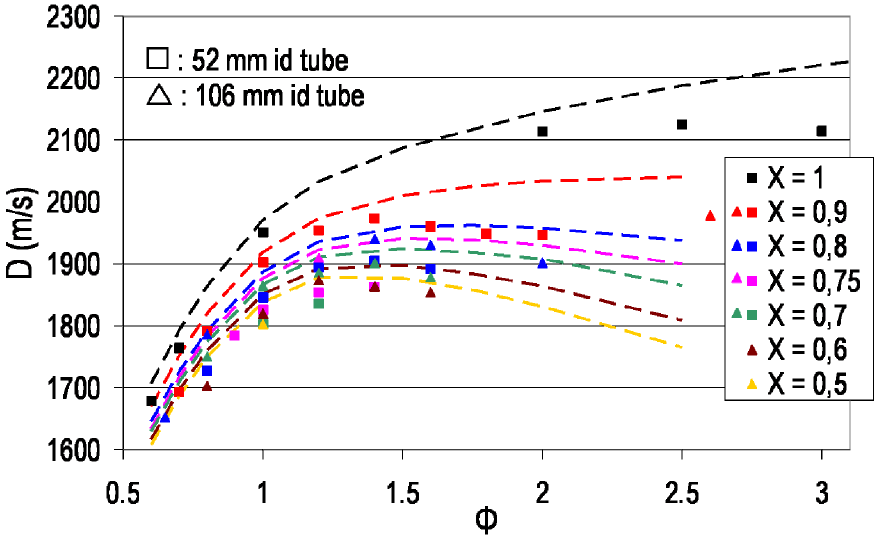

Figure 7: Experimental D (point) and Chapman-Jouguet velocity D_{CJ} (dashed line) in function of Φ for different x and different i.d. tubes (▲ i.d. 106 mm, ■ i.d. 52 mm) at P_0 = 1 bar and T_0 = 293 K.

The detonation pressure *P* is represented in Fig. 8. For given *Φ*, P drops when *x* increases; and for given x, P exhibit also a maximum for *Φ* ~ 1.5.

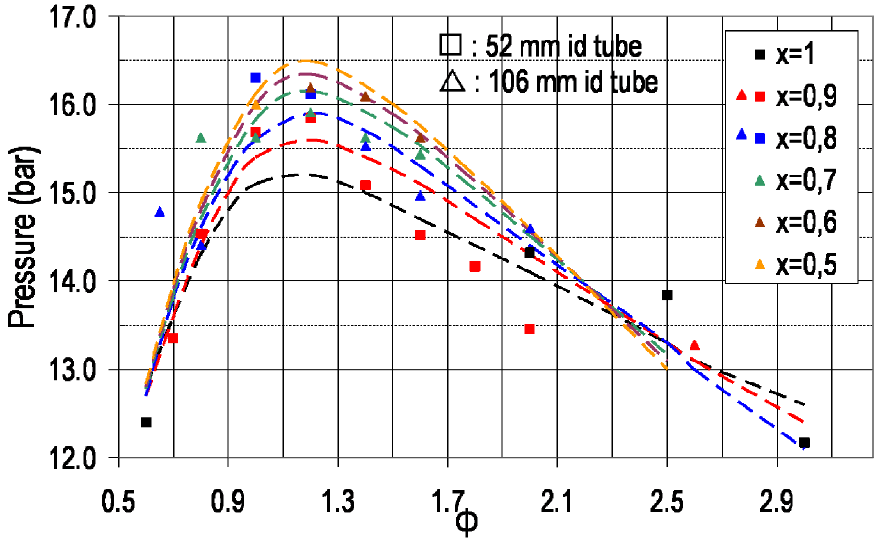

Figure 8: Experimental *P* (point) and Chapman-Jouguet pressure P_{CJ} (dashed line) in function of *Φ* for different *x* and different i.d. tubes (▲ i.d. 106 mm, ■ i.d. 52 mm) at P_0 = 1 bar and T_0 = 293 K.

Variations of cell size *λ* for different *x* in function of *Φ* are reported in Fig. 9. For a given *x*, a typical U-shaped curve is displayed with a minimum close to stoichiometry. For a given *Φ*, *λ* decreases as *x* increases. As evidenced in Fig. 10, for *Φ* = 1, *λ* drops from to 280-300 to 95 when x ranges from 0 to 0.5 and from 95 to 8-10 mm when *x* varies from 0.5 to 1. These results are in good agreement with those of Matignon et al. [8] and [21]. A "sensitive" zone (hatched) is defined in Figs. 9 and 10 for *λ* ≤ 50mm. In this zone, the detonability of the studied mixtures is higher than common hydrocarbon (ethane, propane, butane…) – air mixtures at stoichiometric ratio, i.e.:

- at *Φ* = 1for *x* > 0.65 and,
- on a decreasing range of *Φ* as x decreases from 1. For instance, for *x* = 1, *Φ* ranges from 0.6 to 3. For *x* < 0.65, the mixtures are less detonable independly of *Φ*.

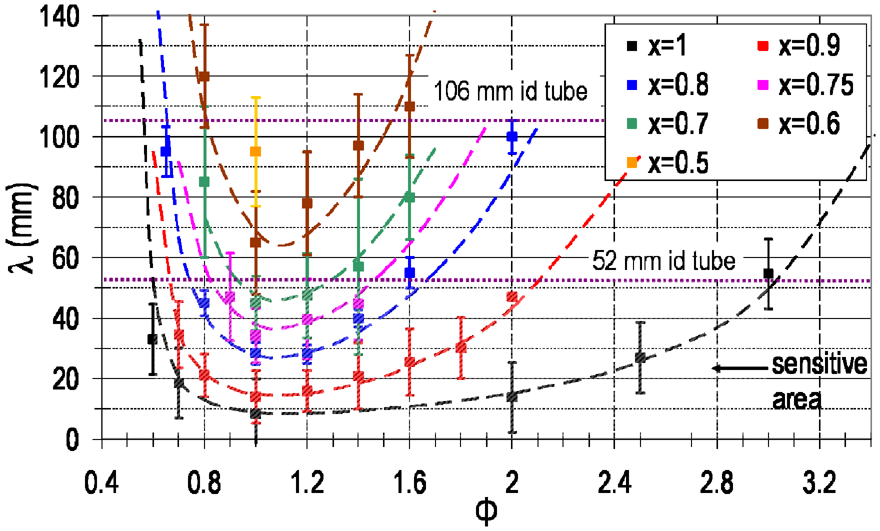

Figure 9: Variation of *λ* as a function of *Φ* for various *x* (P_0 = 1 bar, T_0 = 293 K).

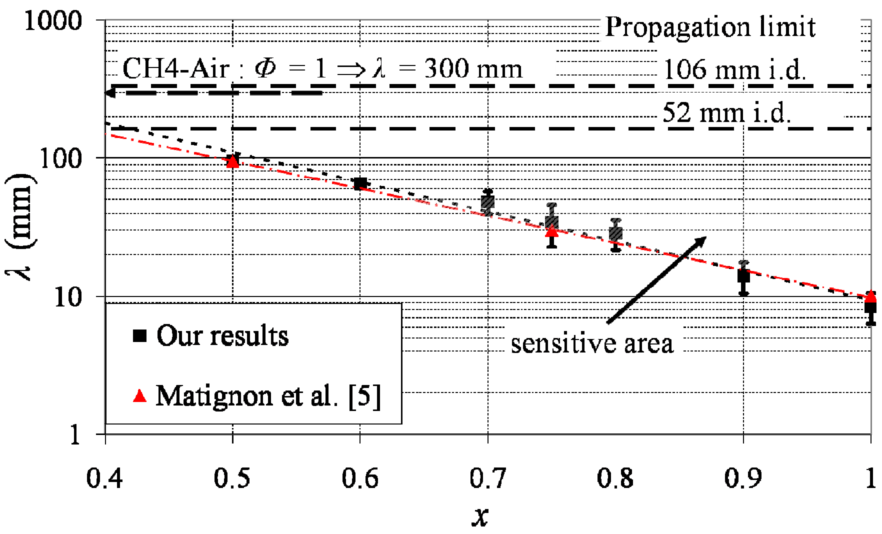

Figure 10: Variation of λ as a function of x ($P_0 = 1$ bar, $T_0 = 293$ K).

Comparison of the normalized induction length $L_i/L_i(\Phi = 1)$ versus equivalence ratio Φ for different hydrogen molar fractions x obtained from Petrova and Williams mechanism [20] among different reaction mechanisms provides the best agreement [22] with the normalized experimental cell size $\lambda/\lambda(\Phi = 1)$. This detailed chemical kinetic scheme was validated for mixtures with hydrogen and methane separately. It involves 55 chemical species and 251 elementary reactions. So, for what follows, numerical kinetics data are provided with this mechanism. Figs. 11 a and b show the evolution of induction length L_i according to (i) the equivalence ratio Φ for various fraction x of H_2 in the binary fuel (Fig. 11.a) and (ii) x at various Φ (Fig 11.b). It is observed that for each x value, induction length presents a minimum for Φ around 1.1. Moreover for each Φ, L_i decreases when the fraction of H_2 increases, which implies that mixture detonability increases, this tendency being reinforced for large fractions of H_2 ($x > 0.8$).

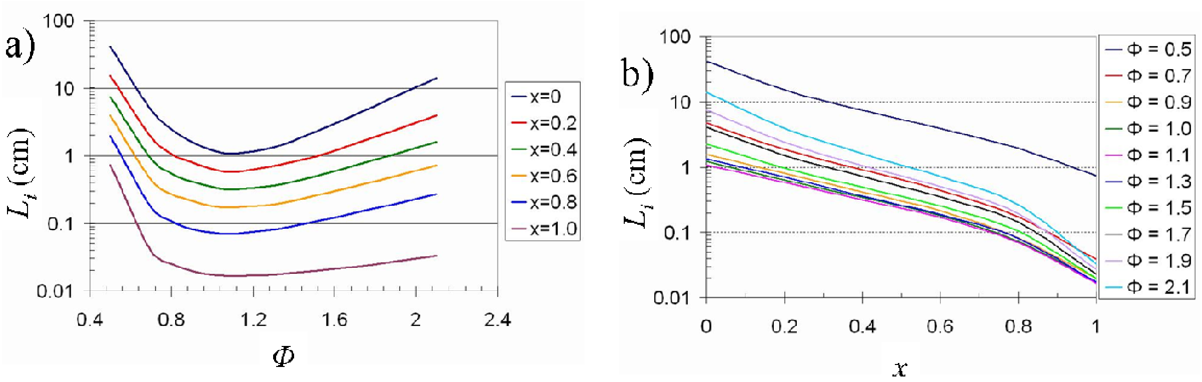

Figure 11: Evolution of induction length L_i according to a) the equivalence ratio Φ at various fraction x of H_2 in the binary fuel and b) x at various Φ.

Direct comparison of L_i and λ in H_2/CH_4 – Air mixtures provides an estimation of the ratio $k(x)$ in the following relationship i.e.:

$$\lambda = k(x) L_i , \tag{3}$$

As shown in [22], k is poorly dependent on Φ. So, for each value of x, the best fit between $\lambda(\Phi)$ and $kL_i(\Phi)$ allows to obtain k. As shown in Fig. 12, $k(x)$:

- remains constant at 40 for $0.5 < x < 0.9$ and,
- increases to 50 for $x = 1$.

The dashed line in Fig. 9 represents the estimated detonation cell size λ using the relationship (3) with the k values issued from Fig. 12.

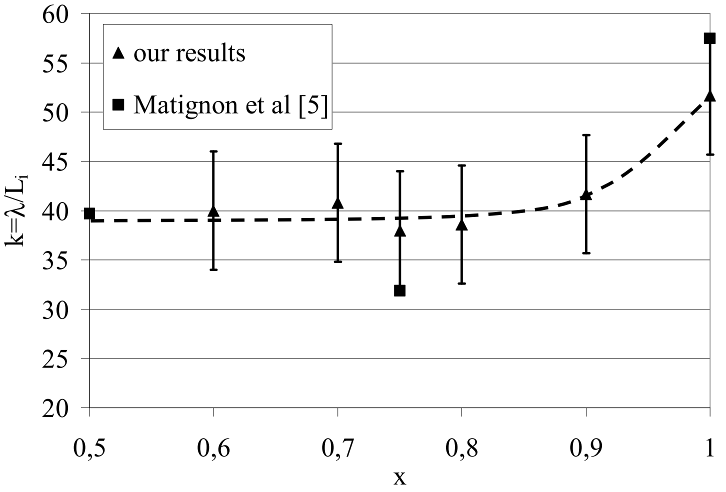

Figure 12: Evolution of λ/L_i according to x.

Results of L_{DDT} in function of P_0 and Φ are respectively reported in Figs. 13 a and b. The dependency of L_{DDT} to P_0 seems to vary like a power -0.8 (i.e. $P_0^{-0.8}$) for the different mixtures studied ($0.8 < x < 1$). It corresponds to the classical trend observed previously in single fuel-oxidizer mixtures. For $x = 0.7$, DDT doesn't occur at all, so this configuration allows the onset of detonation only for $x \geq 0.8$.

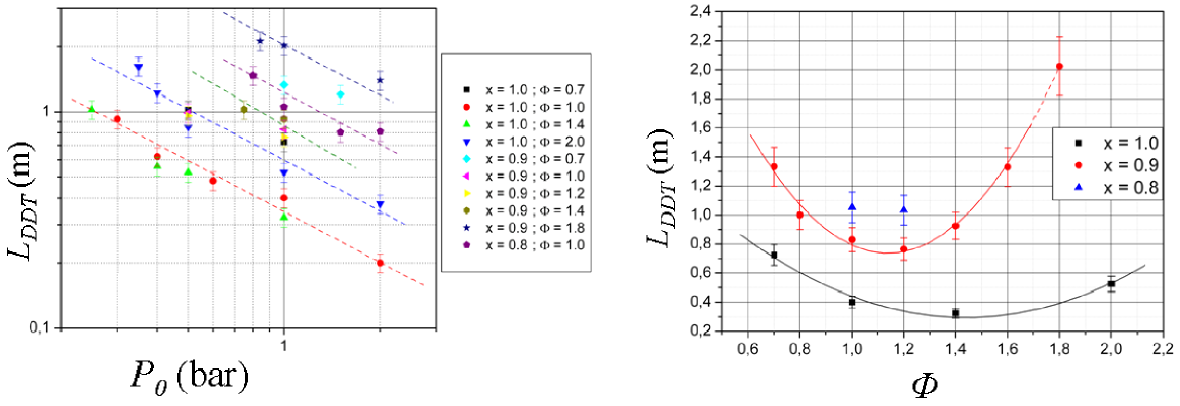

Figure 13 a and b : L_{DDT} versus P_0 (a) and L_{DDT} versus Φ in H_2/CH_4-Air mixtures (b).

Fig 14 summarizes L_{DDT} results as a function of detonation cell size λ. For $P_0 \neq 1$ bar, the reported values of λ are deduced from Fig. 9 assuming the relationship $\lambda \propto P_0^{-1.15}$ [8]. At stoichiometry for example, varying x from 1 to 0.8 makes the cell size to increase from 10 to 30 mm and L_{DDT} from 0.4 to 1.1 m. So the introduction of a weak volume of CH_4 in the mixture in place of H_2 substantially increases the chemical induction time and therefore decreases the detonability. We remark from Figure 14 that, for $x \geq 0.8$, a linear evolution of L_{DDT} with cell size as far as $\lambda \leq 3$ cm. More precisely it corresponds to $L_{DDT} \sim 30 - 40\lambda$. Particularly for $P_0 = 1$ bar, L_{DDT} is close to 40λ. A small amount of CH_4 (up to 20%) added in the fuel does not change the previous correlation $L_{DDT}(\lambda)$ obtained with H_2 - Air mixture [6]. Thus, because L_{DDT}/λ ratio are the same for obstacles laden tubes of different diameters ($d = 26$ mm [3] and 52 mm), we can underline that the ability of the mixture to auto-ignite behind a shock wave (i.e., induction length) influences significantly the DDT run up distance observed in H_2/CH_4 - Air mixtures.

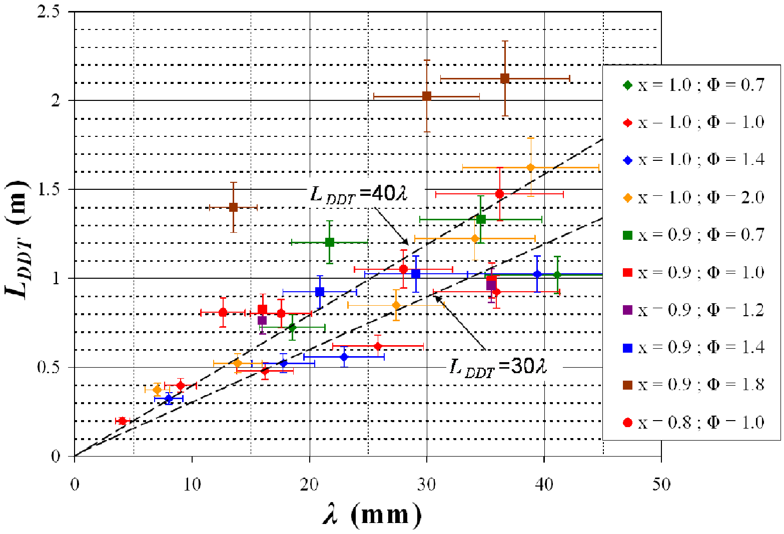

Figure 14: L_{DDT} as a function of detonation cell size λ in H_2/CH_4 - Air mixtures.

CONCLUSION

The aim of this study was to build detonation database of the self sustained mode of detonation propagation and its initiation by DDT, in H_2/Natural Gas – air mixtures according to hydrogen content (higher than 50%). We undertook a thorough experimental study on detonation characteristics for hydrogen molar fraction ratio x ($x = H_2/(H_2 + CH_4)$) varying from 0.5 to 1 within the limit of the possibilities of the experimental devices used, i.e. for mixtures with cell size lower than 106 mm. Deflagration to detonation transition (DDT) was studied in H_2/CH_4 - Air mixtures in a $d = 52$mm i.d. tube with spiral of blockage ratio of 0.5. Different H_2 volume ratio x in binary fuel H_2/CH_4, equivalence ratio Φ and initial pressure P_0 are considered.

Measured detonation velocities and pressures agree mainly with the Chapman Jouguet ones. The cell size λ decreases with the increase in molar fraction of hydrogen x. λ decreases from 95 mm to 8-10 mm for x varying from 0.5 to 1. Our results show that for $x \geq 0.65$, λ becomes lower than 50 mm. Consequently in this domain, these mixtures are more sensitive than common hydrocarbons – Air mixtures and require a more specific attention from a safety point of view. The size of the cellular structure λ is correlated to the chemical induction length L_i by the relation $\lambda = kL_i$. Using kinetic mechanism of [17], we estimate that $k \approx 40$ for $0.5 \leq x < 0.9$ and $k \approx 50$ for $x \geq 0.9$.

L_{DDT} was determined from velocity-distance diagram. It was found that the introduction of a small amount of CH_4 ($x \geq 0.8$) desensitizes the mixture compared to H_2 - Air mixture and increases the run-up distance L_{DDT} to obtain transition to detonation. The fuel binary mixtures studied behaves like H_2 - Air mixture, i.e., the length of transition obeys the linear law $L_{DDT} \sim 30\text{-}40\lambda$. This correlation indicates that, in certain conditions (obstacle laden tube), the deflagration to detonation transition depends strongly on chemical kinetics behind a shock wave propagating in the chocking regime conditions of the mixture.

REFERENCES.

1. Mitrofanov, V.V. and Soloukhin, R.I., On the instantaneous diffraction of detonation, *Soviet Phys. Dokl.*, No.159, 1965, pp. 1003-1006.
2. Schultz, E. and Shepherd, J.E., Detonation Diffraction Through a Mixture Gradient, Caltech, Galcit, EDL Report, 2000.
3. Ciccarelli, G., Critical Tube Measurements at Elevated Initial Mixture Temperatures, Proc 18th ICDERS Seattle, 2001, ISBN 0-9711740-0-8.
4. Desbordes, D., On The Diverging Spherical Detonation and the Critical Tube Diameter, Proc 21th ICDERS Poitiers, 2007.
5. Zel'dovich, Y.B., Kogarko, S.M. and Simonov, N.H., Etude expérimentale de la détonation sphérique dans les gaz, *Z.E.P.T.*, No.26, 1956, pp.1744-1772.
6. Sorin R., Zitoun R., Desbordes D., Optimization of the deflagration to detonation transition: reduction of length and time of transition, *Shock Waves*, No.15, 2005, pp.137-145.
7. Takita, K. and Niioka, T., On detonation behaviour of mixed fuel, *Shock Waves*, No.6, 1996, pp.61-66.
8. Matignon, C., Desbordes, D. and Presles, H.N., Détonabilité de mélanges stoechiométriques méthane-hydrogène-oxygène-azote, *C.R. Mecanique*, No.334, 2006.
9. Komori, M., Yoshida, T., Onoue, K., Kikukawa, S., Mori, T. and Takagi, K., Safety study of hydrogen supply stations for the review of high pressure gas safety law in Japan, Proceeding of the 2nd International Conference on Hydrogen Safety, 8-10 september 2005, Pisa.
10. Smith, P.G., Golden, D.M., Frenklach, M., Moriarty, N.W., Goldenberg, M., Bowman, C.T., Hanson, R.K., Song, S., Gardiner Jr, W.C., Lissianski, V.V. and Oin, Z., http://me.berkeley.edu/gri_mech/, 2002.
11. Kuznetsov M., Ciccarelli G., Dorofeev S., Alekseev V., Yankin Yu., Kim T. H., DDT in methane-Air mixtures, *Shock Waves*, No.12, 2002, pp. 215-220.
12. Dorofeev S.B., Sidorov V.P., Kuznetsov M.S., Matsukov I.D. and Alekseev V.I., Effect of scale on the onset of detonations, *Shock Waves*, No.10, 2000, pp.137-149.
13. Luche, J., Desbordes, D., Presles, H.N., Détonation des mélanges H_2-NO_2/N_2O_4-Ar, *C.R. Mecanique*, No.334, 2006, pp. 323-327.
14. Reynolds, The element potential method for chemical equilibrium analysis: Implementation in the interactive program STANJAN, version 3, Standford University, 1986.
15. Djebailli-Chaumeix, N., Abid, S. and Paillard, C.E., Proceeding of 21st International Symposium on Shock Wave, 20-25 July 1997, Great Keppel, pp. 121-126.
16. Li, J., Zhao, Z., Kazakov, A. and Dryer, F.L., Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, 2004.
17. Konnov A.A. Detailed reaction mechanism for small hydrocarbons combustion 0.5, http://homepages.vub.ac.be/akonnov/, 2000.
18. Hughes, K.J., Turanyi, T. and Pilling, M.J., http://www.chem.leeds.ac.uk/Combustion/Combustion.html, 2001.
19. Juchmann, W., Latzel, H., Shin, D.I., Peiter, G., Dreier, T., Volpp, H.-R., Wolfrum, J., Lindstedt, R.P., and Leung, K.M., Absolute radical concentration measurements and modelling of low-pressure CH_4/O_2/NO flames, 27th Symp. (Int.) on Combustion, 2-7 August 1998, Boulder, pp.469-476.
20. Petrova, M.V. and Williams F.A., *Combustion and Flame*, No.144, 2006, pp.:526-544.
21. Ciccarelli G., Boccio J., Ginsberg T., Tawaga H., The Influence of Initial Temperature and Flame Acceleration and Deflagration to Detonation Transition, 26th Symp. (Int.) on Combustion, 28 July-2 August 1996, Napoly, pp. 2973-2979.
22. Bozier, O., Sorin, R., Zitoun, R. and Desbordes, D., Detonation characteristics of H_2/Natural Gas with Air mixture at various equivalence ratio and molar fraction of hydrogen, 4th European Combustion Meeting, 14-17 April 2009,Vienna.