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The Influence of H₂ Safety Research on Relevant Risk Assessment

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Hydrogen is a valuable option of clean fuel to keep the global temperature rise below 2°C. However, one of the main barriers in its transport and use is to ensure safety levels that are comparable with traditional fuels. In particular, potential liquid hydrogen accidents may not be fully understood (yet) and excluded by relevant risk assessment. For instance, as hydrogen is cryogenically liquefied to increase its energy density during transport, Boiling Liquid Expanding Vapor Explosions (BLEVE) is a potential and critical event that is important addressing in the hazard identification phase. Two past BLEVE accidents involving liquid hydrogen support such thesis. For this reason, results from consequence analysis of hydrogen BLEVE will not only improve the understanding of the related physical phenomenon, but also influence future risk assessment studies. This study aims to show the extent of consequence analysis influence on overall quantitative risk assessment of hydrogen technologies and propose a systematic approach for integration of posterior results. The Dynamic Procedure for Atypical Scenario Identification (DyPASI) is used for this purpose. The work specifically focuses on consequence models that are originally developed for other substances and adapted for liquid hydrogen. Particular attention is given to the parameters affecting the magnitude of the accident, as currently investigated by a number of research projects on hydrogen safety worldwide. A representative example of consequence analysis for liquid hydrogen release is used in this study. Critical conditions identified by the numerical simulation models are identified and considered for subsequent update of the overall system risk assessment.

1. Introduction

Hydrogen is considered a clean fuel and could replace the fossil fuels in order to reduce the environmental pollution. Potentially, its combustion produces only water and heat if the flame temperature is controlled or a catalyst burner is adopted. Moreover, hydrogen has a specific energy value (120 MJ/kg (Verfondern, 2008)) higher than other commercial fuels such as gasoline or natural gas. Despite these and other advantages, hydrogen is considered a dangerous fuel mainly due to its flammability and low ignition energy (0.017 mJ in air (Ono et al., 2007)). Hence, when the transportation and utilization of hydrogen is taken into account, the safety aspects should not be neglected. Furthermore, hydrogen has a low density at atmospheric conditions (0.0838 kg/m³ at 293 K, 101.3 kPa (McCarty et al., 1981)) compared with other fuels. Liquefaction increases the hydrogen density (70.9 kg/m³ at 20.4 K, 101.3 kPa (NIST, 2019)) and that is why liquid hydrogen (LH₂) can be considered both for storage and transportation. For example, in the case of road transportation, a truck with a tube trailer of compressed gaseous hydrogen can be filled with 300-400 kg of hydrogen at 200-250 bar, while a truck with a vacuum insulated tank can hold up to 3.5 tons of LH₂ (Pritchard and Rattigan, 2010). On the other hand, when LH₂ is used, different potential accidents and hazards must to be considered. Some of these have not been fully understood or forecasted yet.

Boiling Liquid Expanding Vapour Explosion (BLEVE) and Rapid Phase Transition (RPT) are two physical explosions as consequence of a loss of containment and these are two atypical accidental scenarios. BLEVE is a very well-known phenomenon for different substances such as water, propane, Liquefied Petroleum Gas (LPG) and Liquefied Natural Gas (LNG). It can happen immediately after a catastrophic rupture of *"a vessel containing a liquid (or liquid plus vapour) at a temperature significantly above its boiling point at atmospheric*

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pressure" (Casal et al., 2016). While RPT can occur if Liquefied Natural Gas (LNG) is spilled onto water "due to the sudden boiling or phase change from liquid to vapor, usually in a way that the LNG penetrates into and mixes well with water" (Woodward and Pitblado, 2010). In the case of LH₂, it is not yet clear if and under which conditions these phenomena can happen, and which is the intensity of the consequences.

Several projects on hydrogen safety have been performed in the last decades. However, some of these studies did not consider BLEVE and RPT, such as the HyRAM tool (Groth and Hecht, 2017). Although, it does not mean these phenomena cannot happen for LH₂. In fact, the IDEALHY project has been focused on the LH₂ risk assessment, considering BLEVE among the potential consequences (Lowesmith et al., 2013). In a recent JRC report on hydrogen safety, it has been concluded that knowledge gaps still exist in hydrogen BLEVE/fire resistance among all the other considered areas (Azkarate et al., 2018). Moreover, LH₂ RPT has been theoretically predicted in a few studies such as in (Verfondern, 2008). This study identifies two past LH₂ BLEVE accidents. On the other hand, RPT never happened for LH₂.

The presented study is a preliminary introduction to the "Safe Hydrogen Fuel Handling and Use for Efficient Implementation" (SH₂IFT) project. This is a Norwegian project coordinated by the research institute SINTEF, in which the safety aspects of both liquid and gaseous hydrogen are studied. In the case of the LH₂, BLEVE and RPT will be analysed carrying out experimental tests and developing models both to forecast the formation and estimate the consequences.

The aim of this work is to integrate atypical accidental scenarios, such as LH₂ BLEVE, into the standard risk assessment of LH₂ technologies. The DyPASI technique was used to update the hazard identification phase, while relevant operational conditions of the LH₂ tank were considered as preliminary input to the consequence analysis phase. Furthermore, all the results obtained in this study will be confirmed during the SH₂IFT project.

2. Methodology

In this study, DyPASI has been applied to LH₂ technologies following the methodology used in (Paltrinieri et al., 2015). In the following, DyPASI and its procedure are briefly described. Furthermore, the methodology adopted to carry out the LH₂ BLEVE consequence analysis has been reported.

2.1 Application of DyPASI technique to LH₂ technologies

In Figure 1, the phases described in the introduction have been schematized. Looking at this scheme, it is noticeable that to apply the DyPASI technique, other tools such as MIMAH (Methodology for the Identification of Major Accident Hazards) and MIRAS (Methodology for the Identification of Reference Accident Scenarios) are needed. As said before, the results obtained in this study will be confirmed during the SH₂IFT project (dashed lines).



Figure 1: Scheme of the phases followed in this study. Dashed line indicates the results will be confirmed during the SH₂IFT project

DyPASI is a hazard identification technique usually coupled with a Dynamic Risk Assessment (DRA) in order to update it taking into account atypical accidental scenarios which are not considered by traditional hazard identification processes (Paltrinieri et al., 2016). For example in (Russo et al., 2018), the explosion scenario has not been considered for the storage unit of the hydrogen refuelling station. MIMAH methodology has been used to develop the conventional bow-tie diagram utilized as input of the first DyPASI step (Delvosalle et al., 2006). DyPASI procedure is structured in different steps and these are described in Table 1. MIRAS methodology has been

used to define the safety barriers for the atypical scenarios in the step 4 of DyPASI (Delvosalle et al., 2006).

Step	Input	Output	Description
0	Input to conventional bow-tie	Generic bow-ties	DyPASI needs a preliminary application of the
	technique	describing potential	conventional bow-tie technique to identify
		accident scenarios	relevant critical events
1	Information from accident	Risk notions on	A search for relevant information concerning
	databases	undetected potential	hazards that may have not been considered in
	and dedicated search systems	hazards	conventional bow-tie development is performed
2	Risk notions from step 1	Early warnings	A determination is made as to whether the data
		triggering further	are significant enough to trigger further action
		analysis	and proceed with risk assessment
3	Bow-ties from step 0 and early warnings from step 2	Bow-tie diagrams	Atypical scenarios are isolated from the early
		considering also	warnings; cause-consequence chains are built
		atypical scenarios	and integrated into the generic bow-ties
4	Integrated bow-ties from step 3	Safety barriers for	Safety measures are defined for the atypical
		the atypical	scenarios identified
		scenarios	

Table 1: DyPASI procedure steps, adapted from (Paltrinieri et al. (2015)

2.2 LH₂ BLEVE consequence analysis

DyPASI technique can identify different kind of accidental scenarios consequences but other tools are needed to estimate these consequences. Hence, a study on LH₂ BLEVE consequences has been carried out.

The BLEVE consequences are the overpressure of the blast wave, the missiles (debrides formed after the vessel rupture) that fly away owing the explosion and the thermal radiation, if a fireball occur due to an ignition source outside the tank, such as fire (Casal, 2008). In this study, only the evaluation of the overpressure of the blast wave has been considered.

The superheat limit temperature theory (Reid, 1979) assumes that the liquid contained in the vessel must be superheated, otherwise the yield of the explosion cannot be compared with a BLEVE. To estimate the superheat temperature of a substance, several formulas have been developed by different authors. One of the most common equation used is the one proposed by Reid (Reid, 1976):

$$T_{shl} = 0.895 \cdot T_c = 29.66 K$$

(1)

Eq(1) is a simple formula that depends only on the critical temperature. According to Eq(1), the superheat temperature of hydrogen is 29.66 K. There are other methods to estimate the superheat temperature, but these are more conservative. Casal et al. (Casal et al., 2016) explained that this theory is valid at small scale but not at large scale where there is always a non-homogeneous distribution of the heat in and around the vessel. Nevertheless, the superheat limit temperature is an important parameter because at this temperature the adiabatic energy transfer between the liquid and vapor interface is maximum (Salla et al., 2006). In this study, the inputs for the estimation of the consequence analysis have been chosen in order to reach a temperature higher than 29.7 K inside the tank. Furthermore, a correlation between the hydrogen mass contained in the tank, its pressure and the yield of the LH₂ BLEVE has been searched. The mass and pressure of hydrogen are operational parameters and, in the case of a storage facility, they can vary during the day.

A representative BLEVE consequence analysis has been carried out using the software PHAST 8.11 developed by DNV-GL. In this software, a BLEVE is simulated as a standalone model, hence the simulation is not time-dependent. The chosen tank has a volume of 1 m³, a cylindrical shape with a diameter of 1.13 m and 1 m of length. The elevation of the tank is 1 m. The tank contains hydrogen in both phases, liquid and vapour. Three different pressures, 9, 11.9 and 31.2 bar gauge (bar_g) have been chosen to simulate the BLEVE. The first pressure, 9 barg, is approx. 1.21 times 7.4 barg, that is the pressure at which the first pressure relief valve (PRV) of the LH₂ vessel opens (Rybin et al., 2005). The same approach is suggested in (Uijt de Haag and Ale, 2005). Then, the yield of the BLEVE have been estimated when the vessel has a pressure of 11.9 bar_a, which is a value close to the hydrogen critical pressure (12.96 bar). The burst pressure of the LH₂ tank has been estimated to calculate the yield of the BLEVE in case of PRVs failure without fire engulfment of the tank (cold BLEVE). In this case, the value of the pressure inside the tank before its rupture is the highest compared with hot BLEVE. When the tank is exposed to fire, the tank material is subjected to thermal stress and the estimated bursting pressure has a lower value than the considered case. To evaluate the bursting pressure, the tank wall thickness has been calculated following the ASME Boiler and Pressure Vessel Code (BPVC) Sec. VIII (ASME, 2001). This code is used to design also cryogenic vessels. Eq(2) is used to calculate the tank wall thickness, t:

$$t = \frac{P \cdot R}{\sigma \cdot e - 6 \cdot P} = 2.76 \, mm \tag{2}$$

where *P* is the design pressure of the tank (7.4 bar_g or 107 psi_g) and *R* its radius (500 mm), σ is the allowable stress equal to 20,000 psi for the AISI Stainless Steel 304 (Rana and Barthelemy, 2003) and *e* is the weld joint efficiency factor considered 1. To estimate the burst pressure *P*, Eq(3) has been used (Casal, 2008):

$$P = P_0 + \frac{S_M \cdot t}{R + 0.6 \cdot t} = 3.22 MPa = 32.2 bar$$
(3)

where P_0 is the atmospheric pressure (0.1 MPa), S_M is the mechanical strength of the material with a value of 565 MPa always for AISI Stainless Steel 304 (Casal, 2008). Eq(3) has been used for LH₂ tank because it is applied for cylindrical vessels with the pressure (P – P₀) lower than 0.385 times S_M (Casal, 2008).

To simulate the BLEVE using PHAST, it is possible to set the pressure inside the tank, the temperature of the substance and the bubble point. The mass of the substance contained inside the tank is not an input, hence, to reach its desire value the other conditions such as pressure, temperature and liquid mole fraction should be changed. When the substance is in the supercritical state, only the temperature can be varied to set the mass at fixed pressure. When the pressure is 11.9 bar_g inside the tank, the minimum and maximum values of the mass that can be reach are almost 26 and 40 kg respectively, due to the density of the vapour and the liquid at this pressure. For this reason, 26, 30 and 40 kg have been chosen as values of the hydrogen mass contained in the tank. In Table 2, the initial conditions of the different simulation have been collected.

Pressure	Mass	Temperature	Liquid mole	Liquid mass
(bar _g)	(kg)	(K)	fraction	fraction
9	26	31.3	0.33	0.64
	30		0.44	0.74
	40		0.71	0.90
11.9	26	33.0	0.05	0.08
	30		0.35	0.46
	40		0.97	0.98
31.2	26	43.0	0	0
	30	40.7	0	0
	40	36.7	0	0

Table 2: Initial conditions of the different BLEVE consequence analysis scenarios

3. Results

3.1 Results of DyPASI application to LH₂ technologies

In the original bow-tie diagram obtained with the MIMAH tool, the catastrophic rupture of the cryogenic tank has been chosen as critical event. MIMAH suggests generic logic trees to build the bow-tie diagram. This methodology considers BLEVE as a domino effect, being the critical event of a secondary event tree.

Applying DyPASI, with the available information regarding the two past BLEVE accidents, this phenomenon becomes an event in the updated bow-tie diagram. Moreover, in the fault tree "improper firefighting technique" has been added as an escalation factor, following the procedure used in the software BowTieXP. This escalation factor triggers the PRV failure, leading to internal overpressure.

In the updated bow-tie diagram, three safety barriers have been added using the MIRAS methodology. These safety barriers are the "training" of the fire fighters and the "PRV" in order to prevent the PRV failures when the LH₂ tank is exposed to a fire and the increase in overcompression inside the tank respectively. The other safety barrier is the "blast walls", usually utilized to mitigate the consequence of an explosion such as the overpressure of the blast wave. Only with the experimental tests that will carried out during the SH₂IFT project, the effectiveness of these safety barriers will be estimated.

In Figure 2, the updated bow-tie diagram is shown. The black branches form the bowtie diagram developed using the MIMAH methodology, while the blue branches have been integrated after the DyPASI application. The red boxes in the figure are the safety barriers.

3.2 LH₂ BLEVE consequence analysis results

The results of the BLEVE consequence analysis obtained with the PHAST software are the overpressure of the blast wave at different distances and the overpressure radii. The latter indicates at which distance the overpressure has a value of 0.02068 barg, which is the lowest value considered.



Figure 2: Bow-tie diagram updated with the DyPASI integrations (light blue dotted line) adapted from (Paltrinieri et al., 2015). Safety barriers in red boxes to avoid the critical event or to limit the consequences

In the presented study, the same overpressure values considered by PHAST that correspond to 3, 2 and 0.3 psi_g (0.2068, 0.1379, 0.0207 bar_g respectively) have been analysed. In the following, these values have been indicated as Overpressure 1, 2 and 3 respectively. In Table 3, the results of the BLEVE consequence analysis have been collected. In particular, the estimated distances at which the 3 values of overpressure occurred have been reported.

Pressure in	Mass	Distance downwind to	Distance downwind to	Distance downwind	Increasing of the
the tank	(kg)	Overpressure 1 (m)	Overpressure 2 (m)	to Overpressure 3	distance to
(bar _g)				(m)	Overpressure 1
9	26	7.65	10.15	40.25	
	30	7.90	10.47	41.55	+3.2 %
	40	8.45	11.20	44.43	+10.4 %
11.9	26	8.38	11.02	43.31	
	30	8.74	11.49	45.14	+4.2 %
	40	9.43	12.39	48.71	+12.4 %
31.2	26	9.64	12.60	48.20	
	30	9.74	12.75	48.74	+1.1 %
	40	9.85	12.88	49.27	+2.2 %

Table 3: Results of the BLEVE consequence analysis at different conditions

As expected, when the hydrogen mass contained inside the vessel increases, the distance to overpressure increases as well. It is possible to note that the increase of mass influence more the distance when the tank pressure is 11.8 bar_g (+12.4 %). Instead, when the hydrogen is in supercritical conditions, the mass has a weak influence on the results of the consequence analysis. The worst-case scenario is the third one, when the tank pressure is 31.2 bar_g, equal to the estimated bursting pressure of the tank.

For the considered cases, it seems that the tank pressure has a higher influence than the hydrogen mass on the consequence results. Comparing the same amount of hydrogen (26 kg) increasing the pressure from 9 to 31.2 bar_{g} , the distance to overpressure increase up to 19.8 %.

These results will be confirmed during the SH₂IFT project when the experimental tests will be carried out to validate this model.

4. Conclusions

Usually, BLEVE is considered as a domino effect and not as a direct consequence of a critical event such as a catastrophic rupture. In this study, an atypical accidental scenario, such as LH₂ BLEVE, has been integrated into the standard risk assessment of LH₂ technologies. This allowed defining appropriate safety barriers to avoid, control, limit or prevent causes and consequences of the critical events are suggested. Moreover, a

preliminary consequence analysis has been carried out. The results of this analysis showed there is a correlation between the hydrogen mass contained in the vessel, its pressure and the distance to BLEVE overpressure. This will represent the very first basis to design robust safety barriers. A more accurate consequence analysis should be carried out, employing and adapting for LH₂ different models validated for other substances. The suggested safety barriers and the results of the BLEVE consequence analysis will be confirmed and validated by the experimental tests that will be carried out during the SH₂IFT project.

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