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H₂ Ignition by Hot Surfaces: Safety Issues and Test Methods

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1 Introduction

Many safety problems associated with the expected diffusion of H₂ energy applications have been addressed in research studies and relevant standards. However, some specific safety aspects or properties remain somehow undefined; one such subject is the ignition of hydrogen-air mixtures by thermal sources. Due to the lack of reliable experimental data, safety rules contained in various technical sheets and standards assume the auto-ignition temperature as a reference. This parameter, though, is quite uncertain itself, as demonstrated by the wide range reported in the literature (1). Moreover, heating the whole gas mixture up to the limit temperature leads to conditions which are far from the most likely scenario of ignition subsequent to an accidental release.

Data on ignition of flammable gas mixtures near ambient temperature by hot sources can also be found in the literature (2-5), but the temperature is obtained by various methods involving undefined uncertainty of the measurement. In addition, the non-uniformity of surface temperature is recognized also for small surfaces. The experimental difficulty in measuring the actual temperature is a major cause of the dispersion of available data on this subject; in fact the range of reported ignition temperature of H₂/air is from 640 to 930 °C (3).

Additional problems are posed by the possible partial consumption of the reactants, with formation of a strong inhibitor as water vapor, during stabilization of the reaction systems, and by the modification of the heating element (strip, rod or filament). Actually, there are very good reasons to refine the methods for the determination of ignition temperature of hydrogen on hot surfaces. In fact, an underestimation of the possible risks can have obvious dramatic effects related to accidents; on the other hand, the overestimation of this parameter can lead to unsustainable costs associated with safety measures, and in the long range to a negative impact on the general acceptance of hydrogen technologies.

An advanced method for the study hot surface ignition should take in due account these problems, and in the same time assure test conditions which realistically reproduce possible scenarios of hydrogen leakage. The method proposed here tries to address these issues.

2 Methods and Results

Previous studies conducted at our Institute on surface reactivity of flammable gas mixtures (6), have suggested that a method for determining the conditions of ignition on hot materials should exhibit the following characteristics:

- Provide an accurate and reliable measurement of the surface temperature under test conditions
Adopt an experimental set-up which reproduces the most likely conditions of accidental H$_2$ release leading to ignition

Utilize state-of-the-art techniques and instruments, and in the same time be simple enough to be easily implemented in the bench scale

A key aspect of these measurements is the controlled heating of the potential ignition source. Since the known region of ignition temperature for H$_2$/air mixtures is relatively high, resistive heating is suitable for metallic materials. In this case a contact method is not recommended for temperature measurement, and infrared imaging with high spatial resolution represents the best option. Imaging of the ignition source also allows a direct control of the history of the sample throughout the test, revealing any physical change (such as deformation or even rupture of the wire or plate) capable of affecting the results. In this experimental study we utilized a FLIR Thermovision SC 4000 camera, operating in the spectral range between 1.5 and 5 micron.

In the proposed method, the test is conducted in dynamic conditions, with the flammable mixture flowing over a metal sheet or wire placed in a sapphire tubular reactor. This relatively expensive material was chosen for the excellent mechanical and optical properties; however a quartz reactor gave also a good performance. For experiments above atmospheric pressure, a proper reaction chamber equipped with a sapphire or quartz window can be used.

The control of the gas flow rate and composition is obtained by electronic mass flow meters and by on line analysis with a Varian CP-4900 micro gas chromatograph equipped with advanced TCD detectors and two capillary columns. The system provides capability of determining the concentration of permanent gases and volatile compounds in 60 to 90 seconds, with relatively high sensitivity (below 100 ppm).

Fig. 1 shows a high-resolution thermal image of a thin steel plate placed in the reactor and resistively heated. Temperature in each point of the surface can be measured, recorded and processed in real time, allowing an accurate evaluation of the real temperature conditions to which the flowing H$_2$/air mixture is exposed.

![Figure 1: Thermal infrared image of a steel sheet during an ignition test.](image-url)
In this way we obtain the plot shown in Fig. 2, where the maximum temperature of the metal surface is recorded as a function of time.

![Figure 2: Evolution of surface temperature in the proximity of H₂/air ignition.](image)

The high temporal resolution of the thermal imager allows the exact detection of the ignition onset (marked with the arrow) and of the corresponding surface temperature.

Table 1 shows some significant results obtained with lean H₂-air mixtures contacted with the hot metal surface. The role of different parameters is clearly evidenced from these data. The sheet of carbon steel provokes ignition of the 5.7 % mixture at 820 °C. A slight increase in hydrogen content lowers the ignition temperature to 760 °C; a higher residence time of the gaseous mixture produces a further decrease in the ignition temperature.

**Table 1: Ignition temperature of H₂/air mixtures on hot metal surfaces.**

<table>
<thead>
<tr>
<th>Metal surface</th>
<th>H₂ concentration (%</th>
<th>Gas flow rate (ml/min)</th>
<th>Ignition Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel*</td>
<td>5.7</td>
<td>100</td>
<td>820</td>
</tr>
<tr>
<td>Carbon steel*</td>
<td>6.5</td>
<td>100</td>
<td>760</td>
</tr>
<tr>
<td>Carbon steel*</td>
<td>6.5</td>
<td>50</td>
<td>720</td>
</tr>
</tbody>
</table>

* exposed to corrosive environment

The metal sheet utilized in these tests had relatively large section: 4x0.4 mm, which required dissipation of significant electric power to reach and maintain high temperatures.

For a more detailed study of the hot surface effects, the sheet was replaced by a thin metal coil or wire, which required quite smaller electrical power. In this way, a simpler and stable electric circuit could be utilized to adjust the metal temperature.
Fig. 3 shows an example of the thermal image of a AISI 302 steel coil resistively heated to high temperature. The sample has a diam. of 0.25 mm and a length of 34 mm. It can be seen that the temperature distribution on the surface can be accurately determined by the IR camera, in spite of the small dimensions, as shown by the axial profile corresponding to the red line. A reliable value of the maximum surface temperature can thus be obtained. Some preliminary results obtained by passing an H₂/air mixture over the heated wire with a residence time of 7 seconds are reported in Fig. 4.

Between 480 and 600 °C, a dramatic increase in H₂ conversion was measured at the reactor outlet. The behavior is similar for the two different H₂ concentrations examined. This conversion can be attributed to surface reactions occurring on the small surface of the metal as well as to gas phase reactions taking place in a heated zone close to the wire. It is
important to notice that ignition of the gas mixture did not take place. For very lean mixtures, 
the hot wire is unable to trigger the propagation of the oxidation throughout the gas. This is in 
accordance with literature data, showing the marked influence of the size of the hot surface 
on ignition (4).

However, even in the absence of ignition, it is possible to estimate a temperature range 
where a high reaction rate is established, with subsequent significant heat release, thus 

determining the conditions for ignition. From the examination of the temperature/conversion 
data, we can deduce that around 620 °C a contact time of about 7 sec is needed to achieve 
an H₂ conversion of 90 %. Above 700 °C conversion is complete. It can be deduced that 
below that temperature a sudden ignition of a lean H₂/air mixture is unlikely. This result is in 
line with the lowest ignition temperatures reported in the literature (3).

3 Conclusions

Experimental techniques and criteria for estimating the temperature of hot surface ignition 
have been proposed. The major features of the method are a fine control of fluodynamic 
conditions, efficient gas analysis, and accurate temperature measurements by real-time 
thermal imaging of the surface representing the potential ignition source.

The ignition phenomenon can be investigated in good detail using resistively heated metal 
sheets exposed to a flammable mixture under controlled environment. However, electric 
power generation and dissipation have to be properly managed.

By scaling down the testing system to thin filaments, a more versatile procedure can be 
defined, which provides detailed information on the kinetics of H₂ oxidation.

These experimental methods can be applied to different metallic materials representing 

potentials ignition sources and to richer hydrogen mixtures, in order to create a 
comprehensive database to be utilized in a wide range of risk analysis scenarios.

References

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