

# Hydrogen Jet-Fire: Accident Investigation and Implementation of Safety Measures for the Design of a Downstream Oil Plant

Daniele Cermelli<sup>a</sup>, Fabio Currò<sup>a</sup>, Tomaso Vairo<sup>b</sup>, Bruno Fabiano<sup>a,\*</sup>

<sup>a</sup>DICCA Civil, Chemical and Environmental Engineering Department, University of Genoa. Via Opera Pia, 15, 16145 Genoa, Italy

<sup>b</sup>ARPAL – UTCR Grandi Rischi, via Bombrini 8 – 16149 Genoa, Italy  
brown@unige.it

As amply known, hydrogen plays a very significant role in the process industry exerting a vital functionality in oil refineries, namely for secondary level refining units such hydro-treating and hydrocracking sections. This paper starts from a statistical analysis on hydrogen accidents and a thorough investigation on the sequence and causes of an accident involving a hydrogen leakage in a downstream oil industry. We present some key features of the accident and comment some practical implications for setting up risk reduction options at the plant level. The applicative phase of the paper states the main prevention strategies and suggest possible mitigation measures for hydrogen leaks events, discussing some practical solutions applied in the design of a large refinery. The experience and lessons learned gained from the event investigation and the comparison of the accident with the predictions of the safety report leads to the formulation of proposals and design modifications aiming at preventing or at least minimizing the consequences.

## 1. Introduction

The possibility of using hydrogen as an energy carrier has gained growing interest in the last decades and is currently regarded as a promising approach towards sustainability, reduction of fossil fuel depletion and greenhouse gases impact. An impressive scientific effort in the recent years was directed towards developing new hydrogen production strategies, e.g., from hydrogen sulphide adopting chemical, or photochemical methods (Reverberi et al., 2016), through thermocatalytic decomposition (TCD) of methane utilizing novel Ni/Al<sub>2</sub>O<sub>3</sub> catalysts (Sow Lock et al., 2017), or from wastes by biological routes employing photochemical processes, or continuous fermentation by large scale bioreactor (Palazzi et al., 2002). Additionally, hydrogen plays a very significant role in many process industries and specifically it represents a vital element for the oil refineries where the products from the primary units like Crude Distillation and Vacuum Distillation Units are hydro-treated before distribution to the market for sale or export. In fact, owing to enhanced demand in light oil, refineries have been increasing the processing ratio of hydrotreating and hydrocracking processes, so that improving the utilization ratio of hydrogen and its reliability are emerging research topics (Zhu et al., 2017). Recent hydrogen leakages resulting in severe accidents have intensified refinery operator attention in both operational plants and during the design of new facilities. Even moderate releases of hydrogen reach mixtures under semi-confined geometry are known to present a serious risk, since flammable mixtures may form and the maximum admissible gas build-up, in connection with possible scenarios must be evaluated to foresee the effectiveness of techniques in reducing the possible adverse consequences (Palazzi et al., 2013). The primary fire and explosion hazards of hydrogen are connected to its inherent properties that can be compared with those of a conventional fuel: explosion limits hydrogen in air: 4,0 – 75%, methane 5,3 – 15%; ignition energy hydrogen/air: 0,02 mJ; methane/air 0,28 mJ; deflagration index,  $(dp/dt) \cdot V^{1/3}$  or  $K_G$  [bar·m/s] H<sub>2</sub>-air 550; CH<sub>4</sub>-air: 55; auto-ignition temperature AIT H<sub>2</sub>-air 572 °C; CH<sub>4</sub>-air 632 °C. For hydrogen, the buoyancy is so strong that it could always be assumed that under confined conditions a flammable cloud is located near the ceiling, or below any other horizontal confinement. For a free jet in unconfined situation, the jet momentum usually dominates the mixing rate of the jet until the hydrogen concentration has become lean. From the hazard comparison, Rigas and Amyotte (2013) argued that hydrogen safety concerns are not normally more severe,

but they are simply different than those we are accustomed to with gasoline, or natural gas. In this paper, we present some key features of hydrogen accident statistics and comment some practical implications for setting up risk reduction options at the plant level, starting from a notable case study occurred in an oil refinery. The applicative phase of the paper is focused on the development of a hydrogen bow-tie centred on the critical release. Conclusions are drawn about some practical solutions applied in the design of a large refinery aiming at jet fire risk prevention and mitigation.

## 2. Hydrogen accident statistics

Newly developed theoretical approaches are available to improve the effectiveness of accident investigations, including dynamic ones (e.g. Fabiano et al., 2016) and systemic cause identification to help define and eliminate the hindsight bias. On this basis, new lessons can be learned by trans-disciplinary approaches also from accidents that have been thoroughly described in the literature, such as Bhopal (Palazzi et al., 2015) and Fukushima (Labib, 2015). Rigas and Amyotte (2013) started from 240 incidents in the Hydrogen database of the U.S. Department of Energy, observing that only a rather small proportion results in loss of human life (4.6 %), especially if compared with human loss from the most frequent HC release scenario represented by pool fire (Palazzi et al., 2017). They concluded that laboratory incidents are by far the most frequent (32.1 %), but this is expected to change in the years to come when moving from the intense hydrogen research of today to the more widespread utilization of hydrogen. The determining role of human factor and the possible escalation from a personnel safety accident to more severe consequences within the working environment is revealed by long-term accident analysis on occupational accidents, in the process sector (Fabiano et al., 1995). A statistical survey on accidents involving hydrogen is here developed starting from FACTS data bank (managed by the Unified Industrial & Harbour Fire Department in Rotterdam-Rozenburg-NL) and including accidents that occurred at the beginning of this century. The database collects information on accidents with hazardous materials that caused, or could have caused serious damage and/ or that constituted a serious threat. Each accident was classified considering three macro-categories: the headline Plant/process collects causative factors directly connected to hardware and inherent characteristics of the process/plant; the area Organization collects causative factors related to human factors at different levels and to the safety management system; the headline Environment includes items related to work place lay-out/environment, machine safety, ergonomics and domino effects (Fabiano and Currò, 2012). As depicted in Fig. 1, the analysis of concurring causes evidences that plant/process accounted for 39.6 % of total entries, organization collected 22.8 % of entries, 1.0 % are connected to environment while the remaining ones have unknown immediate cause. Referring to the main accident scenario classification, as expected from hydrogen inherent hazards and without distinguishing between confined or unconfined geometry, globally the highest percentage of entries corresponds to Explosion (45.0 %), followed by Fire (40.8 %) and Release (14.2 %). Under unconfined conditions, results seem confirming that most frequent scenarios following a hydrogen release are a small flash fire or a jet fire, as due to prompt ignition connected to very low H<sub>2</sub> ignition energy, a flammable hydrogen-air, usually a cloud of significant volume cannot be formed before the mixture is ignited.

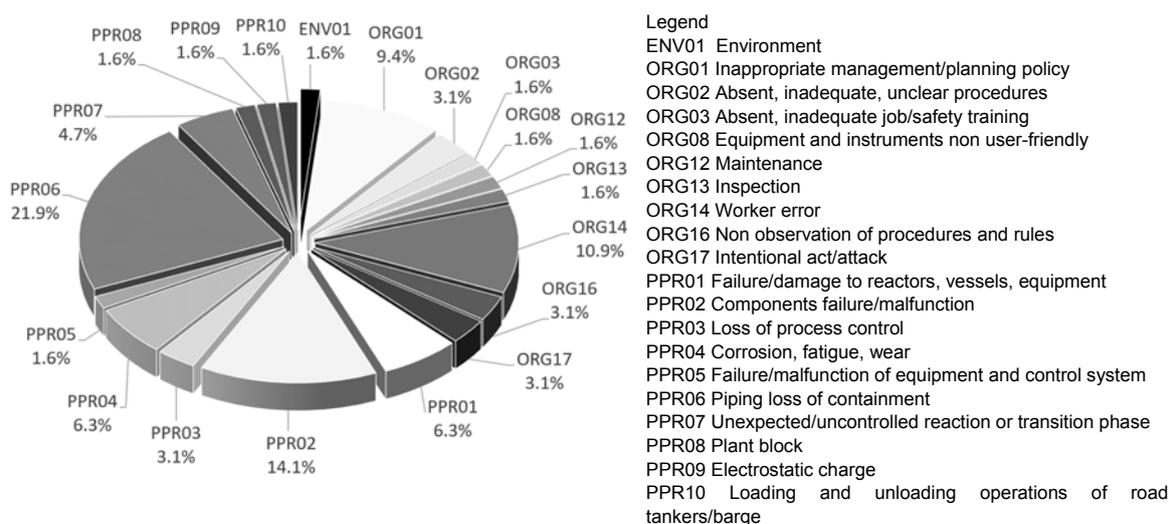


Figure 1: Main immediate causes of accidents involving hydrogen (excluding unknown causes).

However, it should be mentioned that Thomas et al (2015) starting from the analysis of some case-studies, argued that hydrogen buoyancy does not prevent absolutely the formation of significant flammable gas clouds, potentially forming VCEs for release rates of interest for explosion hazard analyses, under particular combination of the release and partial congestion/confinement.

### 2.1 An oil refinery accident

The catalytic hydrotreating unit of the refinery was fed with atmospheric and vacuum gasoil and utilized hydrogen obtained by steam reforming from other units to attain by a process of hydrodesulphurization higher cetano number, lower S content and lower density of the end-products. At local time 21.40 ca. during the re-starting of the hydrodesulphurization reactor, following a routine preventive maintenance, consisting in replacing the catalyst of one of the three catalytic beds, a fire occurred and affected a large area between the reactor itself and the upstream heat exchangers. A picture of the jet fire and escalation fire scenario is provided in Fig. 2. Post-incident investigations were carried out on the heavy fuel oil desulphurisation reactor, originating the primary event and on the light fuel-oil desulphurization reactor involved in the accident escalation. The fire involved mainly heavy fuel oil with an estimated volume of nearly 5 - 6 m<sup>3</sup>. The reboot, which consisted of a gradual rise in temperature and pressure according to a predetermined ramp, started about 10 hours before: at the time of the accident, the set-up was at 90%. In particular, the average reactor temperature was 340-350 °C, and the pressure was 60 bar, being the target set at 355 °C and 65 bar. The replacement of the catalyst represents a minor preventive maintenance intervention, which only stops a part of the process line, so that all other units such as the low-sulfur fuel-oil reactor were regularly running. Maintenance work involves following sequential steps: recharging the reactor, opening it, draining the bed catalyst, and replacing it. The fault was immediately detected by the basic process control system (BPCS) and therefore the automatic shutdown procedure started by plant SIS/ESD, with line disconnection, depressurization and nitrogen injection. The fire lasted about four hours, affected only the area between the heat exchangers and the reactor and caused the complete stop of the whole plant. At the end of the emergency phase, visual and instrumental controls of the surrounding equipment exposed to radiating heat were conducted paying careful attention to the Topping column. There was no recorded anomaly from the on-site integrity inspection, the coat of aluminum had no surface alterations, showing only a chromatic variation and leakage of the paint, while the insulating layer was found intact. Detailed post-incident investigations were carried out on the burned unit) and on the nearby light fuel oil desulphurization reactor, aiming at the identification of the immediate cause of the fire. Empirical evidences were compared also with all the relevant accident scenarios explored and quantified in the Seveso Safety Report of the oil refinery. Results from a very detailed experimental investigation evidenced the failure of a hydrogen quench line to the reactor, representing the starting LOC causing the following chain of events.



Figure 2: Hydrogen jet fire originated at the Hydrodesulphurization reactor and following accident escalation with fire development of diesel oil in the nearby area.

The immediate ignition of the hydrogen jet from the quench line originated the jet fire, generating radiant heat of the order of  $250 \text{ kW m}^{-2}$  affecting the nearby reactor and causing the extensive and long lasting diesel fire. As Kletz reminded us, the learning should result in recommendations: how to prevent the accident, how to avoid or reduce the hazard, and how to improve the management system. In this case, the awareness of the specific hazards of potential hydrogen release would be enhanced, tested and made the subject of training considering that it is a colorless and odorless gas with very low ignition energy and invisible flame. In the following chapter, starting from the statistical analysis on accident immediate causes and relevant scenarios and from first-hand lessons learned by the analyzed hydrogen related accident, we consider safeguarding strategies against hydrogen jet fire, specifically including separation of layout, material selection and various process and piping design solutions.

### 3. Applicative case-study

Notwithstanding technological development, enforcement of new ATEX Directives 153 and 114 and safety management system application, hazardous hydrogen releases and following fire scenarios in the process sector still claim injuries and severe economic losses. As evidenced in the last Loss Prevention Symposium 2016 in Freiburg (Fabiano, 2017) topics of wide scientific interest include preventive and mitigation measures against fires and explosions, ranging from fire and/or explosion resistant design of plants and buildings, to Ex-zoning, fire detection, alarm- and extinguishing, as well as relief systems. It is common practice that large chemical and petrochemical plant designs be comprehensively reviewed for safety at various stages and the plant design here discussed was subjected to such reviews. However, the reviews in some instances may require an additional computational and simulation effort to deal with possible escalation also from minor flammable release events or low rate fugitive emissions. From the analysis performed in the previous chapter, we outline factors that provide warnings to prevent similar hydrogen accidents to occur again, considering the main headlines resulting from accident statistics, namely process/plant and industrial environment. The best chance to reduce risk and increase plant reliability is at the design stage, by properly applying the prevention and mitigation strategies more appropriate for the given context. The approach can be based on a coarse QRA, or damage modelling for events such as potential jet fire impingement on nearby units. Considering hydrogen, peculiar properties such as strong positive buoyancy and enhanced dilution for sonic jets must be exploited during plant design to attain acceptable risk levels. Taking into consideration possible hydrogen releases and their most probable source, during the design phase of a process plant section, a hydrogen bow-tie analysis was developed in order to reduce hydrogen leaks and subsequent ignitions, with possible damages to equipment and injuries to personnel. Starting from API 510 a maximum level of thermal radiation of  $4.7 \text{ kW/m}^2$  is considered in area where emergency actions lasting up to several minutes may be required with protective clothing in the absence of shielding; a thermal radiation of  $12.5 \text{ kW/m}^2$  is considered as a level of thermal stress and structural failure for tank and equipment. The bow-tie shown in Fig. 3 was developed to depict relationship between the critical hydrogen release, immediate causes, consequences and pro-active and reactive barriers. The left part of the bow-tie known as “prevention area” identified three main elements contributing to the generation of the hazardous event, namely the fugitive emission/release sources (flanges, valves and equipment LOCs), mixing process (i.e. ventilation) and at last ignition source. Simulation models coupled with computer-aided design, may facilitate more efficient design and engineering practices identifying safety and loss prevention opportunities before they emerge in practice. A detailed three dimensional representation of the plant section and potential release sources was coupled with accurate simulation of the effects of jet fire scenarios (Van den Bosh and Weterings, 1997) on the nearby structures and working areas.

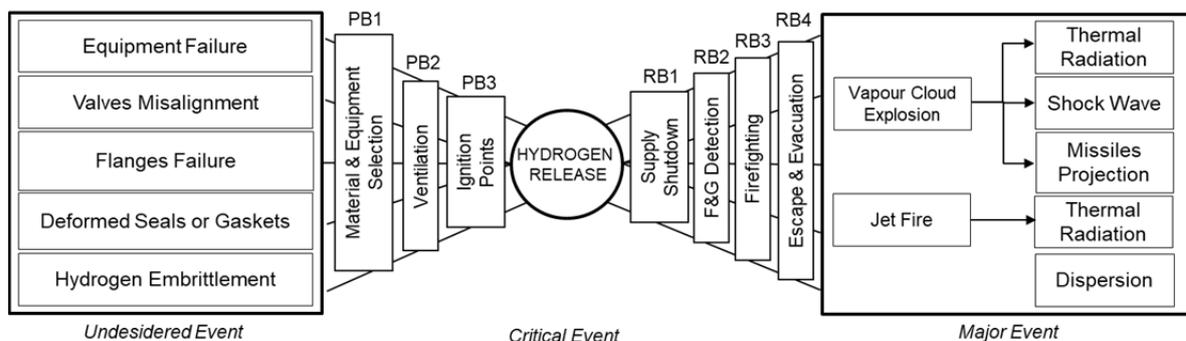


Figure 3: Generic hydrogen safety bow-tie, including proactive and reactive barriers against major events.

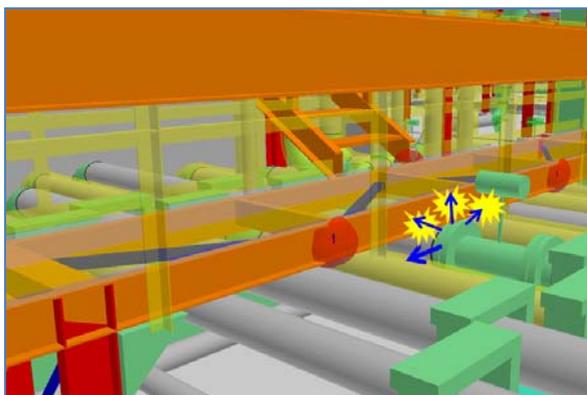


Figure 4: Hydrogen leak from flange and jet fire affecting steel structure and personnel

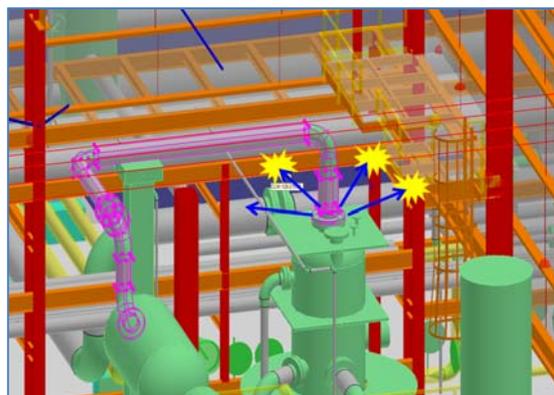


Figure 5: Hydrogen leak from flange and jet fire scenario affecting steel structure

Fig. 4 shows as a representative example a steel structure, which would be impinged by a hydrogen jet fire from a leaking flange. In this case, it was suggested and agreed with plant operation manager to relocate the valve into a more appropriate location where, in event of a leak, hydrogen jet fire would not impinge on the supporting structure. In the second example provided by Fig. 5, given the calculated radiating heat from jet fire up to  $32 \text{ kW m}^{-2}$  under the most critical environmental conditions, the steel structure can be severely damaged and lose integrity up to collapse, thus creating a possible accident escalation. Steel fireproofing, steam rings around the interested flanges were proposed as mitigating measures coupled with the re-design of the length of the nozzle of the vessel to relocate the flange between vessel and piping thus avoiding flame impinging on other equipment, such as other pipelines. A further determining issue is that the length and width of jet fire vary as a function of the pressure upstream of the leak: the easiest way to reduce hydrogen jet fire is by isolation and de-pressurizing the system. This option allows attenuating both pressure and inventories released and therefore length and width of jet-fire, thus reducing the zone of impact, escalation and personnel injuries. In this case, the best strategy was offered by the application of the guideword “minimization”: the proposed solution, which was implemented, was an inventory study where several sectional valves were introduced with the intent of reducing the amount of hydrogen released upon possible LOCs, thus reducing the effects, impact and the escalation probability. Further detailed jet fire simulations were conducted on the hydrogen compression unit, where several flanges are present due to connections with piping and auxiliary equipment. The driver here is minimizing equipment damage and escalation of the incident involving more equipment damage by allowing safe intervention during emergency action. On this basis, considering hydrogen jet fire scenario under worst environmental conditions, it was possible identifying a “red area” where the intensity of thermal radiation may cause a level of thermal stress high enough to cause structural failure and a “blue area” for impact on personnel working in the plant area and provided with appropriate clothing. Therefore, any of the manual operated equipment such as monitors and hydrants for fire-fighting, as well as manual operated shut-off isolation valves have to be located at the boundaries of “the blue area” corresponding to thermal radiation allowing for safe escape and emergency action for a duration up to two minutes.

Table 1: Preventive and mitigative barriers developed from the hydrogen bow-tie, addressing jet fire scenario.

Preventive Barriers		Reactive Barriers	
PB1	Minimize flanges. No insulation on flanges Material selection for embrittlement Hydrogen specific fittings/pipe joints 3D model review for flanges orientation.	RB1	Sectionalizing & depressurizing: jet fires not to be extinguished until supply is shutoff for risk of re-ignition, or explosion.
PB2	Continuous ventilation, even on emergency shutdown.	RB2	Infra-red fire detection for invisible and low emissivity, or catalytic bead detectors. Detectors strategic mapping study.
PB3	Earthing, bonding and grounding. ATEX Hazardous Area Classification	RB3	Water monitors for cooling down impinged equipment, not for extinguishing. Smothering steam (rings and lances).
		RB4	Restricted access and escape routes.

A summary of preventive and mitigative barriers developed from the already mentioned hydrogen bow-tie shown (Fig. 3) is reported in Table 1, referring as major event to only “hydrogen jet fire” in the given context and possible escalation. Globally, the performed safety review allows identifying different safeguarding strategies: separation and segregation of layout, material selection and various process and pipeline solutions. Preventive measures include application of intrinsically safe design, such as flange removal, or alternative design and inventory minimization. Mitigation measures include installation of steam rings/lances and application of fire protection for the structural steel. Proposed solutions were backed-up by extensive jet-fires simulations and possible impact, damage and escalation in which lengths and widths of jet fires were properly assessed in relation to pipelines pressures and isolation/depressurization capabilities.

#### 4. Conclusions

In this paper we analysed an accident occurred in a hydrodesulphurization reactor following a LOC and hydrogen release. Starting from lessons learned, hydrogen jet fire scenario is investigated during the design stage of a process plant in which high pressure hydrogen is handled, so as to identify some key features of possible accidents and given practical solutions and mitigation measures. The approach is based on the construction of a 3D model in sufficient detail to support damage simulations allowing a multi-disciplinary safety review of the plant design. The preventive measures include application of inherent safe design such as flange removal, valve welding, or alternative and innovative design. Extensive 3D-simulations of the possible jet-fires were performed and the impact radius of such jets were plotted in order to understand how to prevent or at least minimize property damages, accident escalation and personnel injury.

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