HOT SURFACE IGNITION IN FLOWING STREAMS OF HYDROGEN-AIR MIXTURES

Proust, C.[1,2] , Daubech J.[2]

[1] Sorbonne Universities, UTC-TIMR, 1 rue Dr Schweitzer, Compiègne, 60200, France, [2] INERIS, PHDS, Parc tech. ALATA, (P.O.Box 2), Verneuil-en-Halatte, 60550, France, christophe.proust@ineris.fr

ABSTRACT

A set of original experiments is presented covering the topic of hydrogen-air mixture ignition by a hot surface. The hot surface is a 30 mm long/10 mm diameter heated coil which temperature is controlled by IR techniques. The coil is placed into the flowing stream of hydrogen air mixtures. The variable parameters are the composition of the flammable atmosphere (4 to 75% H2 v/v), the flow speed (from 0.5 m/s to 30 m/s) and its temperature (from -110°C to ambient). The experimental techniques and results are presented, and a tentative interpretation is proposed based on ignition theories and high-speed video recordings. It is shown that the ignition temperature (600°C) is insensitive to flowing conditions which is a very unexpected result.

1.0 CONTEXT AND OBJECTIVES

It is clear for most of the stakeholders of the "hydrogen energy" economy that ensuring the safety of hydrogen objects is a major constrain [1]. Failing in doing so may seriously jeopardize future developments. Because of the specificities of hydrogen [2], many leakage scenarios may degenerate in escalating accidents [3] and the very details of each scenario need to be described, quantified before designing, calculating the mitigation barriers. Explosion risk is certainly the most important.

With standard hydrocarbons [4], an "ignition probability" is inserted between the appearance of the leakage and the explosion event which typically decreases the explosion risk by one or two decades. With hydrogen, this probability is said to be close to one and it is sometime admitted that ignition is "spontaneous" meaning either the ignition source is undetectable, or the leakage produces its own ignition source (like electrostatic discharges for dust clouds). The everyday practise of experimentalists however is not in line with this assertion and the ignition probability is much lower at least when good practises are used [5]. So, there is definitely a real possibility to control the ignition of hydrogen air clouds.

But to do so, a better knowledge of the ignition processes is required.

For hydrogen-air mixtures, four different "fundamental" ignition processes were identified so far [5]. The well-known "autoignition" [6] theoretically appearing in homogenously heated volumes (thus leading to a volumetric explosion and not to a propagating flame), the spark ignition [6], the hot surface ignition [7] and the "diffusion" ignition [8].

In "practical" ignition phenomena, such as "high pressure release ignition", several of the above-mentioned fundamental ignition mechanisms may intervene and for this particular example…all of them! An analysis of the "practical ignition phenomena" reveals "hot surface ignition" possibility appears in most of them which justifies further investigation of this mechanism.

In this paper, a physical analysis of this ignition mechanism is first proposed. Then, new experimental data are given highlighting the influence of flowing parameters of the atmosphere, often ignored in laboratory experiments.

1.0 HOT SURFACE IGNITION MECHANISMS
1.1 Available data

Hot surface ignition appears when a sufficiently hot object is introduced into a cold atmosphere, cold meaning at a temperature well below the autoignition temperature (585 °C for H_2-air mixtures).

This configuration has been studied experimentally for nearly one century [9-12] but with only limited data for hydrogen air mixtures [13-17]. The influence of the size of the ignition source was identified. When the latter is larger than about the quenching distance (>0.5 mm), the critical hot surface temperature (minimum temperature leading to the ignition) does not seem to depend any more on the size of the hot surface. Nevertheless, the value of this critical temperature is subject to some debate, varying between 930 to 1100 K in quiescent conditions depending on the data source. The reader could find most of the available information in the excellent review recently proposed by Mével et al. [17]. Figure 1 is extracted from this work.
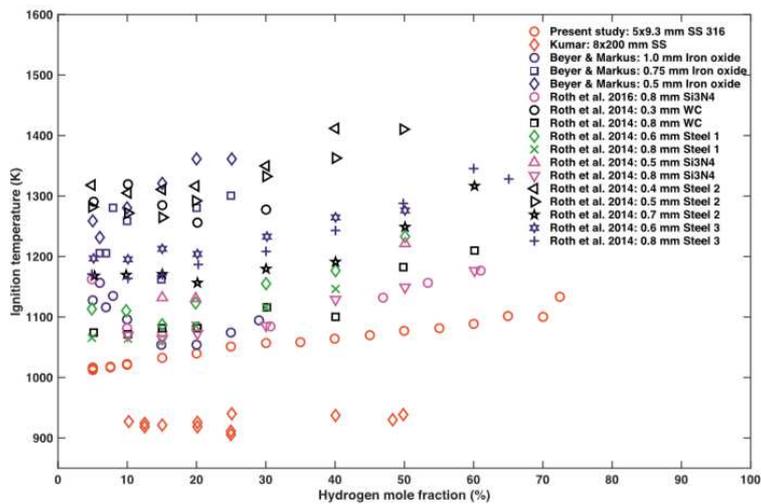

Figure 1 : variability of the hot surface ignition temperature for atmospheric quiescent hydrogen-air mixtures at room temperature (extracted from [17])

To the knowledge of the present author, only Kumar investigated the influence of the "preconditioning" of the atmosphere (pressure, temperature, velocity…). He did that in the specific context of nuclear safety and targeted the influence of the pressure and inerting. He found that a reduction of the initial pressure decreases the hot surface ignition temperature.

1.2 Modelling

Various modelling strategies were attempted. The older ones are analytical and were based on the auto-ignition theory of Semenov [7, 11]. They are "static" models. Ignition is effective once the heat released in the thermal layer attached to the hot surface is larger than the heat lost to the surroundings. As pointed out by Laurendeau [7], this is a necessary condition but not a sufficient one. It does only mean that burning can be produced in the layer but not that the combustion zone will be able to spread out.

Numerical simulations were attempted using CFD and detailed chemistry [13, 17]. Results are somewhat contradictory. Kumar suggests that the convective velocity (natural convection) is of minimal importance and, following, that a 1D model is enough to explain the trends. On the contrary, Mével et al. [17] pointed out the influence of the natural convection and of other details likes the chemical scheme and the temperature distribution.

In research both analytical and numerical approaches are necessary.

In this paper, the emphasis is laid on the analytical step. But a "dynamic model" is proposed instead of a static one. It is assumed that as soon as the local temperature is above the autoignition temperature, combustion occurs (necessary condition) in the thermal boundary. But "ignition" (of the surrounding atmosphere) occurs only if the flame is capable of propagating away.

Following Glassman [18], a flame is able to propagate if the thermal power transferred by conduction from the burning zone towards the reactant ahead of the ignition plane is smaller than the power released in the burning zone. The stable laminar burning velocity, S_l, is obtained when the two powers are equal. With a one-step zero order chemistry, the equations to solve are then :

$$\lambda \cdot \left(\frac{d^2T}{dx^2}\right)_{T:Tign \to Tb} = \rho_0 \cdot A \cdot \Delta H_{comb} \cdot \frac{T_0}{T} \cdot e^{-\frac{E_{act}}{R \cdot T}} \quad \text{and} \quad \lambda \cdot \left(\frac{dT}{dx}\right)_{ign} \approx \rho_0 \cdot Cp \cdot S_l \cdot (T_{ign} - T_0)$$

Where :

- S_l is the laminar burning velocity,
- T_b is the temperature of the combustion gases,
- T_{ign} is the ignition temperature of the reactants,
- T_0 is the initial temperature of the mixture,
- E_{act} is activation energy of the global reaction,
- A is the preexponential coefficient of the global reaction,
- R is the perfect gas constant,
- ρ_0 is the specific mass of the mixture at T_0,
- Cp is the specific heat of the mixture (average between T_0 and T_{ad}),
- λ is the heat conductivity of the mixture (at T_{ad}),
- ΔH_{comb} is the heat released by the combustion.

In the context of high asymptotics, when $E_{act}/R.T$ is large, T_{ign} is always close to T_b. In the particular case of adiabatic flames, $T_b = T_{ad}$ the adiabatic combustion temperature and $S_l = S_{lad}$ such that :

$$S_{lad}{}^2 = 2 \cdot \frac{\lambda}{\rho_0 \cdot \cdot Cp.} \cdot \frac{T_0}{T_{ad} - T_0} \cdot \frac{\Delta H_{comb}}{Cp \cdot (T_{ad} - T_0)} \cdot \frac{R \cdot T_{ad}}{E} \cdot A \cdot e^{-E_{act}/R.T_{ad}}$$

This reasoning can be used to find a sufficient condition for hot surface ignition. In the boundary layer, the heat flowing by conduction equals that transferred by convection to the surroundings :

$$\lambda \cdot \left(\frac{dT}{dx}\right)_p = h_{conv} \cdot (T_p - T_0)$$

Where T_p is the temperature of the hot surface and h_{conv} the convective heat exchange coefficient. It is assumed that T_p is also the temperature of the burning atmosphere in contact with the hot surface at the moment of ignition. Using the flame theory, the combustion zone will be able to escape from the boundary layer only if the conductive heat loss power is smaller than the heat release power. The limiting condition is obtained when both are equal reading :

$$\lambda \cdot \left(\frac{dT}{dx}\right)_p = h_{conv} \cdot (T_p - T_0) = \rho_0 \cdot Cp \cdot S_l \cdot (T_p - T_0)$$

Using the expression for S_{lad} where T_{ad} is replaced by T_p, a general solution can be obtained linking the "process" conditions (nature and composition of the atmosphere, nature of the convection via h_{conv}, T_0 and pressure P_0 via ρ_0) to the combustion/ignition parameters (ΔH_{comb}, E_{act},..). This solution is expressed here as :

$$h_{conv}^2 = \cdot\, 2 \cdot \lambda \cdot \rho_0 \cdot Cp \cdot \frac{T_0}{T_p - T_0} \cdot \frac{\Delta H_{comb}}{Cp \cdot (T_p - T_0)} \cdot \frac{R \cdot T_p}{E} \cdot A \cdot e^{-E_{act}/R.T_p}$$

Because of its simplicity, this model is not meant to be quantitative but may help to illustrate the relative influence of the various "process" parameters. To do so, the logarithm of the equation above is done and differentiated[1]. After some algebra, it comes :

$$\frac{dT_p}{T_p} = \frac{\dfrac{dh_{conv}}{h_{conv}} - \dfrac{dT_0}{T_0} \cdot \dfrac{T_0}{T_p - T_0} - \dfrac{1}{2} \cdot \dfrac{dP_0}{P_0} - \dfrac{1}{2} \cdot \dfrac{d\Delta H_{comb}}{\Delta H_{comb}}}{\dfrac{E_{act}}{R \cdot T_p} - \dfrac{T_0}{T_p - T_0}}$$

T_p is about 1000 K, E_{act}/R on the order of 5000 K ([19]).

The influence of the equivalence ratio is embedded in the value of ΔH_{comb} (figure 2). Towards the rich and the lean mixture zones the heat release drops. This drop is particularly marked towards the lean mixture zone, up to -70%. Since $E_{act}/R\, T_p$ is about 5, this would mean an increase of T_p by about 10% on the lean side. It would be negligible on the rich side. Available data (Figure 1) suggest some resembling variations but trends are not clear.
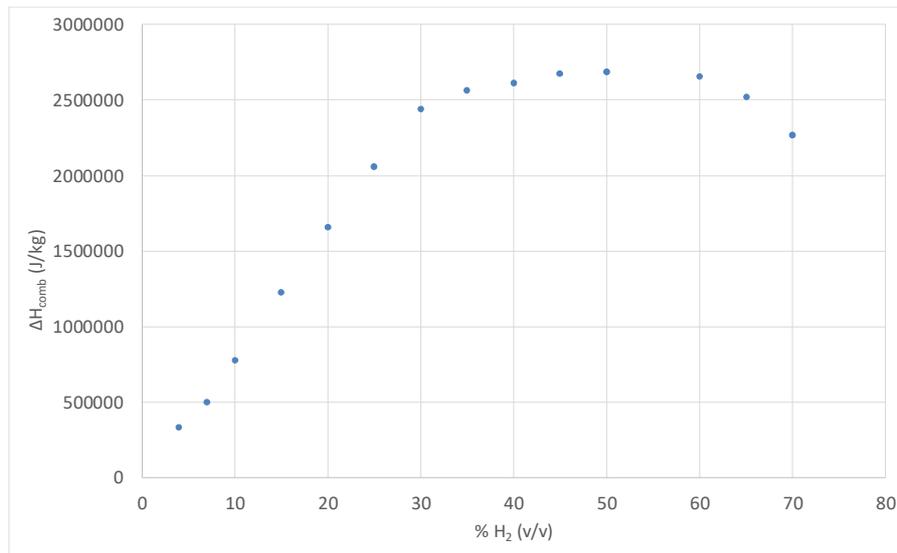

Figure 2: Evolution of the heat release as function of the concentration of hydrogen in the mixture

A decrease of T_0 by -100°C as compared to ambient, so -30%, should result in an increase of T_p by a few % (+3%). A drop in P_0 by -50% would mean a small increase of T_p (+5%). Note this last result seems in contradiction with the results of Kumar, but this may be only an apparent mismatch since in the present reasoning h_{conv} is supposed to be unaffected by P_0 which is not exact. Note also that more complex chemical phenomena (second order reaction rate, cool flames,…) may also be at work.

Using standard correlations to calculate h_{conv}, it is found that for natural convection surrounding a 0.5 mm diameter object[2] at 1000 K in ambient air, h_{conv} is about 120 W/m²K, 100 W/m²K for a 1 mm diameter object, 65 W/m²K for a 5 mm diameter object, 55 W/m²K for a 10 mm diameter object, 40 W/m²K for a 50 mm diameter object and 35 W/m²K for a 100 mm diameter object. For large enough

---

[1] λ is assumed to vary linearly with T_p
[2] cylinder

4

objects, above 5 mm diameter, h_{conv} varies only by ±30% meaning a variation of T_p by about ±5%. Between 5 mm diameter and 0.5mm objects, k_{conv} doubles so that T_p is expected to increase by +40% so typically +400°C. This is in line with available data (figure 1). In the case of <u>forced convection</u>, it can be shown that for a 5 mm cylinder at 1000 K immersed into a flow of ambient air, h_{conv} varies from 65 W/m²K when the flow velocity is zero to 750 W/m²K when the flow velocity is 30 m/s. This would suggest an increase of T_p by a factor of 2 at least !.

So, some influence of the equivalence ratio is expected but a pronounced effect of the forced convection is predicted. Experiments were performed to investigate this.

2.0 EXPERIMENTAL WORK

2.1 Hardware

The parameters to vary are the concentration of hydrogen in air, the flow velocity of this mixture and the temperature.
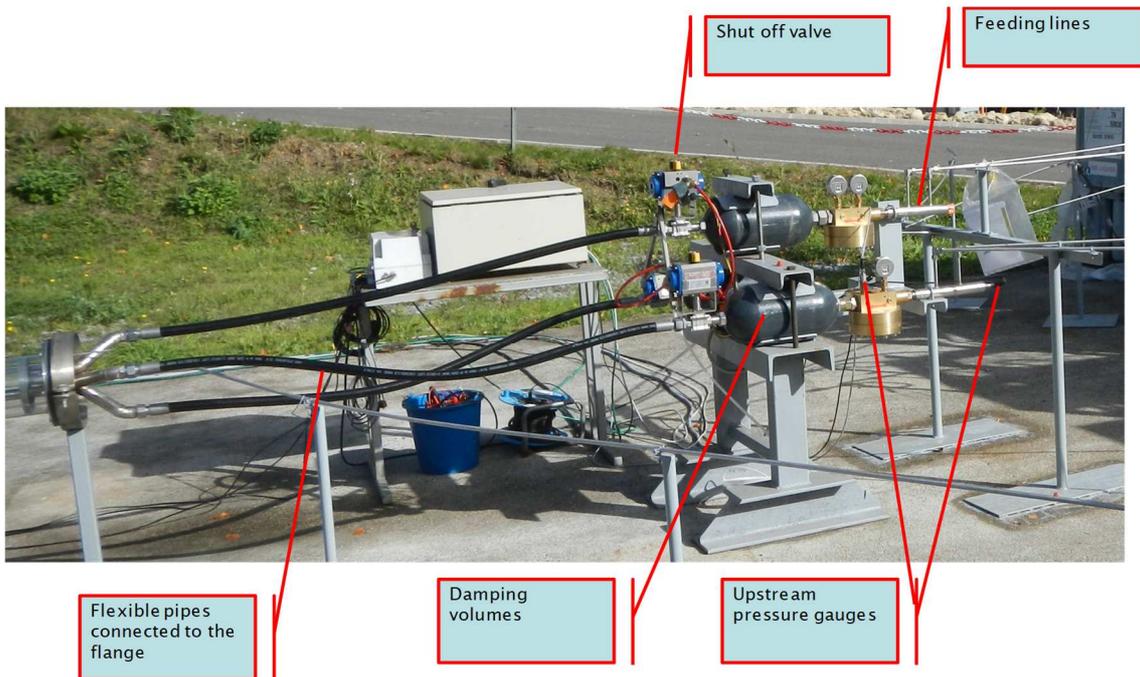
The mixture is continuously flowing in a constant diameter tube (0.1 m inner diameter, 2.5 m long) equipped with a double envelope to ensure thermal insulation (figure 3a). To vary flexibly the composition of the atmosphere and its temperature, gaseous nitrogen, gaseous oxygen, gaseous hydrogen and liquid nitrogen are injected via calibrated ports (figure 3b) in the flange of the pipe. The injection of liquid nitrogen allows to reduce the temperature of the flammable atmosphere. The typical overpressure ahead of the calibrated ports is a few bars insuring a high injection velocity. It was checked that perfect homogeneity was achieved at 1 m from the flange. The flowrate is regulated using high flowrate pressure regulators (figure 3c), carefully calibrated, but as explained later, the composition and temperature of the atmosphere is controlled at the exist of the pipe. All the flammable range could be explored with velocities ranging from nearly zero (0.5 m/s) to 30 m/s and temperature between -120°C to ambient.

a-general view

b-injection ports

Shut off valve

Feeding lines

Flexible pipes connected to the flange

Damping volumes

Upstream pressure gauges

c-pressure regulators arrangment

d-cold cloud emerging from the pipe

Figure 3 : details of the setup

2.1 Ignition source: the heated object

The ignition source is an electrically heated coil (Figure 4). It is basically a 0.7 m long, 0.0008m diameter nichrome wire, tightly spiralled around a 9 mm diameter, 30 mm long alumina core. Surely a better designed source would have been preferred but the present work was performed with the support of an industry, using this kind of rustic but very robust technique. We tried to compensate for this crude conception by carefully controlling the surface temperature of the device.

Figure 4 : hot coil arrangement (0.7 m nichrome wire 0.0008 diameter spiralled over a 9 mm diameter 30 mm long alumina cylinder) – electrically heated

It was thus carefully calibrated using a laboratory 2 colour pyrometer coupled with a field infrared camera (FLIR) used during the experiments. The temperature of the coil is rather homogeneous (Figure 5) and a very accurate reading of the temperature can be obtained with the infrared camera. It is believed the accuracy of the measurement is about ±30°C (at 700°C).
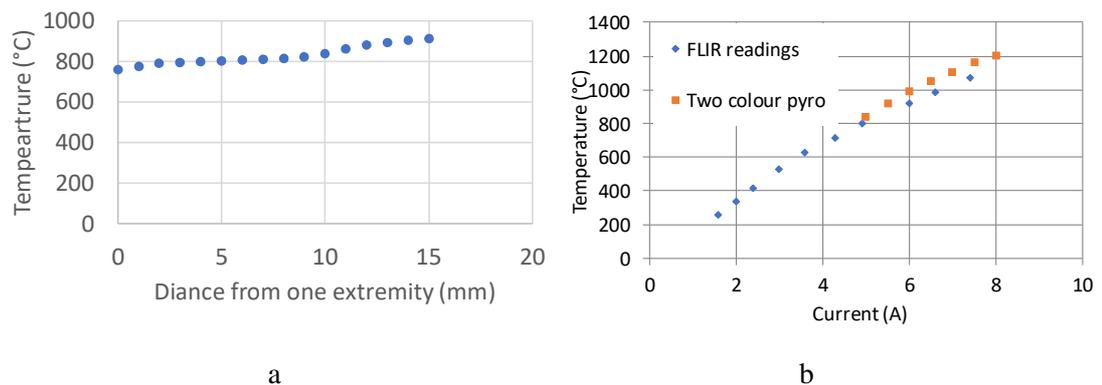

a

b

Figure 5 : two-colour pyrometer calibration (a) and comparison with field measurement infrared camera (b)

The hot coil is inserted inside the pipe in the centre of the open-end cross section.

2.1 Measurements

The temperature of the atmosphere is measured using a K sleeved (0.5 mm diameter) K thermocouple (accuracy on the order of ±1°C) inserted 10 cm upstream from the open-end cross section. The oxygen concentration is measured at the same point using paramagnetic oxygen cells (accuracy ±0.01%O_2 v/v). The hydrogen concentration is deduced, and the expected accuracy of this measurement is ±0.1%H_2 v/v.

The temperature of the coil is measured using the infrared camera.

The pressures upstream of the pressure regulators are controlled using 0-200 bar Kistler gauges (accuracy ±0.1 bar). The flow velocity is deduced from the calibration curves of the pressure regulators and of temperature of the atmosphere (to estimate the quantity of LN_2 injected when used and the specific mass of the mixture). The accuracy of this estimation is not better than ±10%.

The ignition is usually easy to detect either by the noise, the flash and/or the temperature excursion visible on the thermocouple signals. To help a fast detection, an additional K thermocouple is installed 2 cm downstream from the hot coil.

To run an experiment, the flowrates of oxygen and nitrogen are first established, and the oxygen concentration is measured to insure the mixture mimics air. Then hydrogen is admixed to reach the targeted oxygen content in the mixture. Then the coil is slowly heated up until ignition. A typical experiment lasts 15 mn.

2.2 Results

The first point is about the influence of the reactivity of the mixture (figure 6). Given the uncertainty of the measurement of the temperature of the hot coil, the influence of the reactivity seems very small. The critical hot surface ignition temperature is smaller that found up to now (870K) but is coherent with the suspected influence of the size of the hot body. Note also that this temperature is very close to the autoignition temperature.
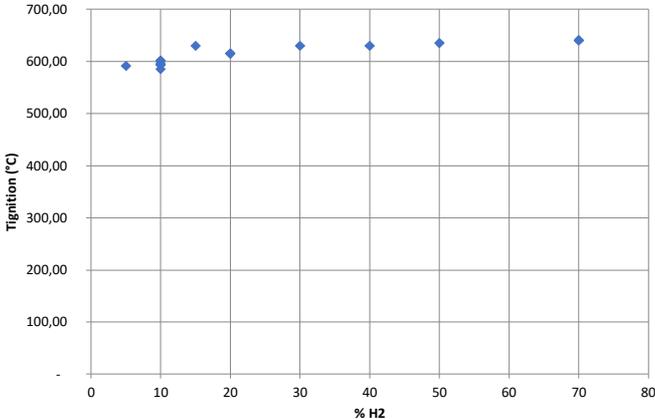

Figure 6 : influence of the proportion of H_2 in the mixture on the hot surface ignition temperature (ambient conditions and at rest)

The second point is about the influence of the temperature of the flammable atmosphere. The data of figure 7 were established for 10% H_2 -air mixtures because for this composition, the hot surface ignition temperature is the lowest and the ignition event is clear (more difficult to judge with leaner mixtures). Again, the influence is not detectable which is in line with the predictions given the measurement uncertainties.
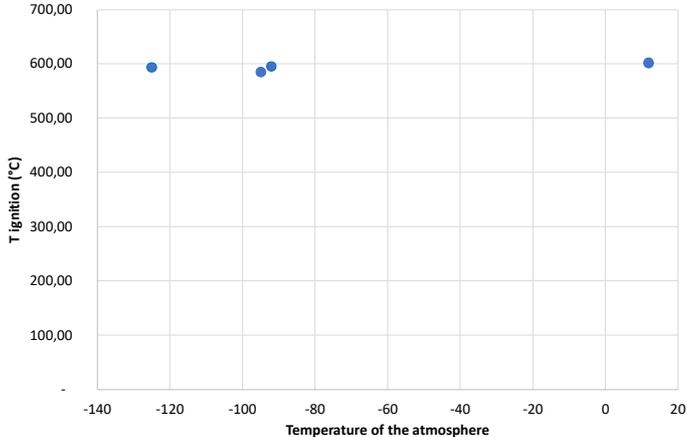
Figure 7 : influence of the temperature of the H_2 air mixture on the hot surface ignition temperature (10% H_2 at rest)

The last point is about the influence of the velocity of the flammable atmosphere. The data of figure 8 were established for 10% H_2 -air mixtures at ambient conditions. The influence is hardly detectable. If any, the influence is far less than postulated.
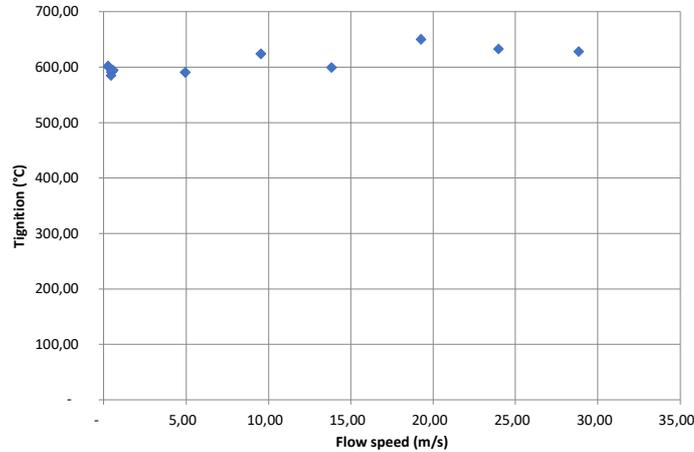

Figure 8 : influence of the velocity of the H_2 air mixture on the hot surface ignition temperature (10 % H_2, ambient conditions)

3.0 DISCUSSION AND CONCLUSION

The present work is devoted to hot surface ignition of hydrogen-air mixtures with a particular focus on the influence of practical process parameters like the flow velocity of the flammable atmosphere, its temperature, pressure … rarely addressed in laboratory experiments. Mével et al. proposed recently a comprehensive work on the subject of H_2-air ignition by heated objects.

From this, it turns out that there is no real consensus about the critical hot surface ignition temperature, which ranges from about 900 K to 1300 K) nor a clear view of the influence of the various influencing phenomena.

A phenomenological representation, based on the flame propagation theory, is exposed on the basis of which the choice of the process parameters to look at in priority was based. The influence of the H_2 concentration, flow velocity and temperature of the atmosphere were targeted.

The mixture is flowing continuously in a straight 10 cm diameter pipe. To obtain the desired temperature and concentration, the mixture is prepared from hydrogen, oxygen, nitrogen gaseous containers and from a liquid nitrogen container. All the flammable range could be explored with velocities ranging from nearly zero to 30 m/s. Temperatures between ambient down to -120°C were obtained. The hot body is a 10 mm diameter hot coil. Its temperature is controlled using a calibrated infrared camera.

It was found that the critical hot surface ignition temperature does hardly vary with any of these parameters, even when the flow is as large as 30 m/s ! This is completely unexpected

One element to consider when trying to solve this problem is that the measured critical hot surface temperature is close to the autoignition temperature. This point is specific to very "ignitable mixtures" like hydrogen and ether. For other hydrocarbons, the gap between both ignition criteria is much larger [12]. It might suggest that the flame propagation theory is not fully applicable to this situation. Autoignition ignition aspects might be incorporated. This might also explain the contradictions between the modelling approaches. There is room for further research on this.

9

REFERENCES

1. Edwards, P. P., Kutnetsov, V. L., David, W. I. F., Hydrogen Energy , *Phil. Trans. R. Soc. A,* **365**, 2007, pp. 1043–1056

2. Crowl, D.A., Jo, Y.D., The hazards and risks of hydrogen, *Journal of Loss Prevention in the Process Industries*, **20**, 2007, pp. 158–164

3. Galassi, M.C., Papanikolaou, E., Baraldi, D., Funnemark, E., Håland, E., Engebø, A., Haugom, G.P., Jordan, J., HIAD – hydrogen incident and accident database, *International Journal of Hydrogen Energy*, **37**, 2012, pp. 17351–17357

4. Astbury, G.R., Hawksworth, S.J., *Spontaneous ignition of hydrogen leaks : A review of postulated mechanisms, Int J Hydrogen Energy,* **32**, 2007, 2178–2185.

5. Proust, C., *Fire and explosion safety in hydrogen containing processes : state of the art and outstanding questions*, ISFEH09 symposium, Saint Peterburg, Russia, April 2019

6. Lewis, B., Von ELBE, G., *Combustion, flames and explosions of gases : 3rd edition*, Academic Press, London, ISBN 0-12-446751-2.

7. Carleton, F.B., Weinberg, F.J., *Correlating minimum ignition criteria, Proc. R. Soc. Lond. A,* **447**, 1994, 513-520.

8. Wolanski, P., Wojcicki, S., *Investigation into the mechanisms of the diffusion ignition of a combustible gas flowing into an oxidizing atmosphere, Proc. Combust. Inst.,* **14**, 1973, 1217-1223.

9. Silver, R.S., *The ignition of gaseous mixtures by hot particles; Phil. Mag. S.7,* **23**,1937.

10. Powell, F., *Ignition of gases and vapors, Industrial and Engineering Chemistry*, **61**, 1969, 29-37.

11. Laurendeau, N., *Thermal ignition of methane-air mixtures by hot surfaces : a critical examination, Comb. and Flame*, **46**, 1982, 26-49.

12. Adler, J., Carleton, F.B., Weinberg, F.J., *Ignition of flammable atmospheres by radiation heated fibrous agglomerates, Proc. R. Soc. Lond. A*, **440**, 1993, 443-460.

13. Kumar, R.K., *Ignitability of Hydrogen/Oxygen/Diluent Mixtures in the Presence of Hot Surfaces, Nuclear Safety*, **36**, 1995, 69-93.

14. Beyer, M., Markus, D., *Ignition of explosive atmospheres by small hot particles: Comparison of experiments and simulations, Science and Technology of Energetic Materials*, **73**, 2012, 1-7.

15. Roth, D., Haber, T., Bockhorn, H., *Experimental and numerical study on the ignition of fuel/air mixtures at laser heated silicon nitride particles, Proceedings of the Combustion Institute*, **36**, 2017, 1475–1484.

16. Buckel, J.W, Chandra, S., *Hot wire ignition of hydrogen-oxygen mixtures, Int. J. Hydrogen Energy*, **21**, 1996, 39-44.

17. Mével, R., Melguizo-Gavilanes, J., Boeck, L.R., Shepherd, J.E., *Experimental and numerical study of the ignition of hydrogen-air mixtures by a localized stationary hot surface, Int. J. of Heat and Fluid Flow*, **73**, 2019, 154-169.

18. Glassman, I., *Combustion, Academic Press*, London, 1977.

19. Coffee, T.P., Kotlar A.J., Miller, M.S., *The Overall Reaction Concept in Premixed, Laminar, Steady-State Flames. I. Stoichiometries, Comb. and Flame,* **54**, 1983, 155-169.