Master's thesis

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Study and Analysis of Fire Safety in Energy Stations in comparison with Traditional Petrol Stations

Master's thesis in TBA4905
Supervisor: Jon Ivar Belghaug Knarud, Professor
Co-Supervisor: Ragni Fjellgaard Mikalsen, RISE Fire Research AS

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Acknowledgements

This master thesis marks the ending of my education at the Higher School of Industrial Engineering (ETSII) of the Polytechnic University of Valencia (UPV) and at the Norwegian University of Science and Technology (NTNU). The thesis was carried out in Trondheim (Norway) during my Erasmus period from January 2019 to June 2019 at the Department of Civil and Environmental Engineering.

The project has been a collaboration of the Department of Civil and Environmental Engineering of the NTNU together with RISE Fire Research A.S. In addition, it has counted on the help of experts in the area of renewable energy development such as hydrogen and conference attendance on future projects related to the use of gas and liquid hydrogen in Norwegian public transport and industry.

Since I started my studies in the Industrial Engineering Faculty at UPV, I have always had an interest in learning and expanding my knowledge in the area of structures, construction and installations both in buildings and industry. During my second year of master I had the opportunity to carry out the specialty in construction and facilities. To which I thank the professors of the specialty for their enthusiasm and motivation towards the students. Especially, Don Antonio Hospitaler Pérez for helping me to choose my Erasmus destination, be my engineering internship tutor and show me his great interest in the construction fire engineering area, which I also share.

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Trondheim, June 2019

Cristina Sanfeliu Meliá

Summary

During the last years the need to find new energy carriers in the automotive sector has increased in order to reduce the greenhouse gases which are poured into the atmosphere due to the use of fossil fuels such as gasoline, diesel and liquefied petroleum gas.

A growing part of the car fleet in Norway and Europe are powered by alternative energy carriers. In this way, traditional gas stations are expected to become energy stations with the main use of electricity and hydrogen.

This work analyses new energy stations where different risks in relation to the fire, leakage and explosion may be compared to that of current gas stations. Currently, the understanding of risks that may appear in hydrogen refueling stations (HRS) are still under development, so it becomes a major challenge for fire safety engineering.

The study is to analyze the hazards, fire causes and its consequences in hydrogen service station, based on incident data collection for petrol service station.

A service station is used as a case study. It will have a supply for gasoline and diesel vehicles, as well as for battery and hydrogen electric vehicles. Fossil fuels are stored in tanks for subsequent supply to the dispensers, while hydrogen is produced from water using electrolysis, where electricity is provided by solar panels located on the station's own roof and from the electrical grid. Regarding the hydrogen production on site, this may be transported by pipelines to on site storage facilities, where it is pressurized in tanks for supplying service.

In order to analyze this new infrastructure and compare its risks with that of traditional petrol stations, different methods for qualitative and quantitative risk assessments [1] are used, thus determining which method that is the most relevant. For this, it was necessary to identify hazards [2] in the hydrogen infrastructure by PHA (Preliminary Hazard Analysis). Moreover, development of better assessments necessitated use methods like FMECA (Failure Modes, Effects, and Criticality Analysis) and HazOp (Hazard and Operability). These last methods are used when the functional breakdown is sufficiently detailed. The objective was to find the consequences caused by deviations or hazards in the systems regarding to fire and/or explosion, and furthermore, to make an evaluation of whether the refueling station design taken into consideration was safe.

Deviations related to flow and pressures of the system were analysed. Overpressures, fatigue of materials and valves failures were identified as causes of hydrogen leakage.

In addition to focusing on the risks, accident scenarios were described in connection with hydrogen leakages in storage and dispensing, detected by means of risk assessment. These scenarios were simulated in FDS modelling software, where the concentration of hydrogen was studied in order to analyze different flow leakage rates. Finally, different ventilation rates were investigated to reduce the possibility of generating an explosive atmosphere.

Sammendrag

I løpet av de siste årene har behovet for å finne nye energibærere i bilbransjen økt for å redusere utslippet av drivhusgasser til atmosfæren, fra bruk av fossile brensler som bensin, diesel og flytende petroleumsgass.

En voksende del av bilflåten i Norge og Europa drives av alternative energibærere. Av den grunn forventes tradisjonelle bensinstasjoner å bli energistasjoner med hovedbruk av elektrisitet og hydrogen.

Dette arbeidet analyserer nye energistasjoner hvor ulike farer i forhold til brann, lekkasje og eksplosjon sammenlignes med dagens bensinstasjoner. For tiden er forståelsen av risiko som finnes i hydrogenstasjoner (HRS) fortsatt under utvikling, og er dermed en stor utfordring for brannsikkerhetsingeniører.

Studien analyserer farer, brannårsaker og konsekvenser i hydrogenstasjoner, basert på henting av datainnsamling for bensinstasjon.

En energistasjon brukes som en case studie. Det vil ha en forsyning for bensin og diesel kjøretøy, samt for batteri og hydrogen-elektriske kjøretøy. Fossilt brennstoff lagres i tanker for etterfølgende tilførsel til dispensere, mens hydrogen produseres fra vann ved hjelp av elektrolyse, hvor elektrisitet leveres av solcellepaneler på stasjonens eget tak og fra EL-nettet. Når det gjelder hydrogenproduksjon på stedet, kan dette transporteres via rørledninger til oppbevaringsanlegg på stedet, hvor det trykkes i tanker for levering av service.

For å analysere denne nye infrastrukturen og sammenligne risikoen med tradisjonelle bensinstasjoner, har det blitt brukt ulike metoder for kvalitative og kvantitative risikovurderinger [1], for deretter å bestemme hvilken metode som er mest relevant. For dette var det nødvendig å identifisere farer [2] i hydrogeninfrastrukturen ved hjelp av PHA (Preliminary Hazard Analysis). Utviklingen av bedre vurderinger nødvendiggjorde bruksmetoder som FMECA (Failure Modes, Effects, and Criticality Analysis) og HazOp (Hazard and Operability). Disse siste metodene brukes når funksjonell sammenbrudd er tilstrekkelig detaljert. Målet var å finne konsekvensene som følge av avvik eller farer i brann- og / eller eksplosjons i systemene, og dessuten å foreta en vurdering av hvorvidt designet av tankstasjonen, som ble tatt i betraktning, hadde lav nok risiko.

Avvik knyttet til strømning og trykk i systemet ble analysert. Overtrykk, utmattelse av materialer og ventiler ble identifisert som årsaker til hydrogenlekkasje.

I tillegg til å fokusere på risikoene ble det beskrevet ulykkescenarier, identifisert gjennom risikovurdering, i forbindelse med hydrogenlekkasje i lagring og dispensering. Disse scenariene ble simulert i FDS modelleringsprogramvare, hvor konsentrasjonen av hydrogen ble studert for å analysere ulike strømningslekkasjer. Til slutt ble forskjellige ventilasjonshastigheter undersøkt for å redusere muligheten for å få generert en eksplosiv atmosfære.

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Figures and Tables

Abbreviations

ATEX	Potentially Explosive Atmospheres (EU)
BP	Boiling Point
CFD	Computational Fluid Dynamics
CGH2	Compressed Gaseous Hydrogen
FDS	Fire Dynamics Simulator
FMEA	Failure modes and effects analysis
GH2	Gaseous Hydrogen
HAZOP	Hazards and Operability
H2	Hydrogen
HRS	Hydrogen Refuelling Station
HSS	Hydrogen Storage System
HIAD	Hydrogen Incidents and Accidents Database
ISO	International Organization for Standardization
LEL	Lower Explosivity Limit
LFL	Lower Flammability Limit
NFPA	National Fire Protection Agency (USA)
ODIN	Online Data and Information Network for Energy
PFS	Petrol Filling Station
PHA	Preliminary Hazard Analysis
PRD	Pressure Relief Device
QRA	Quantitative risk assessment
SWIFT	Structured What-IF checklisT
FTA	Fault tree analysis

Definitions

- Consequence: Severity of the harms caused to people, equipment or effects in the common operation of the process due to an accident.
- Harm: Physical injury or damage to the health of people, or damage to property or the environment.
- Hazard: Potential source of harm.
- Probability: Likelihood of occurrence of a determined event. Normally, it is expressed as expected period needed to the event to occur in common operation.
- Risk: Combination of the probability of occurrence of harm and the severity of that harm.
- Risk analysis: Systematic use of available information to identify hazards and to estimate risk.
- Risk assessment: A risk analysis followed by a risk evaluation.
- Risk evaluation: Procedure based on the comparison of risk achieved with tolerable risk.

1 Introduction

This master thesis is a survey of risks regarding fire and explosion in energy stations carried out in connection with RISE Fire research A.S. Nowadays, traditional petrol stations are becoming energy stations which including alternative energy carriers. In this project, hydrogen production and its leakage consequence in the station is studied and discussed.

1.1 Background

Currently, 81% of the total energy consumed in the world comes from oil, coal and gas. By 2030 [3], the world is projected to consume two-thirds more energy than today, with developing countries replacing the industrialized world as the largest group of energy consumers. Fossil fuels, including oil, coal, and gas, will remain the dominant sources of energy, accounting for more than 90% of the expected increase in demand, according to the International Energy Agency (IEA) of Paris (2004)[4]. Oil will continue to rise, with much of the increase in demand geared to the transport sector, nevertheless new energies in vehicles like hydrogen and electric cars would replace in the future the fossils of fuels in automobile sector.

Nowadays, hydrogen market is relatively small. While the technology exists, widespread production and adoption face significant challenges. Germany, Japan, United States and South Korea are among the pioneering countries in terms of the construction of hydrogen-based power stations and electric charge.

Hydrogen can be derived or produced from a variety of primary sources like ammonia, syngas, renewables, methanol and fossil fuels. It is likely to be the most important future energy carrier for many stations with the potential to produce reductions in carbon dioxide emissions as well as improvements of the efficiency at the global scale, if renewable primary energy sources are coupled with fuel cells. Nowadays, the options for the on-board storage of hydrogen are as a compressed gas, a cryogenic liquid, synthesis of ammonia or as a hydrocarbon reformed to produce a hydrogen stream.

The idea of combining fuels at the same fuelling station is due to the fact that it is possible to reduce costs and increase efficiency. Also, some improvements would be to use the same grid connection for both fast charging and production of hydrogen via electrolysis. One way to achieve this is to combine fast charging with on-site production of hydrogen at the fuelling station and regulate the electrolyser to reduce production when power is needed for fast charging.

The use of hydrogen vehicles requires appropriate infrastructure for production, storage and refuelling stages, which presents many safety problems due to hydrogen physical properties. The most dangerous physical properties are its low ignition temperature and its wide flammability range [5]. Because of this, in case of leakage in an enclosed space there is an explosion risk, generating dangerous overpressures for the structure, the materials and for the people. Other problems arise when the storage of the hydrogen in the gas state is required. It has a low density, so large volumes are needed to store it at high pressures.

In addition, normally hydrogen production facilities have limited space in urban area, so situated together with oil and electric charge still presents more challenges. Therefore, it is of great interest to build an appropriate infrastructure at the station, which maintains safety against fire and explosion hazards when in operation and along with other fuels.

Different hydrogen production plant typologies exist like hydrogen by water-electrolysis and gas reforming of hydrocarbons (e.g. natural gas). Each plant typology shows different safety problems. However, focusing in hydrogen production by means of water electrolysis requires an in-depth investigation from possible dangers and accidental risks. This accidental risk can expose damages to plant operators, people using the dispenser during refuelling, and people outside the station.

To reduce hazards, during the study and development of the station, all possible threats in the station's systems are identified through methodologies such as PHA (Preliminary hazard analysis), FMEA (Failure Mode and Effect Analysis) and HAZOP (Hazard Operability Analysis). These methodologies are standard engineering safety techniques. PHA describes possible hazard events in general, FMEA helps to minimize the effects of failure through appropriate corrective actions. HAZOP allows to identify hazards and accidental scenarios after PHA analysis. For this reason, it is crucial to have a broad knowledge about each part of the process, modes of operation, maintenance and security systems.

This project presents the results of risk assessment at the service station and the results of safety analysis by means of the techniques described, with special interest in hydrogen, as well as failure and deviations in its installations.

1.2 Challenges

This thesis studies hydrogen gas behaviour in refuelling station, during its production and supply, in order to reduce fire and explosion risks. Hydrogen leaks are very common in small amounts at stations, so if left uncontrolled, an amount of gas may accumulate in closed areas prone to explosion hazard. For this reason, the focus will be on studying what hydrogen concentration can create fire and explosion risk in the station, as well as, the proximity in the same station of petrol fuel supplies and fast charging of electric cars. The study attempts to answer the following questions:

1. What hazards exist in an energy station with respect to the risk of fire and explosion? Which parts of the system are most vulnerable?

2. Under what conditions can hydrogen gas be released? What levels or concentrations of gas can generate an explosive atmosphere? Where will more accumulations occur in case of leaks?

3. What consequences can an explosion of hydrogen gas cause at the energy station where other fuels are operated? How to mitigate this type of risk?

1.3 Objective

The main objective of this thesis is to study and analyse what hazards and what accidental situations related to fire and explosion could generate an explosive atmosphere in an energy station. This study is essential to reduce and mitigate any risk that occurs in an energy station, so that it becomes as safe as a traditional service station. Each hazard is determined by different risk assessment methods, while each method allows to describe the cause and consequence of each dangerous event in different states of the system.

The main difference with traditional service stations is the incorporation of hydrogen and electric fast charging. The use of hydrogen will increase the risk in the station, so it will be necessary to analyse what risk assessment methodology is the most appropriate and what are the worst scenarios that can occur in its facilities.

For the energy station to be safe, it will be necessary to study what concentration levels of hydrogen in closed spaces will generate a risk of fire and explosion. The simulation in FDS will allow to analyse what is the behaviour of gas and how it accumulates in closed spaces, in this way it will be investigated how different designs of ventilation affect gas dispersion.

1.3.1 Scope

The scope in this project is to detect what levels of hydrogen leakage could create an explosive atmosphere in the station and what is the risk having fuel petrol supply, fast charging and external fire near to hydrogen storage and dispensing. The aim is that this information will contribute with a basis for new regulations and guidelines regarding energy stations.

1.3.2 Limitations

Analysing all risks in an energy station with hydrogen refuelling and fast charging is not an easy task. It involves finding specific information about the equipment, its operating systems, control system and facilities. The limitations found in the project are detailed in the following paragraphs:

First, it is difficult to analyse the hazard identification phase, then there are difficulties when it comes to decide what risk assessment techniques is appropriated and finally, there are difficulties in finding available resources.

In order to study and analyse all the risks, it is necessary to have feedback and help from experts in the area, who contribute their knowledge in risk analysis, sequence studies, frequency and consequence of any dangerous event. Due to the lack of information in the risk assessment during the execution of the project, this has implied difficulty in the study of frequency and consequence of the events.

2 Methodology

Figure 1 shows the methodology of this master thesis which begins with a literature of study about hazards and risks in an energy station, as well as the theoretical qualitative and quantitative risk assessment methods. The process, operation, facilities and equipment at energies stations based on examples of energies stations in Norway, Germany, South Korea, United States and technical guidelines about hydrogen refuelling station are found in scientific documents.

Subsequently, hazardous areas and safety distance in an energy station are defined based on *guidelines chapter 3.4.* In addition, it is explained *fuels properties regarding fire and explosion risk in chapter 4* - which help to understand what its physical behaviour in terms of flammability and possible causes and consequences in the hazard identification phase is.

Database of historical accidents is used as a basis for hazardous events at the station. Different risk assessment methods are used to identify, evaluate and mitigate hazardous events.

According to the objective, the worst-scenarios are related to hydrogen leakages, which can create explosive atmospheres. Different leakage rates are released in an enclosed area and hydrogen concentration is measured. This study is simulated in CFD (Computational Fluid Dynamics) to investigate hydrogen gas dispersion and hydrogen concentration through different design configurations.

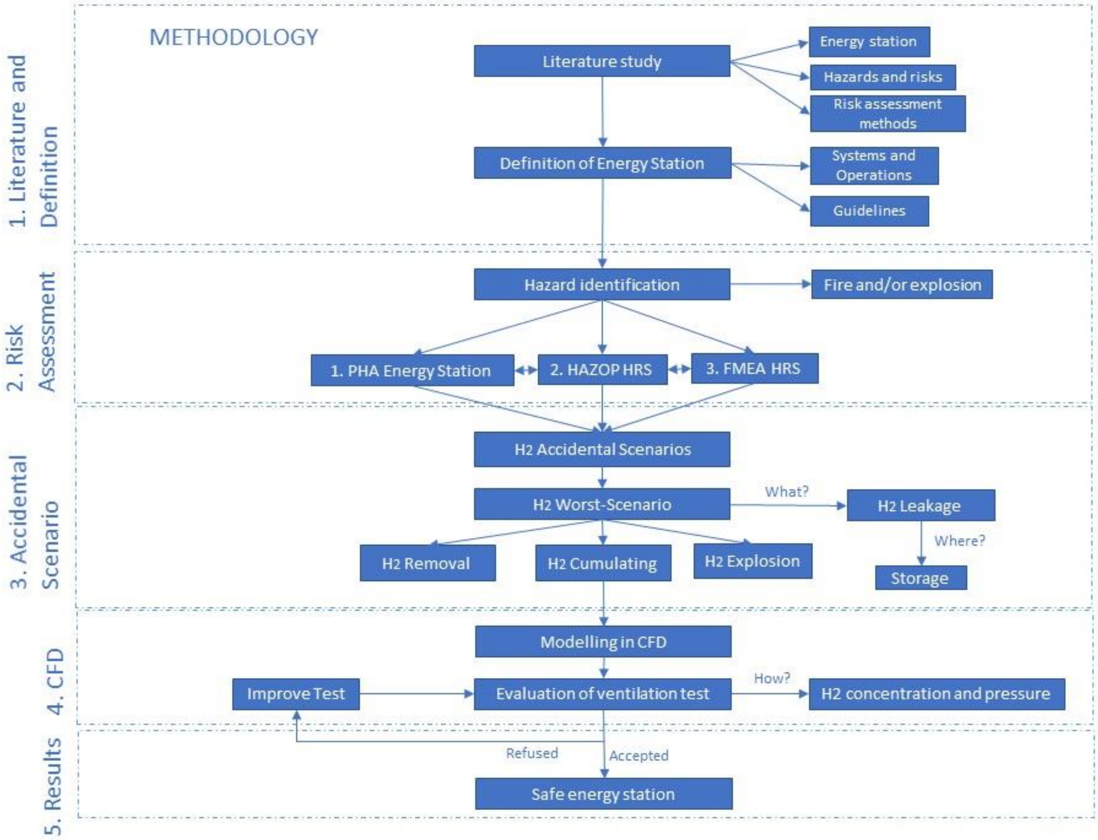


Figure 1. Methodology developed in this master thesis. (Autor design)

2.1 Literature study

A literature study was conducted in order to find information about risks in fire and explosion in refuelling hydrogen gas, petrol and fast charging. The theorical risks found in science articles, book, projects and official websites will be used as a basis for the discussion of simulation results.

In the search for literature, the same keywords were used, such as *petrol station, hydrogen refueling station, hazards, risk assessment, FMEA, HazOp, leakage rate, CFD and ventilation*. Not all databases include the same library of literature, so different databases have been taken. In addition, all the keywords have been used in different combinations so that the search was as concrete as possible with the treated area. The databases and search engines used was Oria, Science Direct, Google Scholar, HIAD website and Hydrogen Europe. Articles and reports without online access were ordered through NTNU *University Library*.

2.2 Definition of energy station

The study is based on an energy station which has the supply of several fuels for its users. According to **InterReg project funded by the EU** [6] this type of station is known as multifuel energy station, where the term “multifuel” implies that there are at least two types of renewable fuel in the station, including the term “energy” to indicate the fact that there are poles of electric charge.

As a starting point it is known that the station will serve cars, light trucks and buses. Their fuel can be hydrogen, diesel, gasoline or electricity. The fuels considered are compressed hydrogen (CH2), liquid gasoline and gasoil and fast charging. In addition, it will have photovoltaic cells located on the roof to supply electricity for the load, the hydrogen production process and service functions.

The energy station systems, hazardous areas, regulations and safety distances are described in *chapter 3*. Hydrogen refuelling station has an infrastructure formed by production and transport by means of pipes, storage and dispensers. At the same time, the refuelling of petrol is transported and stored in a tank, where it is connected by means of pipes to the dispensers. Meanwhile the electric charging poles will connect directly with the vehicles.

2.3 Fuels behaviour regarding fire and/or explosion

The physical properties of hydrogen are described and compared with other fuels (e.g. gasoline, methane, propane) in *chapter 4.1*. On the other hand, the properties of fuels, which can generate high fire and / or explosion risks in the facilities of the station, are described in *chapter 4.2.1* and *4.2.2.*

2.4 Risk assessment methods

Risk assessment is a process of identifying and analysing possible hazards where the main aim is the prevention and mitigation of accidents in potentially hazardous facilities.

This project is based on a study of the energy station by means of the methodology described in *1.1 Background*. A preliminary hazard analysis (PHA) is performed in combination with HAZOP and FMEA. These methods are developed in *chapter 6.1 Case of Study and Appendices*. A PHA is a preliminary method to analyse hazards that can appear when petrol, hydrogen and fast charging are staying at the same place. Since the objective is to identified hazards in hydrogen facilities, which can affect to the other installations, qualitative and quantitative methods are used to describe in detail hydrogen risks. A HAZOP method is used to evaluate and complete system hazards by assuming deviations in hydrogen process. A FMEA is used to describe failure modes that generate the hydrogen deviations states.

This project does not analyze failures mode probabilities, but it is based on the three-point scale used in TIAX studies project [7] which is described in *chapter 6.1.3*.

The main difference between risk-assessment methods is presented in *table 1*.

Table 1. Risk assessment methodology: PHA, HAZOP and FMEA [2].

Method	Qualitative/quantitative	When to be used
PHA	Qualitative	Early in the design process when little detail about design is available.
HAZOP	Qualitative	During detailed design, verify a safe and reliable process design.
FMEA	Semi-quantitative	Detailed design review with focus on safe design. An effort to rank the risk contributors is included.

2.5 Scenarios

The selection of accidental scenarios has been based on the study of the systems and operations that presented the highest risk in hydrogen leakage after conducting HAZOP and FMEA analyses. The analysis of the hydrogen installations, by means of these methods, present a higher accident risk when occur a hydrogen leakage and explosion

In *chapter 7.1 Potential accidental scenarios* for each equipment of the hydrogen installation, possible scenarios that will produce leaks and/or explosions due to malfunction in valves are described.

In *chapter 7.2 worsts cases scenarios* are described. These scenarios are related to malfunction in valves at storage, malfunction in safety valve in dispenser or hose rupture. Small leakage will generate large accumulations in hydrogen production area, meanwhile hydrogen leakage in dispensing area may accumulate hydrogen on the roof of the station.

In *chapter 5.2 and 5.5* hydrogen leakage in a closed area, events and consequences are described.

2.6 CFD

Describing the worst scenarios in *chapter 7.2*, computational fluid dynamics (CFD) is used to study hydrogen behaviour when a release occurs in the production unit's enclosure.

CFD allows to provide the concentration of gas in the area of interest and has the ability to investigate different parameters such as ventilation, obstacle configurations and sources of ignition.

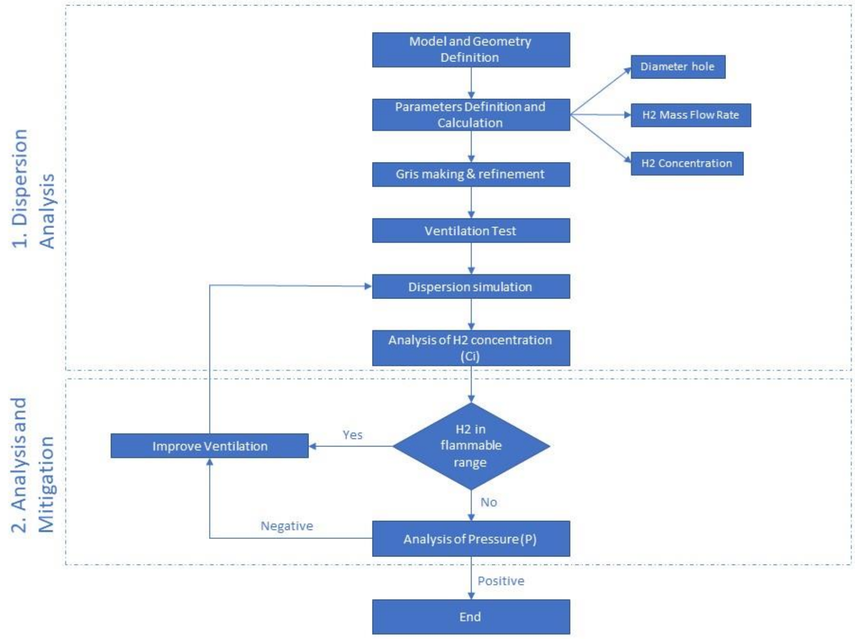


Figure 2. The proposed methodology for the safe design of confined spaces exposed to a hydrogen release. (Autor design)

Figure 2 shows a CFD-based approach to evaluate the dispersion behaviour of the hydrogen gas, its accumulation and concentration level after a release of hydrogen jet without ignition at unit production. Through different configurations described in *chapter 8.4 Simulation Strategy*, the ventilation condition is improved and the fuel concentration is reduced below the flammable level (4-75 v/v%).

2.6.1 Software of simulation

In this master's thesis the simulator FDS used is ***Pyrosim***. Dynamic fire simulator (FDS) was developed for the first time by the **National Institute of Standards and Technology (NIST)** to simulate a fire and the consequences of smoke [8]. Currently, there are many software that perform this type of computational analysis. ***Pyrosim*** is a graphical interface of FDS that allows studying the substances that are emitted in a fire, the behaviour of the fire and allows modelling where it does not include fire, such as ventilation.

2.6.2 Dispersion modelling using FDS

The implemented FDS model solves Navier-Stokes equations for low Mach numbers. In three-dimensional tetrahedral elements FDS uses the finite difference method to estimate the derivation of the conservative equations of mass, momentum and energy in an iteration scheme as described in [8]. Large Eddy Simulations (LES) formulation of conservation laws is adopted to solve the equations.

2.6.3 Modelling and simulation strategy

For the analysis in FDS different meshes have been distributed in the station model. Therefore, a further study can be carried out in hydrogen production area when hydrogen leakage occurs. In the modelling of hydrogen production area, six meshes have been chosen and the minimum cell size has been 0.2m as can be seen in *Figure 3*. *Table 2* shows the number of cells used in each case:

Table 2. Number of cells for mesh in hydrogen unit production.

Mesh Name in Unit Production	Number of cells for mesh
Mesh01-f-a	33.660
Mesh01-f-b	28.710
Mesh01-f-c	35.700
Mesh01-f-d	30.450
Mesh01-f-e	33.660
Mesh01-f-f	28.710

Five tests are studied with natural ventilation, meanwhile twelve are studied like a combination of natural and forced ventilation for 3mm diameter as is described in *chapter 8.3.1 Scenarios Definition*. Hydrogen concentration and pressure parameters inside the enclosure are evaluated. Seven tests are selected to be studied with hydrogen leakage for 1mm and 5mm diameter.

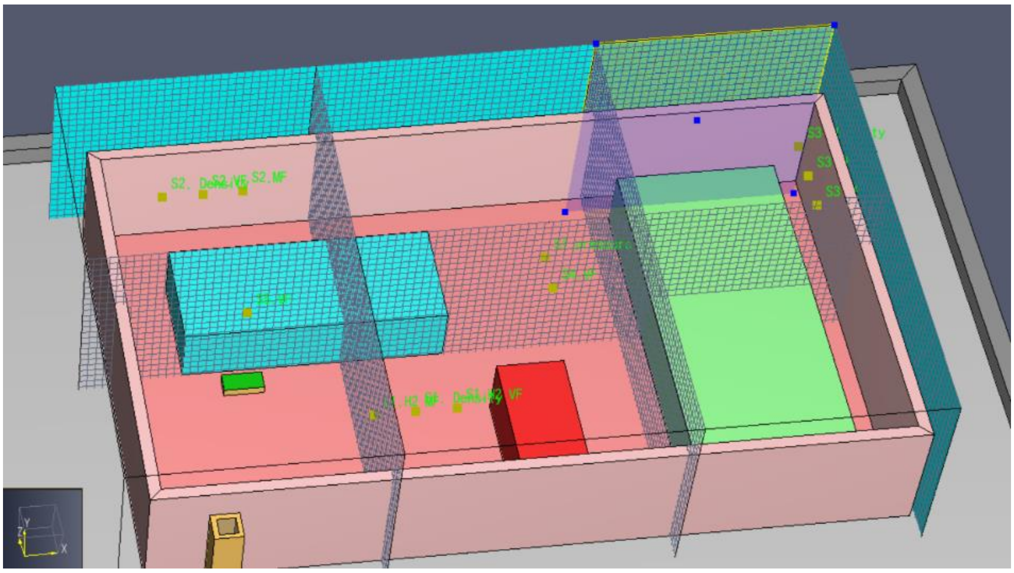


Figure 3. Different mesh in hydrogen unit production at the energy station.

The simulation time for each hydrogen leakage rate depends on the leakage diameter and the storage capacity as described in *chapter 8.2 Theoretical Calculations* and *table 19*. Tank emptying times for 1mm, 3mm and 5mm is respectively 60 min, 6.5 min and 4.3 min.

In relation to forced ventilation by extraction, like is described in *chapter 8.2 Theoretical calculations* and the results expressed in *table 23*, different configurations of forced ventilation are studied under values of extraction of hydrogen of 2.56 m^3/s, 4.6 m3 / s, 5.12 m^3/s and 9.22 m^3/s per exhaust. The value of 4.6 m^3/s is used due to the occurrence of negative pressures in production area when the flow is 9.22 m^3/s, so that it is an average extraction value between 2.56 m^3/s and 9.22 m^3/s.

3 Energy station systems

In the following chapter is described the station infrastructure, combustible/energies supply process, equipment and installations of energy station study case.

3.1 Petrol Refuelling Process

General Description

The station counts on petrol and diesel fuel supply. The petrol station equipment is roughly divided into an underground tank and dispensers. The gasoline and diesel are transported by a truck to the petrol station. The storage is connected to the dispenser. The fuels are pumped upward due to a pump inside the dispenser which working when the nozzle is activated.

The process and operation of the system are detailed in chapters *3.1.1 Storage* and *3.1.2 Dispenser.*

3.1.1 Storage

The storage tank is located underground in the station, where the fuel is a pressure of 0.3 MPa. This storage is connected with petrol dispenser by means of pipelines, which have security valves, meters and pumping equipment.

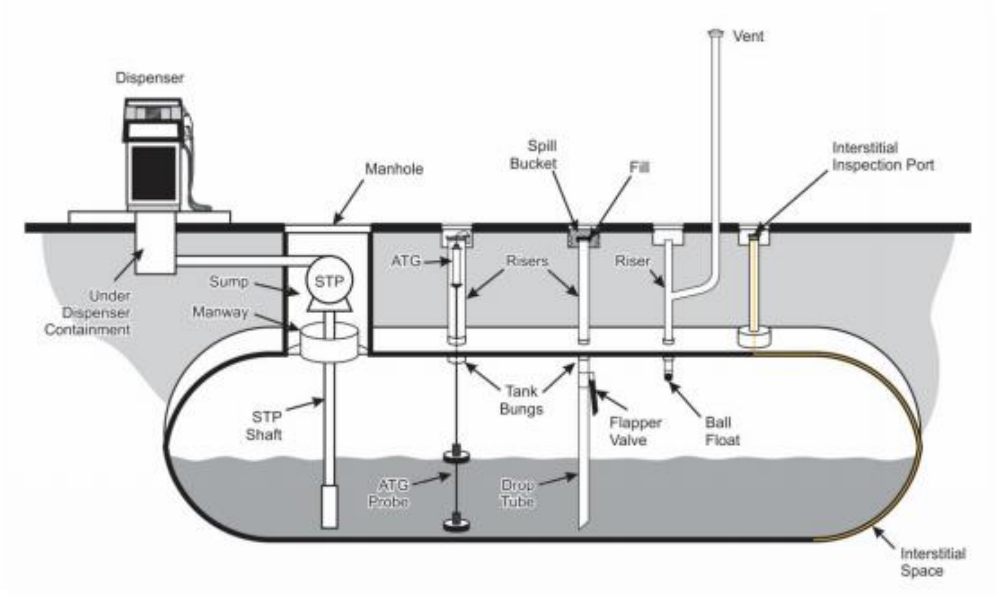


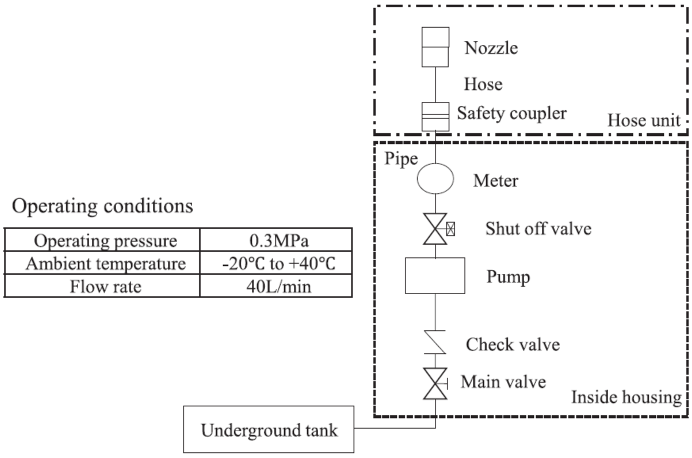
Figure 4. Simplified Diagram of Diesel Underground Storage and System Equipment [9].

3.1.2 Dispenser

The dispenser is divided into two parts, inside housing and hose unit. Normally, the pressure is 0.3 MPa, the maximum flow rate of dispensing is 40L/min and the ambient operating temperature is from -20 to 40ºC [10], [11] .

Onside housing is located the security valves, meters and pumping equipment as it is shown in *figure 5*. When the pump is in the off state, the check valve prevents the internal gasoline / diesel from returning to the underground tank. The shutoff valve is normally closed and opens only during refuelling. The shutoff valve is closed only when the emergency stop button is pressed during refuelling. This emergency button is pressed when leaks or malfunctions appear.

On the other hand, the hose unit is the equipment to supply the vehicle and a safety coupler is incorporated.



Operating conditions

Operating pressure	0.3MPa
Ambient temperature	-20℃ to +40℃
Flow rate	40L/min

Figure 5. Gasoline dispenser model [11]

3.2 Electric Cars Posts

General Description

The station has an infrastructure combined with electric vehicles charging. The fast charging posts support high voltage and high current. The electricity is obtained by facilities in the station (Transformers) and part of the photovoltaic panels in the roof of the shop service station.

The charging is produced by means of a cable and plug connected with the electric car. These electric cars posts have DC Charge System [12], where the time needed to charge the battery is around 20-30 minutes (Fast Charging). In addition, the voltage is around 400-500V and the power ≥ 50kW, depending on the vehicle. The infrastructure is composed of multiple fast charging points in order to delivery electricity in sudden surges in demand.

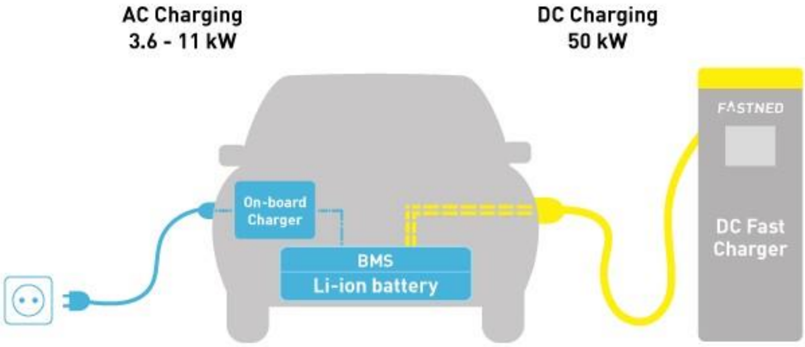


Figure 6. AC and DC charging in electric vehicle [13].

3.3 Hydrogen Refuelling Process

Hydrogen can be produced from many primary energy sources and through various technical processes, but not all techniques reduce greenhouse gases [14]. Previous studies [15], [16] explain that reforming (Gas-mix, Biogas-mix or LNG) produces higher greenhouse gas emissions than electrolysis when electrolysis is produced by renewable energy like photovoltaic panels.

The study presented [17] for the **International Journal of Hydrogen Energy** reveals that the transport of hydrogen is stored in liquid state because needs less tank volume and its gas compression demands a small amount of energy at the station. However, liquid hydrogen demands more energy during transport because it must heat at temperature of -33ºC to -40ºC. The hydrogen in gas state needs greater energy consumption in compression stage, but lower consumption in pre-cooling system. In summary, the transport of liquefied hydrogen consumes more energy than compression in a tube trailer. For this reason, hydrogen will be produced at the station and the process to obtain hydrogen will be carried out by water electrolysis.

General Description:

The hydrogen refuelling is an infrastructure designed for filling a vehicle with hydrogen fuel. Hydrogen is produced in gaseous state on-site and the facilities are composed by the following equipment (*Figure 7*).

- Water Electrolysis Cells
- Low-Pressure Storage
- Compressors which brings the hydrogen to the desired gas pressure level
- High-Pressure Storage
- Precooling system
- Dispensers for delivering the fuel

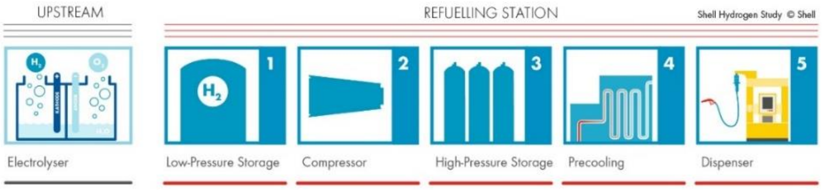


Figure 7. Components of a Hydrogen Refuelling Station [15]. *Shell Hydrogen Study. Supply Hydrogen (https://hydrogeneurope.eu/hydrogen-production-0)*

The process begins with hydrogen is produced by water electrolysis. Electrolysis is a process based on electricity, oxygen and water together with electrolyte solution [18] (34% KOH). At the station, electrolysis is produced inside a container, which is composed of the equipment to purify and prepare hydrogen under conditions. This equipment is constituted of deoxider (O2 seal/demister), hydrogen ballast, hydrogen purification, hydrogen drying and auxiliary cooling as is shown in manufactures [19] and *figure 9*.

The compression stages required are shown in *figure 9: Stages 1 & 2 and Stages 3 & 4*. The first stage compresses at a suitable pressure to perform the purification and drying of hydrogen. In the second stage, hydrogen is compressed into three states to store it at low, medium and high pressure. The connection is by means of pipes which have different valves such as pressure switch (PS), pressure relief system (PRD), solenoid valve (SV) and pressure and flow meters as shown in *figure 11*. In addition to this, indicators of level, temperature, pressure and conductivity are located in its corresponding equipment. These systems control the proper functioning of the process to guarantee its safety.

The storage is connected to the dispenser, where the pressurized gas is sent from three storage. The medium pressure is around 70MPa and at a temperature of -40ºC [11][15]. This is because the gas when it is compressed at high pressure raises its temperature and should be controlled by gas coolers.

The process and operation of the system are detailed in the following sections. In addition to this, it is shown an ***example of Piping and Instrumentation Diagram for Electrolyser-Based Refuelling*** [7] *and a* ***simplified process flow schematic for a hydrogen fuelling station with an on-site electrolyser*** [20].

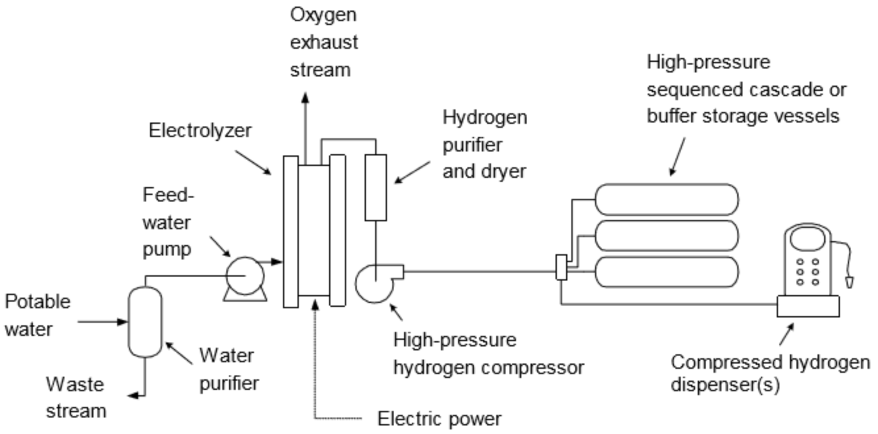


Figure 8. Simplified process flow schematic for a hydrogen fuelling station with an on-site electrolyser [20].

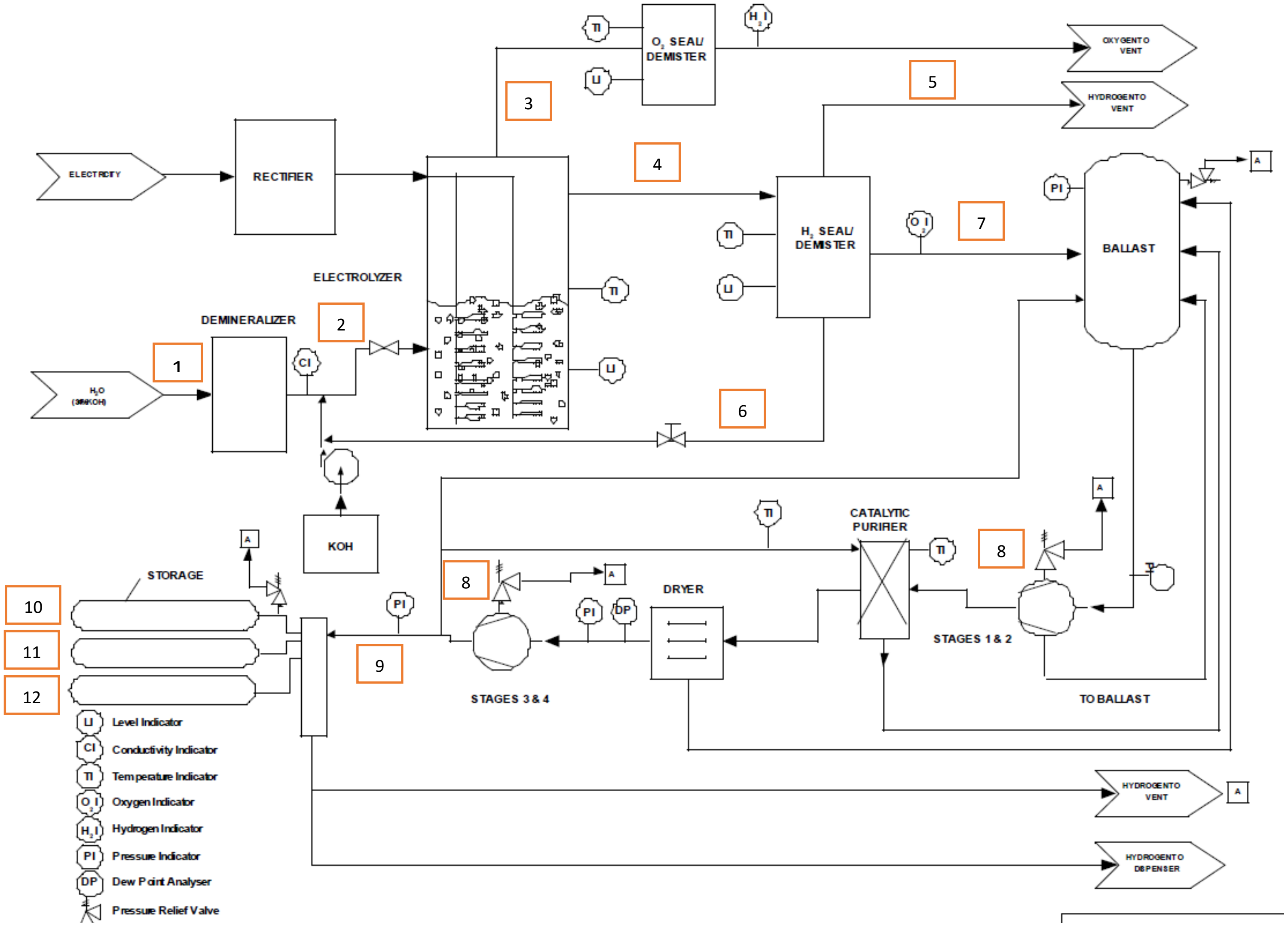


Figure 9. Example of Piping and Instrumentation Diagram for Electrolyser-Based Refuelling [7].

3.3.1 Production

Description electrolysis process:

Hydrogen is produced by water electrolysis at the station. The electrolyser consists of a DC source and two noble-metal-coated electrodes, which are separated by an electrolyte. The electrolysers are differentiated by the electrolyte materials and the temperature at which they are operated. The most common are alkaline electrolysis (AE) and proton exchange membrane (PEM) electrolysis.

Alkaline electrolysis has benefits in comparison with PEM due to reaching up to 60% efficiency and the circulating liquid electrolyte (KOH) has a freezing temperature of below -40 ºC allowing the start up in sub-freezing conditions. PEM typically require water for membrane hydration; therefore, must operate in conditions above freezing (4°C) or be placed in a heated and insulated enclosure [15], [21].

Alkaline electrolysis is characterized by having two electrodes immersed in a liquid alkaline electrolyte consisting of a caustic potash solution (KOH). KOH is preferred over sodium hydroxide (NaOH) because the former electrolyte solutions have higher conductivity [22].

The electrodes are separated by a diaphragm, separating the product gases and transporting the hydroxide ions (OH^-) from one electrode to the other. When enough voltage is applied between the two electrodes, at the cathode water molecules take electrons to make OH^- ions and H_2 molecule. OH^- ions travel through the 34% KOH electrolyte towards the anode where they are combines and give up their extra electrons to make water, electrons, and O_2.

Conventional alkaline water electrolyzes are designed to run at temperatures of around 80-90 ºC [23] [24]. The pressure at which the electrolyser operates should depend on the end use of the produced hydrogen, normally 8 bar. In addition, it is essential for the electrode materials to be stable in highly corrosive alkaline environments, to minimize the electrolyser's operation and maintenance costs [25].

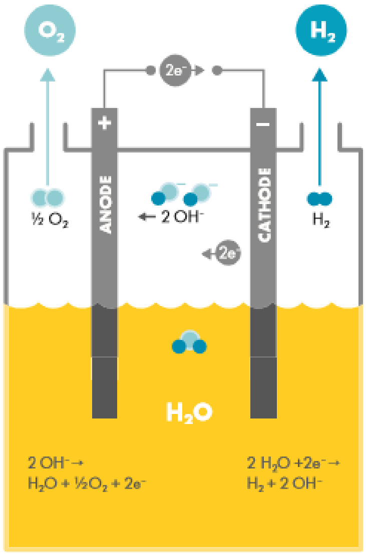


Figure 10. Principles of electrolysis [15]

The water quality is a central factor to ensure long-life operation of an electrolyser. The highly alkaline environment in the electrolysis cell requires the concentrations of magnesium and calcium ions to be sufficiently low to avoid precipitation of their hydroxides [22]. In addition, when the current density exceeds the so-called limiting current of hydroxyl ions,[26] chloride ions present in solution are oxidized to chlorine at the anode surface, which is extremely corrosive to most metallic components of the electrolyser.

3.3.1.1 Unit production systems, valves and controls

Figure 9 shows the valves (through orange squares) that will have the pipes of the electrolyser, compressor, storage and dispenser of hydrogen. The content of each orange square is explained in *Tables 3, 4 and 5*. In case of the electrolytic hydrogen generation system [27] and purification, their valves and vent lines is described in *Table 3*.

Table 3. Vales, shut-off and vent line in piping contents of hydrogen unit production [27] *.*

System	Contents of piping	Pressure (MPa)	Configuration
1	Water+Air	Air 0.1	Check valve included
2	Water demineralizered	-	Check valve and safety valve included
3	Oxygen gas	-	Safety valve and shut off valve included
4	Hydrogen gas	20	Check valve and safety valve included
5	Hydrogen gas	Small quantity	Pressure reducing valve, shut-off valve and Vent line
6	Water	0.9	Back pressure valve included, safety valve and shut-off valve
7	Hydrogen gas to compress-purifier and dry	20	Back pressure valve, check valve and safety valve included.

3.3.2 Compression

Hydrogen is produced in gaseous state and it is stored by a three-state compressor arriving at 5-10MPa until 70-85 MPa. The arriving pressure is insufficient to supply hydrogen in fuel cells; therefore, it is compressed around 85MPa of pressure [15]. The equipment is buffer, compressor and precooling system.

Buffer:

The buffer helps compressor capacity in order to this can be used for many hours per day.

Compressor:

Two stages of compression are necessary in order to hydrogen gas has an appropriate pressure. At first stage, hydrogen gas is compressed at a low pressure to perform its purification and drying. While, on second stage, hydrogen gas is compressed into three states to store it at low, medium and high pressure.

Precooling system:

Hydrogen is heated when is compressed during refuelling. Depending on ambient temperature, fuel delivery temperature and target pressure in the vehicle tank. Precooling is necessary to stay in within the limits (overpressure/overheat) of the vehicle's fuel storage system. For 70 MPa, hydrogen refuelling is generally precooled to -40ºC [15] ***(according to SAE J2601).*** The low temperature required is usually generated by means of a compression refrigerating machine and a suitable heat exchanger.

3.3.2.1 Compressor pipeline, valves and controls

The compressor is connected to storage by pipelines. The compressor pipeline is equipped with internal and external pressure switches that operate based on downstream pressure.

In order to control the pressure and flow, *table 4* shows a list of control systems. These control systems are valves, pressure regulators and switch. Like an example case, *figure 11* shows a compression and storage equipment in a ***hydrogen refuelling station in Eureka, California.***

According to *figure 8*, in compressor pipeline is located an external pressure switch (PS2), which ensures that the compressor switches off when the storage pressure equals the set point value. In addition, a pressure regulator (PR) and the pressure relief system (PRD1) reduces unwanted higher gas pressure in the line [28].

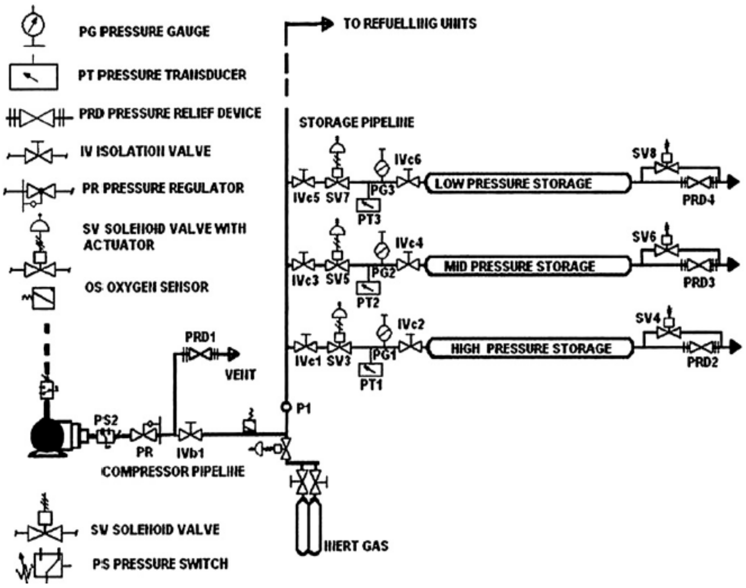


Figure 11. Example of Compression and storage units of a Plant in California [29] [28].

Table 4. Devices, valves and controls in hydrogen compressor and storage.

System	**Contents**	**Pressure (MPa)** [30]	**Configuration** [29][28]
8	Compressor vent		Pressure relief device (PRD)
9	Hydrogen in three-stages compressor pipeline	5-85MPa	External Pressure switch (PS) Pressure regulator (PR)
10	Hydrogen at low-pressure in storage pipeline	5-10 MPa	Solenoid valve (SV) Pressure relief device (PRD)
11	Hydrogen at medium-pressure in storage pipeline	20-50MPa	Solenoid valve (SV) Pressure relief device (PRD)
12	Hydrogen at high-pressure in storage pipeline	50-85MPa	Solenoid valve (SV) Pressure relief device (PRD)

3.3.3 Storage

The hydrogen compressed gas is send to three storage. Each tank has different pressures. Usually, the pressure levels at a refuelling station are at low-pressure storage (5-10 MPa), medium-pressure (20-50 MPa) and high-pressure storage (50-85 MPa).

3.3.3.1 On-board hydrogen storage

Hydrogen gas storage in vehicles is in high-pressure (around 70 MPa); therefore, it is necessary a large storage volume to maintain steady. The reason is because hydrogen gas has a low volumetric energy density in comparison with hydrogen liquid.

On-board hydrogen storage is required greater volume capacities than the full range of light-duty vehicle platforms (e.g. Gasoline and diesel cars).

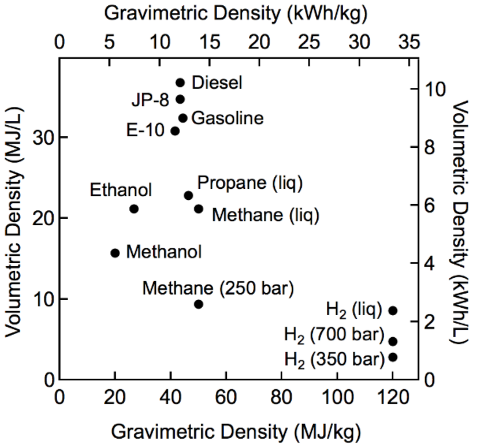


Figure 12. Comparison of specific energy (energy per mass or gravimetric density) and energy density (energy per volume or volumetric density) for several fuels based on lower heating values [31]. *https://www.energy.gov/eere/fuelcells/hydrogen-storage*

- Cars: store up to 6 kg of hydrogen on-board needed to provide a driving range in the region of 400-500 km [15][32].

- Buses: store up to 50kg of hydrogen on-board due to several tanks situated on the roof [15][32].

- Trucks: are heavier, requires more power for a longer distance which results in a larger amount of energy needed on board [6].

3.3.3.2 Storage pipeline, valves and controls

Figure 6 shows valves and controls in storage. Each storage is protected by pressure relief devices which help to assure that the maximum allowable pressure is not exceeded. Such devices are composed by mechanical valve (PRD) and solenoid one (SV), which act when the pressure excess or control system malfunction.

Storage pipelines are equipped with pressure gauges (PG), connected with pressure transducers (PT), and solenoid valves actuated (SV) by a programmable logic controller (PLC). This PLC is also used to control major safety functions of the station, including regulation of the dispenser interactions.

Hydrogen is supplied when the vehicle is connected to the dispenser. The PLC makes solenoid valve (SV7) of the storage low pressure gas line to open. If it is necessary, the operation is completed by the other stages at higher pressures. Hydrogen outflow is regulated from storage vessel in order to optimizing the refuelling time [28].

In addition, a manual emergency shut-down is placed inside as well outside the facility to initiate immediate shut-down of all process hydrogen lines.

3.3.4 Dispenser

The hydrogen is refuelled to a vehicle through a dispenser. According to the pressure supply, different times of filling exist. On-board storage will be 70MPa; therefore, the dispenser will work around at 85 MPa to control the pressure drop. In addition, the maximum flow rate will be 5 kg/min and a delivery temperature at -40ºC [11].

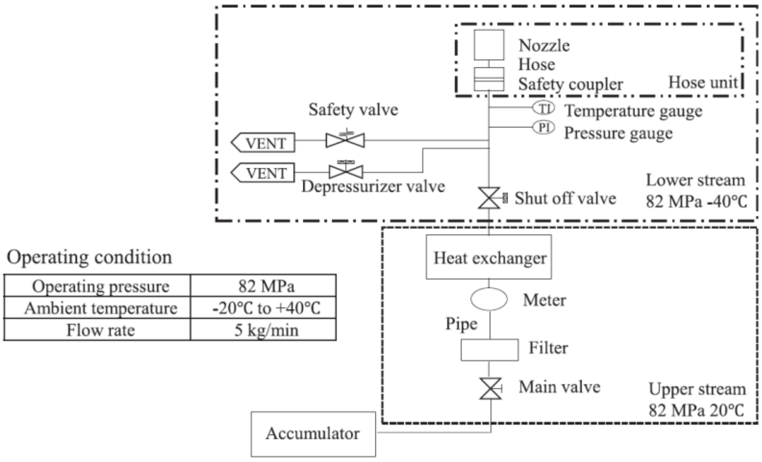
3.3.4.1 Dispenser devices, valves and controls

Hydrogen is introduced to the dispenser by differential pressure through the main valve. On this way, the dispenser model is divided into two parts like is shown in *figure 10*: upper stream section and lower stream section [11]. This information about filling is based ***on SAE J2600 (Compressed Hydrogen Surface Vehicle Fuelling Connection Devices)***[33] which explains the design and control on dispensers.

In the upper stream is used a filter to block foreign particles during the transfer and a meter where the mass of the flowing gas is measured. A heat exchanger is used to cool the hydrogen. This heat exchanger controls the temperature rises that results from adiabatic compression during high-speed filling.

In the lower stream section is situated a shutoff valve which is closed if the pressure or temperature exceeds the set value. The temperature and pressure are monitored by the pressure gauge (PI) and the thermometer (TI)[33].

Hydrogen is transferred to the vehicle tank through the hose unit which is composed of safety coupler, hose and nozzle. Safety coupler is designed to protect the entire structure in front of leakage.



Operating condition

Operating pressure	82 MPa
Ambient temperature	-20°C to +40°C
Flow rate	5 kg/min

Figure 13. Hydrogen dispenser model [11]

To control the flow, a valve is installed between dispenser and accumulator. The safety valve opens when the preset pressure level is exceeded and will release hydrogen safely from the upper part of the dispenser into the atmosphere. Also, a depressurized valve is installed to release the pressure between the shutoff valve and the nozzle after filling is complete. In case of the leak detector is triggered, the dispenser shutoff valve is closed automatically, reducing the amount of the leakage and minimizing the scale of any fire or explosion.

3.4 Guidelines

In this thesis, as well as using scientific literature, has also found the following regulations and technical considerations in reference to the design, location, storage, fuelling and fire safety of the use of hydrogen, petrol and electric charging posts.

The regulations found to analyse the *supply of petrol* have been:

- The guidance issued by the Health and Safety Executive (HSE, United States): **The Dangerous Substances and Explosive Atmospheres Regulations 2002 (DSEAR)**[34].
- Petrol Filling Stations: Guidance on Managing the Risk of Fire & Explosion (**The Red Guide created by The Energy Institute (EI), London**)[35] .

- Design, construction, modification, maintenance and decommissioning of filling stations (**The Blue Book created by the Association for Petroleum and Explosives Administration (APEA) and Energy Institute (EI)**) [36] :
    - Hazardous Area Classification
    - Planning and Design

The guidelines found to analyse the *supply of hydrogen* have been:

- ISO / TS 19880-1: 2016 Gaseous H2 - Fueling Stations. Part 1: General requirements. *Risk-reducing measure* [37].
- ISO / IEC 60079-10-1: 2015 Explosive Atmospheres - Part 10-1 (Classification of areas - Explosive gas atmospheres) [38].
- NFPA 55: Compressed Gases and Cryogenic Fluids Code. Standard for Gaseous Hydrogen Systems at Consumer Sites. (**National Fire Protection Association (NFPA), United States**) [39].
    - Incorporation of the requirements of NFPA 50A, *Standard for Gaseous Hydrogen Systems at Consumer Sites*, into Chapter 10.
- Guidance on hydrogen delivery systems for refuelling of motor vehicles, co-located with petrol fuelling stations (**Supplement to Blue Book created by the Association for Petroleum and Explosives Administration (APEA) and Energy Institute (EI)**) [40].

The regulations found to analyse *fast charging* have been:

- ISO EN 60079-14: 2014 Explosive Atmospheres – Part 14 Electrical installations design, selection and erection [41].

3.5 Hazardous areas

Dangerous areas are necessary to identify at hydrogen installations to reduce the risks regarding fire and explosion. These areas will consider the elements of the following operations:

- On-site generation equipment
- Vents lines
- Hydrogen storage facility
- Transfer piping from storage to dispenser
- The hydrogen dispenser
- The vehicle filling procedure at possible locations
- The hydrogen fuel delivery vehicle
- The fuel unloading procedure, including hoses

The hazardous areas of petrol near the hydrogen facilities should be studied. As ***The Blue Book*** [40] well describes, the road tanker unloading of petrol, drainage systems, vapour petrol venting and petrol dispensers should be taken into account.

The methodology defined to protect petrol areas is equivalent to the zone definitions given in DSEAR. In contrast, hazardous areas in hydrogen installations can be identified using the example presented in *section 3.4 of the Supplement to Blue Book*, which refers to the ***Guidance BCGA CP 41*** [42]. In addition, methodologies such as described in ***BS EN 60079 Explosive Atmospheres - Part 10-1 (Classification of areas - Explosive gas atmospheres)*** [38] may be applied.

Table 5 shows the hazardous areas for each hydrogen equipment. These hazardous areas are considered in the layout explained in *chapter 3.6 Safety distances*.

Table 5. Hazardous area in hydrogen equipment: compressor, storage, dispense, relief valves and vent line.

Potential area of flammable/explosive atmosphere in hydrogen equipment	The area is expressed in meters terms
Around compressor unit	5-4.6m
Around storage unit	5-4.6m
Around dispenser	1.5m
Outdoor discharge for relief valves or vents	1.5-4.6m

3.6 Safety distances

The safety distances are the minimum recommended separations between systems. As it is the case of traditional gasoline stations, these are governed by regulations and studies. Petrol station regulations develop the minimum safety distances between the filling of underground tank, the gas vapor ventilation systems and the use of the dispensers. The incorporation of hydrogen production and its facilities will increase the risks in the station.

This chapter compiles what guidelines could be used at the station. It also explains a brief comparison between the existing guidelines and which distances are taken for the model of the energy station.

3.6.1 Comparison of guidelines

In ***annex A of ISO / TS 19880-1: 2016*** [37], examples of safety distances are collected depending on the country where it is applied. Currently, there is no list detailing international values [43] due to the lack of consensus between countries. The guidelines differ in minimum safety distances because it uses different leakage rates [44].

Different guidelines have been used to describe the layout of the station:

- US (United States): **NFPA 2 Code 2** (Gaseous hydrogen systems of a pressure between 51.5 MPa to 100 MPa), and also NFPA 55 (Compressed gases and cryogenic fluids code) [39].
- UK (United Kingdom): British Compressed Gases Association (**BCGA**) Code of Practice CP41, 2014- The design, construction, maintenance and operation of filling stations dispensing gaseous fuels[42].
- Table 1. Hydrogen filling site safety separation distances, consideration of Appendix 1 Guidance in **BCGA CoP CP 41** [42].

According to the guidelines, *Table 6* shows the minimum safety distances between each equipment of the energy station.

Table 6. Minimum safety distances between each equipment at the energy station

Location	US	UK	Appendix 1 CoP CP 41
Dispenser to occupied buildings, footpaths, highway and potential ignition sources	1.5m	-	3m (during vehicle is filling)
Potential release point from storage or compression equipment to buildings (Shop Service)	10.7m	8m	5m
H_2 storage and compression equipment, to footpath	10m (Although not is very specified)	8m	5m
H_2 storage or compression equipment to dispensing	-	-	8m
H_2 storage or compression equipment to H_2 vents	8m	8m	2m

H_2 storage or compression equipment to above-ground fuel storage tank or Petrol Tanker Delivery	15m	8m	8m
H_2 storage to gasoline storage	15m	8m	8m
Gasoline to H_2 dispensing	3m	-	3m

Some regulations agree in the distances. This is for example; the storage of h_2 compared to petrol tanker delivery, underground storage of gasoline, gasoline dispensers and nearby buildings. On the other hand, other locations differ in distances.

In case of fast charging poles, the EX zones for gasoline and hydrogen installations are considered; therefore, it will be located at a conservative distance from the hazardous areas. EX regulations can be found in ***Norwegian regulation NEK400-7-722.*** This guidelines states that chargers may be located outside EX zones. Also, some literature considers that fast charging poles should be located at a distance equal or greater than 18m from the petrol dispensers [45].

3.6.2 Distances hydrogen supply co-located with petrol supply and fast charging

An example of energy station has been developed as was described *chapter 3.6.2 Minimum safety distances*. This design is also based on risk identification developed in *chapter 6*, together with the information performed in scientific documents [46], [47], [48]. The distances used at the energy station are shown in *figure 14*:

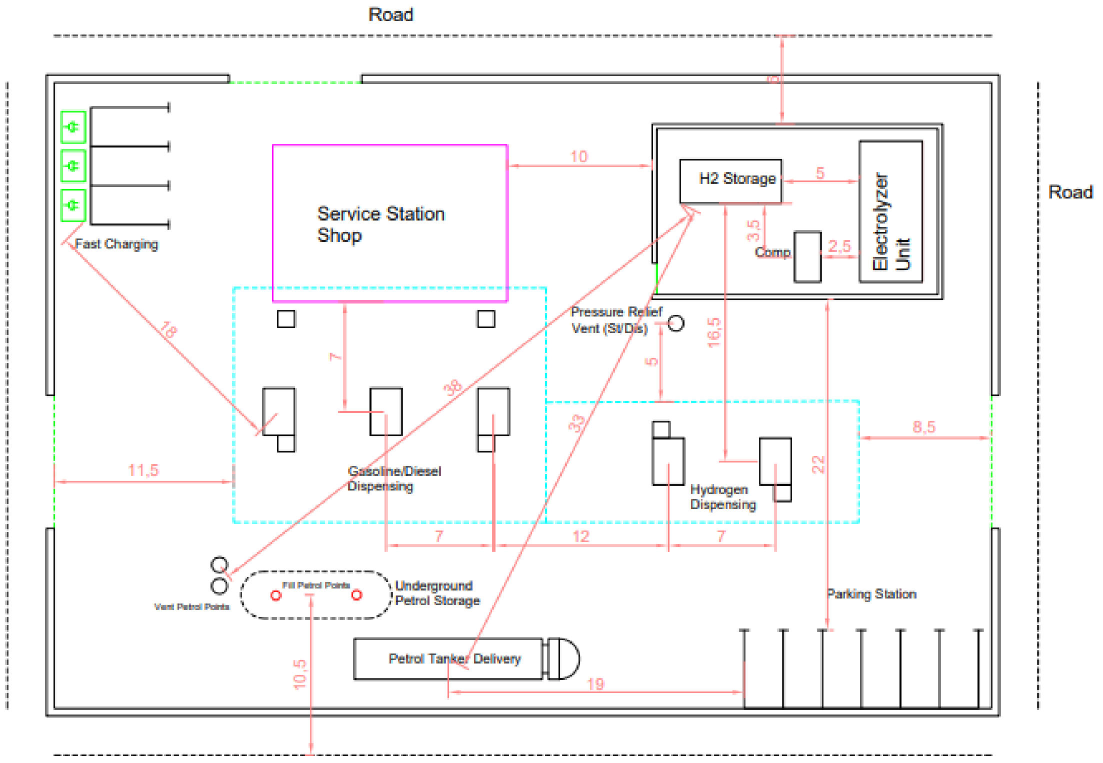


Figure 14. Distances between operations at the Energy Station.

Table 7 shows the area of each hydrogen systems at the energy station according to NEL hydrogen manufacturer.

Table 7. Area of the different hydrogen systems and operations at the Energy Station (NEL manufacturer [19], [49]*).*

Location	Quantity	Area (m2)	Height (m)
Unit Production	1	190	2.5
Electrolyzer	1	36	1.5
Compressor	1	5.28	1.5
H2 Storage	1	18.2	1.4
H2 Dispenser	4	3	2

4 Properties of fuels

4.1 Hydrogen physical properties

Hydrogen is the lightest and abundant element in the universe. Hydrogen does not present greater or lesser hazards than other flammable fuels, such as gasoline or natural gas. Some hydrogen properties provide more security against other fuels; however, hydrogen conditions are necessary to study and to analyze. Both hydrogen and gasoline are flammable, therefore, the main basis for understanding fuels behavior is to study their properties.

The main physical properties of the hydrogen are listed in *table 8* [18], [50].

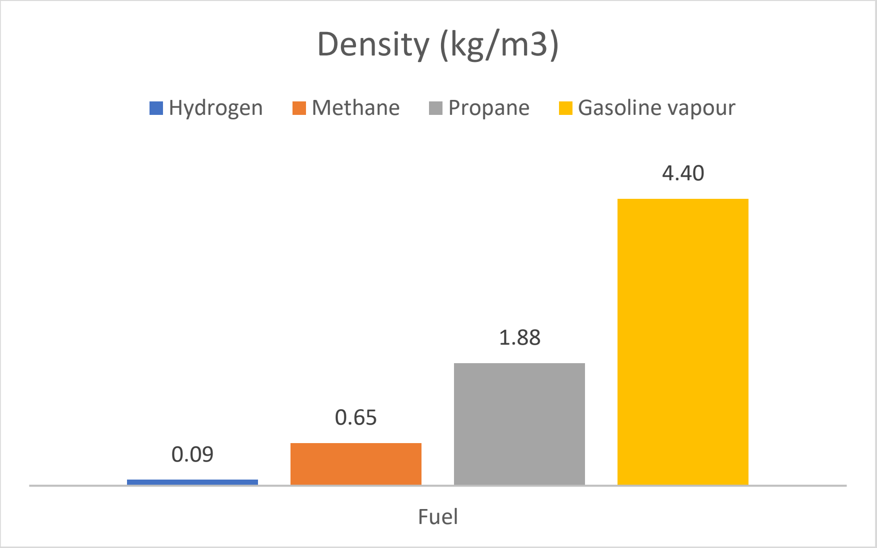
Table 8. Hydrogen physical properties [50].

Property	Value	Unit
Molecular weight	2.016	g/mol
Boiling point	20.27	K
Melting point	14.01	K
Critical temperature	33.25	K
Critical pressure	1.297	MPa
Density of gas	0.08376	kg/m3
Density of liquid	70.78	kg/m3

Below standard conditions, such as 1 bar and 0 ° C, the hydrogen is in gaseous state. Hydrogen is liquid at 20.3K (-252.9 ° C, boiling point) in atmospheric pressure. The boiling point increases with the pressure and solidifies at 13.8 K (-259 ° C, melting point). Hydrogen density is very low, both in gas and liquid, where in gas state its density is 7% air density. The density of usual fuels is shown in *table 9* and *graph 1* shows absolute density of hydrogen, methane, propane and gasoline vapour.

Table 9. Absolute density, relative density to hydrogen and air of different fuels [50].

Fuel	Gas/Vapour		
	Absolute (kg/m3)	Relative to hydrogen	Relative to air
Hydrogen	0.09	1	0.07
Methane	0.65	8.13	0.57
Gasoline	4.4	55	3.85
Propane	1.88	20	1.4

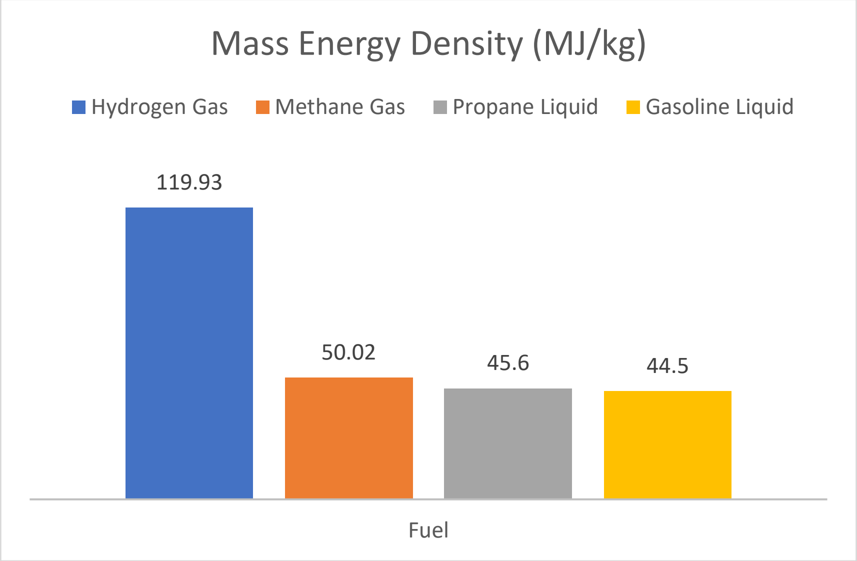


Graph 1. Absolute density of different fuels [50].

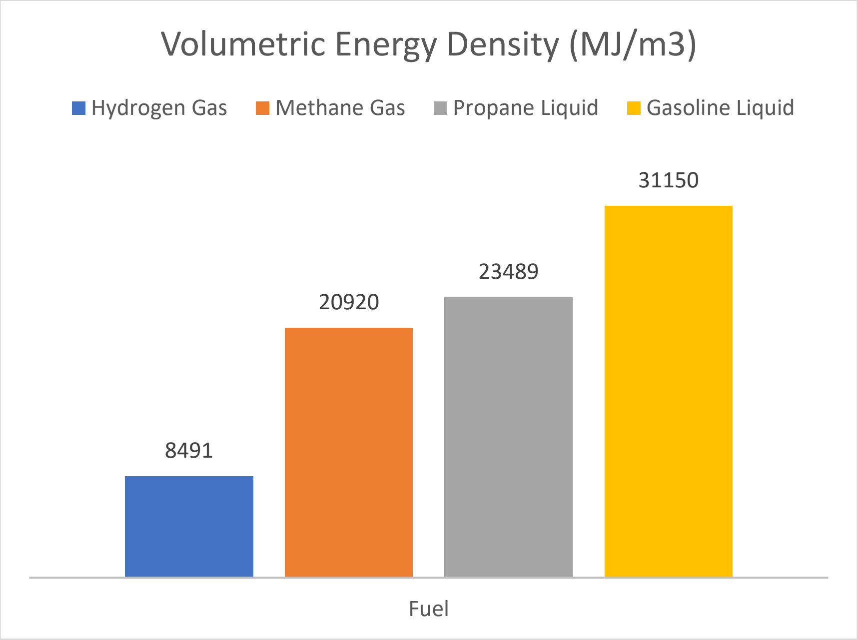
Comparison with other fuels

Hydrogen has the highest mass energy density in comparison with other conventional fuels, at least 2.5 times higher than that of other fuels. On the other hand, hydrogen has the lowest volumetric energy density affecting the volume of storage needed. This factor is important both in road transportation and hydrogen production at the energy station because larger volume of tank will be needed to store hydrogen gas.

The mass energy and volumetric energy of various fuels are summarized in *graph 2 and graph 3*:



Graph 2. Mass energy density of different combustibles [50].



Graph 3. Volumetric energy density of different combustibles [50].

4.2 Properties related to explosion risks

The properties of fuels can generate high risks in the facilities of the station. Fuels properties regarding fire and explosion should be studied for the fuelling station design. There is to distinguish between gas state and liquid state, because petrol is supplied in liquid state in comparison with hydrogen which is supplied in gas state. However, next points are referring about petrol in vapour state.

Fuels properties relation to fire and explosion are described in the following points:

- **Auto-ignition temperature (ºC):** Minimum temperature required to initiate self-sustained combustion in a combustible fuel mixture in the absence of a source of ignition. The fuel is heated until it bursts into flame [5]. **(Regulation ISO/IEC 60079-20-1:2017 Explosive Atmospheres – Part 20-1)**

- **Flammability range (volume %):** To ignite a flammable gas requires the gas to be mixed with a certain minimum amount of air and requires also the concentration of gas to not be very high. This is defined in terms of its lower flammability limit (LFL) and its upper flammability limit (UFL). LFL is the lowest gas concentration and UFL is the highest gas concentration that will support a self-propagating flame when mixed with air and ignited [5]. **(Regulation ISO/IEC 60079-10-1:2015 Explosive Atmospheres – Part 10-1)**

- **Relative density of a gas or a vapour:** Density of a gas or a vapour relative to the density of air at the same pressure and temperature (air being equal to 1.0). A gas with lower density than air (<1) tends to move upwards, while a gas with higher density than air tends to move downwards. If the temperature of the gas differs from the temperature of air, the gas may have other densities which affect the behaviour [5]. **(Regulation ISO/IEC 60079-10-1:2015 Explosive Atmospheres – Part 10-1)**

- **Minimum ignition energy, MIE (mJ), in air:** Amount to external energy that must be applied in order to ignite a combustible fuel mixture. Energy from an external source must be higher than the autoignition temperature and be of enough duration to heat the fuel vapour to its ignition temperature. This common ignition sources are flames and sparks [5].

4.2.1 Safety Petrol properties

Petrol is a mixture of organic substances characterized by the octane number. Petrol is a fuel which presents fire risks, explosion risks, health risks and environmental risks. Petrol physical properties can vary depending on source, product specification and additives. This fuel is a volatile liquid which gives off flammable vapour at very low temperature, down to about -40ºC [51], and is known as flash point temperature. Petrol vapour can create a highly flammable atmosphere when mixed in certain proportions with air. This mixture could burn or explode if an ignition source is presented.

A mixture containing about 1-8 v/v% of petrol vapour [52] in air is flammable. The flammability limits for gases and the flash point temperature for liquids can be related because of the flash point temperature occurs when the vapor concentration above the liquid is at the flammability limit.

Petrol vapor is heavier than air, where its relative density with respect to air is 4 as described *graph 1*. This is the reason why petrol does not disperse easily and tends to sink to the lowest level. In case of accumulate vapour in enclosed spaces or other poorly ventilated areas will cause risk of explosion.

Petrol has an ignition temperature of 440 ºC [52] and this is affected by chemical properties of the flammable liquid. Petrol in liquid state will no ignite only when it is gaseous state in lower flammability limit. In addition, the minimum ignition energy is 0.25 mJ [53], like other fossil fuels and higher than hydrogen. This mean that the external energy applied to produce ignition will be greater than in the case of hydrogen.

As a relevant physical property, petrol has a lower auto-ignition temperature compared to hydrogen and when combustion takes place emits a large amount of heat and radiation. The flame burn is visible but produces an exothermic reaction [53].

- It is odorous. A stream of gasoline from a leak can be detected due to their smell and visualization.
- Non-toxic, does not support life and may act as an asphyxiant by replacing the oxygen content in a confined space.
- Narrow flammability limits than hydrogen.
- Ignition energy bigger than hydrogen.
- Lower auto-ignition temperature than hydrogen.
- Highest heat of combustion.
- Not easy dispersion.

4.2.2 Safety Hydrogen properties

Hydrogen is a density of 0.009 g/l (at 298K and 1 bar), is liquid below its boiling point of 20K (-423 ºF; -253ºC) and is solid below its melting point of 14K (-434ºF; -259ºC) to atmospheric pressure [18].

Hydrogen is 14 times lighter than air and disperses rapidly. The small molecule size increases the likelihood of a leak through material and systems. Hydrogen results in very high buoyancy and diffusivity [5], [15], where the diffusion is more pronounced at elevated temperatures. It is also extremely flammable in air (flammability limits 4 % to 75 % by volume [52]) and explosive over a wide range of concentrations. This range is much larger than range for the other fuels, therefore poses a higher risk for the occurrence of explosive gas mixture.

Hydrogen gas at normal ambient temperature has lower density than air, in this way it rises much faster than other gases. The high diffusion coefficient contributes to a high dispersion in the air. However, hydrogen mixture with air could generate an explosive mixture easily.

Hydrogen needs along with the air to reach an explosive mixture compared to gasoline because the lowest limit of flammability for hydrogen is 4% and for gasoline is 1.3%.

Hydrogen has a minimum ignition energy 0.018 mJ [54]. This implies that the amount of external energy applied for the ignition of the hydrogen is lower than other fuels, such as gasoline.

Other hydrogen properties are important for adequate security measures:

- It is colourless, odourless and tasteless. Hydrogen leakage is almost invisible in daylight.
- Non-toxic, does not support life and may act as an asphyxiant by replacing the oxygen content in a confined space.
- It is non-corrosive, but it can embrittlement some metals which may cause loss of ductility.

Table 10. Comparison safety-relevant properties with other fuels [50].

Property	**Unit**	**Hydrogen**	**Methane**	**Gasoline**	**Propane**
Lower Flammability Limit	% volume	4	5.3	1.3	1,7
Lower Detonation Limit	% volume	18.3	6.3	1.1	3.1
Upper Detonation Limit	% volume	59	13.5	3.3	9.2
Upper Flammability limit	% volume	75	17	6	10.9
Autoignition temperature	K	858	810	488	723
Minimum igntion energy	mJ	0.017	0.274	0.24	0.24
Diffusion coefficient in air	(cm^2/s)	0.61	0.16	0.05	0.12

4.3 Ignition sources and general principals to avoid fire and explosions

A description of possible ignition sources can be found **in the standard EN 1127-1:2011 (Explosive atmospheres – Explosion prevention and protection – Part 1: Basic concepts and methodology)** [50].

- Hot surface: i.e heating pipe or casing of an electrical apparatus
- Flames and hot gases: i.e autogenous welding, exhaust gases
- Mechanical sparks: abrasive cutting, flint gas lighter
- Electrical equipment: electrical sparks at make and break
- Stray electric current and cathodic corrosion protection: sneak current, short circuit
- Static electricity: spark discharge
- Lightning strike
- Exothermic reaction

Safety measures are a priority to prevent and to protect against fire and explosion. In general, the principles to be kept are the following:

1. Minimize the probability of an explosive atmosphere
2. Minimize the likelihood of an ignition source
3. If the explosion cannot be avoided, try to stop immediately and limit the explosion flames and pressure to an enough level of safety

4.3.1 Typical ignition sources in Energy Station

- **For electrical equipment:**
  - Sparks and arcs due to short circuits or breaks in electrical circuits
  - High surface temperature caused by electric power
  - Lighting
- **For mechanical equipment:**
  - Sparks caused by mechanical impact
  - High surface temperature caused by friction for moving parts
- **Open fire**

5 Hydrogen leakage in unconfined area

Hydrogen gas is composed of small molecules which is more likely to escape easily through materials and seals. Hydrogen leakages will cause deviations and problems at the HRS if they are not controlled. This is because any leakage could lead to fire, flash fire or explosion [50].

The consequences are different depending on the amount of hydrogen leakage is released and its accumulation in a closed area. As main consequences could be; ignition with explosion, flash fire after a built-up of an ignitable gas cloud of hydrogen in unconfined spaces, or to jet fire caused by direct ignition.

The fact that an escape happens is not easy to know what kind of phenomenon will occur. In order to analyze the phenomenon is always necessary to simulate different hydrogen leakage rates and validate their consequences in a FDS (Fire Dynamics Simulator) software.

5.1 Leakage incident and accident database

During the last years the growth of hydrogen as fuel for vehicles has increased at the stations. The use of this fuel is still great challenges in its research area. Hydrogen is being investigated daily to incorporate higher safety measures.

Database of hydrogen refueling stations accidents are important to study what accidents occurred in the last years. Different web pages such as: https://h2tools.org/lessons, HIAD database and https://odin.jrc.ec.europa.eu/odin/index.jsp, collect information about accident database. In greater proportion, most accidents take place due to hydrogen leakage.

Examples:

1) Hydrogen Delivery Truck Causes Hydrogen Leak at Fill Station Due to Improperly Stored Hydrogen Fill Line at Departure (https://h2tools.org/lessons/hydrogen-delivery-truck-causes-hydrogen-leak-fill-station-due-improperly-stored-hydrogen).
2) Hydrogen Cylinder Leak at Fueling Station (https://h2tools.org/lessons/hydrogen-cylinder-leak-fueling-station).
3) Pressure Relief Device Fails at Fueling Station (https://h2tools.org/lessons/pressure-relief-device-fails-fueling-station).

In these events the following consequences occurred after leaks:

1) Hydrogen leakage occurred, but no ignition.
2) Hydrogen leakage occurred, but no ignition.
3) Hydrogen leakage and ignition occurred, due to static electricity or spark from escaping particle.

Other examples of incidents related to escapes can be found on the web pages. Some of them are related in the operations of the compressor and in the use of the h_2 dispenser. (Leak on compressor due to a failure of one of the compressor bearings, discharge valve installation due to human error, hydrogen boosting compressor fails due to loss of seal in the diaphragm or to vehicle left to filling point without disconnecting the hose).

5.2 Possible leakage scenarios

The leaks can present different scenarios according to the events that occur, which will be studied in *section 6. Risk assessment in energy stations.*

- Leak – immediate ignition – shutdown failure – jet fire
- Leak – immediate ignition – shutdown – short lived jet fire

- Leak – no immediate ignition – shutdown failure (hydrogen accumulation) – delayed ignition – flash fire and explosion
- Leak – no immediate ignition – shutdown failure (Hydrogen accumulation) – no delayed ignition – no effect
- Leak – no immediate ignition – shutdown (Minor hydrogen accumulation)– delayed ignition – flash fire and explosion
- Leak – no immediate ignition – shutdown (Minor hydrogen accumulation)– no delayed ignition – no effect

In the event of a leak in an enclosed space, different phenomena and consequences could happen as well detailed in the reference [55] ***Hyindoor Work Package 5: Guidelines on Fuel Cell indoor installation and use, chapter 2.1.2 Phenomena and consequence diagram***. Once the release of hydrogen begins, it could ignite immediately due to the presence of an open fire, hot surfaces, electric sparks or other factors ... In case it does not ignite immediately, there would be a gradual accumulation of hydrogen inside the enclosure. The high flow rate exceeding the ventilation capacity could produce a hydrogen concentration higher than 4% by volume, which creates a possibility of delayed ignition in one layer and its deflagration. In contrast, lower hydrogen release rates that do not produce a concentration above 4% can cause delayed ignition in a jet. Both types of delayed ignition can cause the deflagration of the mixture of air and hydrogen, with an overpressure capable of destroying the enclosure.

5.3 Accumulation of hydrogen

Hydrogen tends to escape easily when it is stored at high pressures. Hydrogen disperses more easily than other gases since it has a high buoyancy. However, its accumulation in closed areas can cause high levels of concentration, putting at risk human safety, facilities, structure and the environment.

Different studies [56], [57] show that event leak in the hydrogen gas storage at high pressure (70 MPa/700 bar) could produce levels of concentrations greater than 10%.

For hydrogen accumulations to be non-hazardous, according to ***Norm EN-60079-10*** [38], an event of a foreseeable leak, the concentration of hydrogen in air will not exceed **50% of LFL** (Lower flammability limit).

5.4 Ventilation

The ventilation of enclosures with hydrogen systems is an essential requirement to prevent the hazards associated with accumulations of flammable atmospheres. Mainly natural or mechanical ventilation is used.

In ventilation design, several authors [55], [58] detail what type of ventilation configurations are more efficient with respect to others. Some recommendations are the following:

- In order to avoid the accumulation of flammable concentrations of H_2, an enclosure may have adequate passive ventilation.

- Two (or more) vents located at different heights is preferable to use; this configuration is more efficient than a single ventilation (or more) located only in the upper part of the enclosure, considering the same area of total ventilation.

- A vent configuration of an opening can be used when a two-vent ventilation configuration is not possible.

- Vertically stretched vents (height> width) provide better ventilation compared to vents stretched horizontally from the same area.

- Several vents distributed on all sides of the enclosure, both above and below, help ensure that the wind improves ventilation regardless of direction.

- Consider the preferential use of side vents over roof vents to improve passive ventilation.

- Obstructions should be avoided, such as grilles or ducts near ventilation areas.

- Forced ventilation could be applied in cases where purely passive ventilation is not practical. However, these systems are not secure against fail-safe and the reliability of the system must be considered.

There are different methodologies to calculate the parameters of the ventilation system using engineering tools described in ***Appendix 4.2 of Hyindoor Work Package 5*** [58], where it is proposed:

- In *Appendix 4.2.2.2 for the ventilation mode of an opening* the calculation of passive ventilation using the method proposed by Linden (1999) and the simple expressions developed by Cariteau and Tkatschenko (2013). And for the ventilation mode of two openings is another model also presented by Linden (1999).
- Forced ventilation in an enclosure with an opening in *Appendix 4.2.2.3*.
- Computational fluid dynamics (CFD) for complex geometries, multiple ventilations and release parameters at high pressures.

5.5 Consequences of leakage

The concentration of hydrogen is sometimes not possible to reduce below LFL, in this case the ignition of a flammable atmosphere may occur and lead to dangerous consequences due to combustion.

If ignition occurs at high pressure, it will generate overpressures and high thermal radiation during combustion, affecting equipment, nearby buildings and the safety of people.

According to [55], typical pressure values to destroy the civil structure are between 10-20kPa, while different levels of heat flow emitted will affect both the equipment and people around the installation.

6 Risk assessment in energy stations

Risk assessment procedure consists in an analysis of system operations followed by a risk evaluation as described *chapter 2.4*. This methodology defines hazard like any harm action or event, while risk like a combination of probability of occurrence of harm together with severity of that harm. In addition, this includes a risk control that is composed by actions, measures or protections which reduces risks.

Figure 15 shows the procedure of risk assessment at the energy station which consists of an interactive process. First of all, the energy station is defined, followed by hazards identification and risk estimation. Secondly, each of risk is evaluated and is studied. Whether risk evaluation is not tolerable will have to risk reduction adding measures to mitigate its consequences.

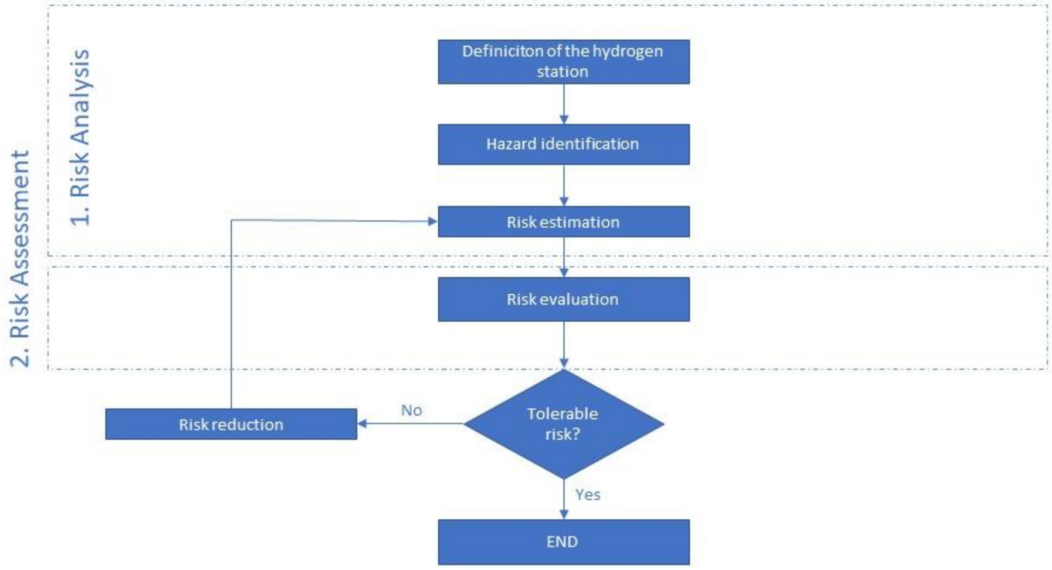


Figure 15. Interactive process in risk assessment procedure at the energy station. (Autor design)

6.1 Case of study

The methods used to analyze the hazards regarding fire and/or explosion at the station are described in *chapter 2.4*. A lot of information exists about potential risks in traditional petrol station in comparison with hydrogen station. **Guidelines like Petrol Filling Stations: Guidance on Managing the Risk of Fire & Explosion (The Red Guide)** [35] will be used to present hazards in petrol and will be a base to study hydrogen installations risks.

The analysis starts with PHA methodology which evaluate all the facilities at the energy station. The deviations will be studied by means of HAZOP and will be completed with a FMEA. This FMEA will be used to evaluate quantitatively the failure modes which could generate leakages and other potential risks.

6.1.1 Preliminary hazard analysis (PHA)

The methodology PHA identifies all possible hazards that can appear at the energy station and estimates how much each hazard contributes to the safety of the station.

In any traditional petrol station, the risk arising due to failures in operation and failure in maintenance, putting at risk the employees, the public that uses the facilities and the proximity to be occupied buildings.

A brief explains about possible hazards and accidental events in traditional petrol station are described, which are used as a basic in a wide description about hydrogen hazards at the station.

6.1.1.1 Petrol supply

According to [35] activities involving petrol are potentially dangerous because of the vapours given off by the substance are highly flammable and easily ignited. Fuels such as gasoline and diesel can present dangers either due to leaks, spills, ignition sources or open fires. These dangers could happen in petrol equipment (Fill points, tanks, pipework and dispensers).

Flammable vapours could be released when petrol is handled or transferred between storage tanks and containers. A flammable atmosphere may exist above in tanks containing petrol and in those where petrol is removed. On the same way, leaks could be liberated into the ground due to a corrosion or fatigue in the underground storage, or leaks and spills next to the dispensers when it is used by public.

A summary of most important risks in traditional petrol station is shown in the following points, which it should be consider at the energy station.

1) **Tanker unloading:**
    - Overfilling
    - Impact/Collision
    - Spillage
    - Leak and uncontrolled vapour release
    - Ignition sources
2) **Underground storage of fuel:**
    - Leak and uncontrolled vapour release
    - Accumulation of vapour in drainage areas near the tank
3) **Pipework connection:**
    - Leak (Corrosion and fitting damages)
4) **Dispensing of fuel by members public:**
    - Leak
    - Vapour release
    - Spillage
    - Vehicle impact
    - Members of public
    - Equipment failure
    - Ignition sources
5) **Carrying out repair, maintenance or modification:**
    - Leak
    - Spillage
    - Vapour release
    - Impacts
    - Ignition sources

General causes:

Human errors, mechanical and electrical equipment failures, bad maintenance, bad ventilation, damages in pipes, failure safety valves, failure vapour emission control, ignition sources and fire from an external source.

General consequences:

Any leakage and uncontrolled vapour release will deliver the product in the atmosphere. If the vapour is in its lower flammability range could create ignition as long as an ignition source is presented. This vapour leakage can occur through the walls of the pipe, filtering through the ground and affecting neighbouring properties.

On the other hand, any leak in dispenser should have an installation that disperses and quickly ventilates any accumulation of vapour. Also, any safety valves failure in storage could generate over pressurization in the tank, cracking, explosion, vapour release and generate pool fire.

General risk-reducing measures:

- To locate tanker standing area away from other traffic.
- To provide physical protection such as bollards or fencing.
- Vehicles must have a clear route.
- Protect tank with an insulating material.
- To provide additional fire protection measures such as automatic fire detection and firefighter equipment.
- Ensure that there is adequate separation between tanks and other features.

- Consider location of vent pipes, repair or replacing of corroded or damaged pipes.
- Regularly maintain and test monitoring/leak detection systems. Install a leak prevention and detection systems. Stop fuelling operation when the valve safety or detection system detect leak.
- Training staff in the operating principles of vapour recovery.

6.1.1.2 Fast charging

Electric charging poles are generally not protected against explosions. This could cause the ignition of any nearby flammable gas or vapour. Therefore, electric charging stations should be located at the energy station outside hazardous areas, as well as vehicles that park to be refuelled.

The charging stations have electronic equipment that can produce sources of ignition. These sources of ignition can be sparks caused by short circuits and breakage of electrical circuits. Also, the electric power could give rise high temperature surfaces.

According to **InterReg project funded by the EU** [6] an accident could occur when the charger of the electric vehicle (BEV) is disconnected and the circuit transports current. Cables could be broken and make a spark jump at the connection point. This spark could be a source of ignition in an explosive gas mixture. Charging places should not be in the following places:

- Low ground points, where liquid fuels or liquefied gas may accumulate upon a release.
- Underground sewages and drainage canals, where liquid fuels or liquefied gas may flow or accumulate upon a release.
- Places close to access and exit roads for tankers and trailers supplying the station with fuel.
- Fire due to high charging currents at unattended fast charging. This fire can affect the installations which contain fuels.

Therefore, according to *chapter 4.5.2 Comparison of regulation*, the poles should be located outside EX zones. In this way, in case of emergency, all the equipment will be turned off and vehicles will not be supplied with electricity.

6.1.1.3 Hydrogen supply

Hydrogen leakage is more likely to appear in the facilities. These leaks, in small concentrations (below 4% of limit flammability range) are not dangerous, however, an accumulation superior to 4% is prone to create an explosive atmosphere. These dangers could happen in hydrogen equipment like electrolyser, compressor, storage, pipework and dispenser.

According to **HyApproval Handbook of HRS** [50] in case of a release of hydrogen at high pressure in parts of the facilities (storage and dispensers), adequate ventilation should be available to reduce any accumulation.

Table 11 shows a general idea about hazard identification at HRS. Hydrogen leakage could generate three consequences such as vapour cloud accumulation in enclosed area when the ignition is delayed, explosion and flash fire when hydrogen is ignited, and finally rapid ignition of hydrogen (auto ignition) producing a jet fire.

Table 11. Hazard equipment and potential hazard in Hydrogen Refueling Station [50].

	Hazard equipment	**Potential Hazard**
Hydrogen leakage	Electrolyser Compressor Tank Pipes	Causing (Vapour cloud) Explosions (Flash fires) Jet fires
	Tank	Burst of a pressurized tank
Other combustible materials (Shops, cars…) and external impacts		Causing fires

At the following points is detailed accidental events for each activity related to hydrogen supply. These details can be found in table described on ***Appendix A***. In addition, transformer evaluating is included in the study because it is an important ignition source.

- Transformer
- Electrolysis Unit Production
- Compressor
- Pipework connection compressor-storage and storage-dispenser
- Storage
- Dispenser

Transformer [59]

Hazardous event, cause and consequence:

Description:

The transformer supplies electricity in medium and low voltage to the electrical equipment and electrolysis unit. This transformer is situated in a close area at the energy station and it is accessible only for specialists. According to **Guide for Transformer Fire Safety Practices** [59] the area must protect, because excessive overheating, severe short circuits, oil faults and lighting strokes are phenomena which would help to generate fire and/or explosion.

Electrical heat energy is a hazard caused by **(Appendix A. PHA table 1.1)**:

- Resistance heating in electrical equipment: high resistance joints develop, overloading occurs, cooling diminishes due to failure in cooling equipment or obstruction of flow of cooling.
- Induction heating in transformer tank and structure: due to magnetic fields from leakage flux and high currents in conductors in proximity to magnetic metals. It could be worst if overloading occurs or cooling diminish.
- Dielectric materials heating when exposed to dielectric stress, properties deteriorates or cooling inadequate in bushing.
- Heating from arcing when dielectric materials cannot withstand the dielectric stress and a breakdown resulting in an arc.
- Heating from static electricity due to dielectric breakdown.
- Heating from lighting strikes, because this is an overvoltage and create dielectric breakdown.

The most important hazard is an internal arcing in an oil immersed transformer [59]. This will cause a high temperature in the arcing gases and the surrounding oil, but it will be necessary having oxygen inside the tank to cause fire. If high energy arc is not disconnected, tank may rupture, high temperature gases will release, and oil then gets access to oxygen. On the other hand, if the temperature is high for auto ignition or contacting with metal which has a high temperature, it could cause ignition and produce combustion.

Hazard event example [59]**:**

Diagram process of internal fault is shown in *figure 16*. Electrical stress in insulation material exceeds its dielectric strength, so it may break down and produce a high energy electrical arcing. The energy is transferred between arc and liquid oil inducing high temperature at the arc. The arc heats and vaporises surrounding oil, producing flammables gases. It will increase the pressure within the gas surrounding the arc due to the much-localized phase change. It will generate pressure waves that propagate at finite speed and start over-pressure in the tank. If the tank rupture, flammable gases will be released to the atmosphere and get in contact with oxygen will create hydrocarbons. This gas could auto ignite, ignite by an external energy source (hot metals parts, sparks, external arcing…) or energy transfer to metals.

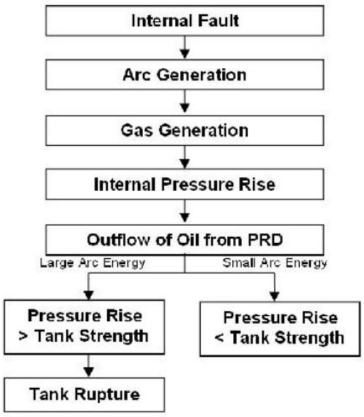


Figure 16. Diagram process of internal fault in Transformer [59].

Risk-reducing measure:

- Use transformers do not use mineral oil as insulation and cooling.
- Transformers for mineral oil and non-mineral oil filled, the choice of low explosion types of bushings, avoiding cable terminations.
- Prevention measure of tank rupture and uncontrol release of oil and arcing gases.
- Indoor installation avoiding oil and arcing gases encountering oxygen.

Hydrogen Production Unit (Electrolyser) [27]

Hazardous event, cause and consequence:

Chemical damage is a hazard caused by **(Appendix A. PHA table 2.2)**:

- Water supply in electrolysis contains impurities due to filter water failure. If the water contains impurities, it can damage the electrolytic cell, since it incorporates minerals such as magnesium and calcium. These minerals could generate precipitation of hydroxides at diaphragm of the electrolyte, appearance of chlorine on anode surface and corrode of metallic components [22].

The ***consequences*** are degradation alkaline electrolyte, release toxic gases like chlorine and reactivity with other components.

Interruption hydrogen flow is caused by **(Appendix A. PHA table 2.3)**:

- Within electrolysis unit exists high concentration levels of hydrogen and oxygen.
- Low maintenance.
- Hydrogen release because exist overpressure to the container.
- Leak in connections and seals of the electrolyser.
- Electric communication shut-off or electrical fault in wires due to overheating or jumping arcs, ground faults or overloading.
- Failure in heat evacuation.

The ***consequence*** is high concentration levels of hydrogen and oxygen in electrolyser. The pressure could increase and pressure relief valve releasing hydrogen at the container. If hydrogen concentration is in flammability limit range, could be ignite as long as an ignition source is presented.

Risk-reducing measure:

- Maintain and replace water filters.
- Control concentrations inside electrolyser.

- Enough ventilation and unconfined area.
- Prevent release of hydrogen with sensors and emergency shut down.

Compressor [60]

Hazardous event, cause and consequence

Hydrogen flow is interrupted at compressor by **(Appendix A. PHA table 3.1)**:

- Overtemperature and overpressure due to bad cooling and insulation.
- Inadequate maintenance, fatigue and equipment failure.

The ***consequence*** could be material degradation, weakness in compressor walls, possible leaks and compressor rupture.

Risk-reducing measure:

- Check cooling system.
- Pressure and temperature controls.
- Continuous maintenance.
- Prevent release of hydrogen with sensors and emergency shutdown.

Pipework connection compressor-storage and storage-dispenser [61]

Hazardous event, cause and consequence:

Hydrogen flow is interrupted in pipeline by **(Appendix A. PHA table 4.1)**:

- Leak through pipe wall due to corrosive and mechanical damage.
- Leak from pipework fitting due to a low maintenance in valves, fitting, pumps and connectors.

The ***consequence*** could be a leakage close hydrogen unit production, dispensing area or service station putting the facilities of the station at risk of fire and/ or explosion.

Risk-reducing measure:

- Regular maintenance and test monitoring/leak detection systems.
- Install a leak prevention and detection systems.
- To use non-corrodible or double skin pipework.

Hydrogen storage [60]

Hazardous event, cause and consequence:

Mechanical failure caused by **(Appendix A. PHA table 5.1)**:

- Leakage in tank safety valves due to high pressure and temperature.
- Bad maintenance in gaskets sealing.
- Non-functioning of pressure relief valves can cause hydrogen embrittlement.

Human error caused by **(Appendix A. PHA table 5.2)**:

- Impact damage, such as collision or vandalism.

Thermal hazard caused by **(Appendix A. PHA table 5.3)**:

- Fire involving tanks and fire from an external source.

The ***consequence*** would be the releasing of hydrogen at the unconfined area and could generate ignition as long as an ignition source is presented. In case of extern fire, the storage may be degraded with possible rupture and a blast wave.

Risk-reducing measure:

- Mechanical failure:
    - ➢ Install a suitable leak prevention or detection system.
    - ➢ Regular maintenance.
- Human error:
    - ➢ Locate or re-locate tank away from normal site traffic route.
    - ➢ Provide physical protection such as bollards or fencing.
- Thermal hazard:
    - ➢ Protect tank with an insulating material
    - ➢ Automatic fire detection equipment.
    - ➢ Adequate separation between tanks and other features.

Dispenser [11] [60]

Hazardous event, cause and consequence:

The dispenser is composed of different equipment like pump, valves, meters, include hoses and nozzle. Any failure at the equipment, bad maintenance in hoses or bad use of nozzles by customers could result in hydrogen leakage.

Hydrogen flow is interrupted in dispenser by **(Appendix A. PHA table 6.1)**:

- ➢ Leakage from hose rupture or bad use of nozzle.
- ➢ Vehicle collision with hydrogen dispenser.
- ➢ Member of public drives away during refuelling.
- ➢ Failure in pumps and safety valves.
- ➢ Static electricity in pump and junction boxes.

The ***consequence*** would be hydrogen leakage at dispensing area which could generate a possible explosive atmosphere.

Risk-reducing measure:

- ➢ The vehicles should have a clear route at the station.
- ➢ The dispenser should have a barrier to protect it.
- ➢ Stopping fuelling operation when the valve safety or detection system detect leak.
- ➢ Using dispenser with volume or time limited cut-offs, limiting devices and shear valves.
- ➢ Isolate electrical supply.

In general, ***risk-reducing measures*** are necessary to reduce hydrogen leakage at the equipment and protect it in case of fire. These measures include hydrogen detectors, daily maintenance and control of valves and pumps, fire extinguishers installation, flame and fumes detector, emergency procedure, control of ignition sources, protection of hazardous areas and safety distances measures.

In summary, the most important hazards are hydrogen leakage, bad ventilation in unit production, overpressure in storage, rupture of the storage, external fire and uncontrol of ignition sources.

6.1.2 Hazard and operability (HAZOP)

According to *chapter 2.4* HAZOP methodology helps to identify problems in systems operability during design. In *chapter 6.1.1* was shown a preliminary study about hazards in HRS. In this chapter is investigated what deviations can occur in the operability of each system (Electrolyser, Compressor, Storage and Dispenser). In keeping with Risk Assessment Book [2] *Table of Appendix B* shows deviation of each system based on variables and guide words.

The variables used to describe HRS are defined depend on hydrogen process and hydrogen equipment. The variables in hydrogen process could be; voltage and static electricity; in hydrogen production unit; level of water, level of oxygen and level of hydrogen in electrolyser, hydrogen purifier tank, level of moisture in purifier and problems in cooling system; while in compression stage, storage and dispensing; hydrogen flow and hydrogen pressure. These variables are completed by word guides such as more, less, none ... and enable to analyse all the deviations in each system.

The main deviations in each system have been developed based on PHA, information collection and previous studies in hydrogen production [27], hydrogen compression[28][62], hydrogen storage [28][63] and hydrogen dispensing [11]. The table in *appendix B* is a compilation of all deviations, explaining their causes and consequences. These deviations are examined based on two criteria. The possibility that the deviation will produce hydrogen leakage and / or generate the risk of fire and explosion. This means that if these two conditions are met, its will be studied in FMEA methodology.

A compilation of deviations in each system is developed in the following points:

1. **General Process**

- High voltage. **(Appendix B. HAZOP table G.1)**
- Static electricity accumulation. **(Appendix B. HAZOP table G.2)**

2. **Electrolysis Unit Production**

- More water level than expected in electrolyser. **(Appendix B. HAZOP table P.1.1)**
- More oxygen level than expected in electrolyser. **(Appendix B. HAZOP table P.1.2 and P.1.3)**
- More hydrogen level than expected in hydrogen production. **(Appendix B. HAZOP table P.1.4)**
- Reduction of hydrogen purification in tank. **(Appendix B. HAZOP table P.2)**
- High moisture in hydrogen dryer. **(Appendix B. HAZOP table P.3)**
- No cooling of hydrogen after compression. **(Appendix B. HAZOP table P.4)**

3. **Hydrogen Compression**

- High quantity of hydrogen flow. **(Appendix B. HAZOP table C.1.1, C.1.2)**
- Low quantity of hydrogen flow. **(Appendix B. HAZOP table C.2)**
- No hydrogen flow. **(Appendix B. HAZOP table C.3)**
- High pressure of hydrogen. **(Appendix B. HAZOP table C.5.1, C.5.2)**

4. **Hydrogen storage**

- No hydrogen flow. **(Appendix B. HAZOP table S.1.1, S.1.2)**
- High quantity of hydrogen flow. **(Appendix B. HAZOP table S.2.1, S.2.2)**
- Low quantity of hydrogen flow. **(Appendix B. HAZOP table S.3.1, S.3.2, S.3.3)**
- High pressure of hydrogen. **(Appendix B. HAZOP table S.4.1, S.4.2)**
- Low pressure of hydrogen. **(Appendix B. HAZOP table S.5.1, S.5.2)**

5. **Dispenser**

- High quantity of hydrogen flow. **(Appendix B. HAZOP table D.1)**
- Low quantity of hydrogen flow. **(Appendix B. HAZOP table D.2.1, D.2.2)**
- No hydrogen flow. **(Appendix B. HAZOP table D.3)**
- High pressure of hydrogen. **(Appendix B. HAZOP table D.4.1, D.4.2)**
- Low pressure of hydrogen. **(Appendix B. HAZOP table D.5)**

The information described in tables of *Appendix B* is very detailed. In the following paragraph a HAZOP methodology is developed in hydrogen compression process.

During hydrogen compression stage is possible to have a high quantity of hydrogen flow, a low quantity of hydrogen flow or no hydrogen flow. In the first case, this may be due to the fact that there is a high pressure in the input line to the compressor C.1.1 or compressor exceeds its capacity limit C.1.2. Consequently, it will become warmer due to the high pressure, it will be able to produce overloads and break some connecting pipe. Both consequences may cause hydrogen leakage and risk of fire / explosion, so it is studied in FMEA methodology as a failure mode. In the second case, if hydrogen flow is low C.2, it may be because there is an escape in some pipe or compressor is not operating correctly. Consequently, hydrogen leakage will occur and is also evaluated in FMEA. In the third case, if there is no hydrogen flow may be due to malfunction of the valves or compressor has broken. This last case will not produce hydrogen leakage, therefore is not considered in FMEA study.

In addition, higher hydrogen pressure is also possible due to a failure in pressure relief valve (PRD) at compressor C.5.1. This will generate a higher pressure in both pipes and compressor. Another failure could be in pressure interruption valve (PS) at compressor C.5.2. These cases will cause hydrogen leakage, as well as the risk of fire and explosion and will be analysed FMEA.

6.1.3 Failure modes and effects analysis (FMEA)

The following methodology to develop is FMEA. The main objective in FMEA is to reduce the risk of hydrogen leakage by failure in operations, overpressure in equipment and other potential risks. Normally, probability criteria are applied to assess the level of risk in this method. These probabilities are based on two criteria: frequency of occurrence and frequency of consequence. This project does not analyze failures mode probabilities, but it is based on the three-point scale used in **TIAX studies project** [7].

TIAX studies are based on failure modes analysis providing by contributors in an example of hydrogen refueling station.

The scale consists in three-points appointed like low (L), medium (M), and high (H) to rank both the frequency of occurrence (F) of the failure mode and the consequence of the failure mode (C). Frequency and consequence determinate the relative risk of potential failures.

The consequence and frequency ratings for each FMEA are combined in the risk binning matrix to estimate risk. Each hazard is plotted on a frequency vs. consequence matrix that yields an estimate of risk as high, moderate, low, or negligible. **High risks** are considered combinations of M x H, H x M, and H x H ratings. **Moderate risks** are combinations of L x H, H x L, and M x M. Finally, **low risks** are combinations of L x M, M x L, L x L.

Table in *Appendix C* describes an example of failure in HRS systems related to hydrogen leakage and other risks in fire/explosion. In the following paragraph is described a brief detail about failure modes:

1. **<u>Electrolysis Unit Production</u>**

Failure mode which can produce hydrogen leakage:

- Valve reducing pressure or shut-off valve in the vent line of hydrogen failure. **(Appendix C. FMEA table 1.4 FMEA)**
- Catalytic purifier aftercooler failure. **(Appendix C. FMEA table 1.5 FMEA)**

Failure mode to produce high fire and explosion potential risks:

- Safety valve or shut-off valve in the vent line of oxygen failure. **(Appendix C. FMEA table 1.3 FMEA)**

- Catalytic purifier failure when H2 is in purification. **(Appendix C. FMEA table 1.2 FMEA)**

2. **Hydrogen Compression**

Failure mode which can produce hydrogen leakage:

- Mechanical failure of line or fittings in the compressor suction. **(Appendix C. FMEA table 2.1 FMEA)**
- Lubrication compression system failure. **(Appendix C. FMEA table 2.2 FMEA)**
- Seals failure. **(Appendix C. FMEA table 2.3 FMEA)**
- Pressure relief valve in compressor fails (PRD). **(Appendix C. FMEA table 2.4)**
- Pressure switch valve in compressor failure (PS). **(Appendix C. FMEA table 2.5)**

3. **Hydrogen storage**

Failure mode which can produce hydrogen leakage:

- Overpressure in the tank (Rupture). **(Appendix C. FMEA table 3.1)**
- Pressure relief valve or solenoid valve in storage failure. **(Appendix C. FMEA table 3.2)**
- Piping leak. **(Appendix C. FMEA table 3.3)**

4. **Dispenser**

Failure mode which can produce hydrogen leakage:

- Pressure relief valve or general shut-off on disperser failure. **(Appendix C. FMEA table 4.2)**
- Failure or rupture in the connection of nozzle. Safety valves failure. **(Appendix C. FMEA table 4.6)**
- Vehicle pressure relief valve failure. **(Appendix C. FMEA table 4.3)**
- Vehicle tank isolation valve fails. **(Appendix C. FMEA table 4.4)**
- Depressurize dispenser valve failure. **(Appendix C. FMEA table 4.5)**

Failure mode to produce high fire and explosion potential risks:

- Another: human errors using dispensers.
  - ➢ Drive away while connected to dispenser.
  - ➢ Collision in dispenser.

7 Accidental Scenarios

Different accidental scenarios were detected after developing the risk assessment methodologies described in *chapter 6.1 Case of study*. Most hydrogen systems in the energy station are at high pressures, and this why any small failure in the process would lead to the release of hydrogen.

If the release of this gas happens in a closed room, the accumulation of it would generate consequences as described in *chapter 5.3 Accumulation of Hydrogen*.

7.1 Potential accidental scenarios

The possible accidental scenarios described evaluate both hydrogen leakage and hydrogen explosion. This is due to malfunction in the pressure relief devices located in electrolyser systems, compression system, tank storage and dispensing area.

Table 12. Location of potential accidental scenarios

Scenarios	Where
Leakage	Production: Electrolyzer, compressor and storage
	Pipeline connection
	Dispenser
Explosion	Storage

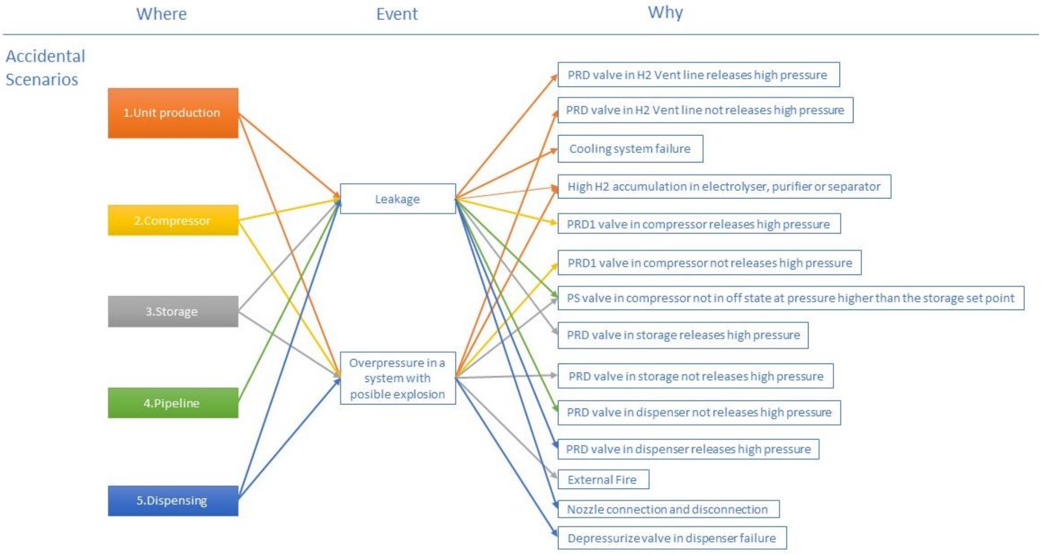


Figure 17. Potential accidental scenarios at the energy station. (Autor design)

Unit H2 Production:

1) A large quantity of H_2 accumulates in the electrolyser, in the catalytic purifier or in the H_2/O_2 separator. These scenarios mixed with an enough quantity of O_2 would produce an inflammable mixture.
2) In normal operation, H_2 leakage occurs when pressure relief valve PRD in the H_2 vent line, releases high hydrogen pressure.
3) Overpressure occurs in the electrolyser when the PRD valve does not release the pressure.
4) System cooling fails.

Compressor:

1) Overpressure occurs in the compressor, with possible breakdown of the line, when the mechanical valve (PRD1) in compressor is not able to open and not release the hydrogen high pressure.
2) In normal operation, pressure relief valve (PRD1) releases the hydrogen high pressure in the enclosure.
3) On the compressor inlet line generate leaks when a large accumulation of H_2 is produced.

Pipeline:

1) The pressure rises in the line of connections between compressor-storage due to a failure in pressure switch valve (PS) at the compressor. Pipes can be damaged and fatigued causing gas leaks.

2) The pressure rises in the connection line between storage-dispenser due to failure in pressure relief valve (PRD) at the dispenser.

Storage:

1) Overpressure in the storage with possible rupture because the mechanical valve PRD in a rack is closed and does not release the high pressure.
2) Overpressure in the storage with possible rupture of pipes, when the pressure switch valve (PS) in compressor is not in off state at pressure higher than the storage set point. The storage is not able to release the high pressure.
3) In normal operation, pressure relief valve (PRD) in a rack of the storage releases the high pressure.
4) Overpressure in storage due to an external fire.

Dispenser:

1) Bad connection and disconnection of the nozzle produce an escape.
2) The safety valve in the dispenser is not able to open when the pressure is high, generating the rupture of the hose and releasing hydrogen.
3) Depressurize dispenser valve is closed when the nozzle is used.

7.2 Worst-accidental scenario

Different accidental scenarios have been presented in *chapter 7.1 Potential accidental scenarios*. All of them describe possible malfunction in the pressure relief devices located in the compression system, in the storage, in the safety valve of dispenser and in the depressurizer valve of dispenser. In some cases, hydrogen leakage occurs directly, while in other cases the high pressure in the storage will cause an explosion when is not possible releasing the high hydrogen pressure.

The objective of the project is to study the concentrations of hydrogen leakage that could accumulate in closed spaces. This is the reason why in the following section reference is made to potential events of hydrogen leakage both in the storage and in the dispensers.

7.2.1 Potential event of H2 leakage

Relevant scientific documents [56] consider that the most serious leak is pressure relief device open (PRD) in a confined space when the storage has a high pressure. PRD intends to vent the high pressure of hydrogen before rupture occurs preventing disastrous explosions [64].

The releasing of hydrogen gas is in tens of seconds; therefore, a good ventilation system will be essential. If the ventilation system takes a long time to dilute the gas cloud, hydrogen will be accumulated and could ignite immediately.

Any leakage in the hose of the dispenser would cause accumulations of hydrogen on the roof of the station. In this way, this are also considered as a potential hydrogen leakage event with possible explosion.

Table 13. Worst-accidental scenario. Potential event of hydrogen leakage.

Potential event of leakage	Where
Pressure relief valve (PRD) in a rack open	Production and Storage
Rupture of hose or Safety dispenser valve is opened to liberate pressure.	Dispensing area

Figure 18 presents the event tree used for derivation of this possible incident scenarios (Storage in Unit production). As the initiating event, the continuous release of hydrogen from storage. The explosion is the worst-case scenario and can be presented in two situations in each of them (shown in blue lines on

the event tree). An important parameter is the ignition source, as long as ventilation system does not work, and this can happen when there is a lack of detection and ventilation systems.

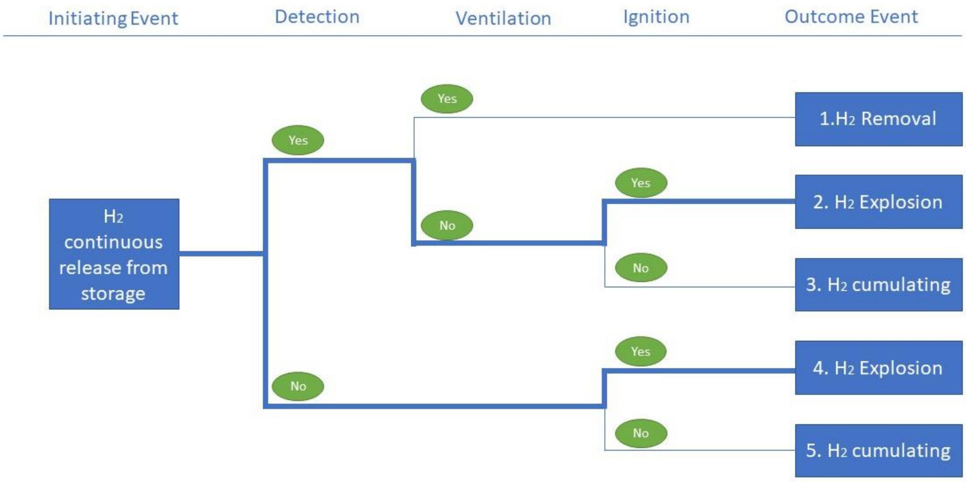


Figure 18. Event tree used for the derivation of possible incident scenarios. (Autor design)

7.2.1.1 Hydrogen leakage rates

The hydrogen leakage rates used to analyze hydrogen concentrations are calculated based on gas storage pressure and leak diameter.

ATEX European directive guidelines [65] provides diameters values for gas releases in pipes and in tanks. Studies on hydrogen leakage in vehicles use the diameter of the pressure relief valve as a base, while ***Korean Gas Safety Corporation (KGS) guidelines*** consider different percentages in the diameter of the pipe (10, 20 and 30%).

In this case leakage diameters will be considered in accordance with possible diameters of valves for storage, such as 3mm and 5mm, as well as possible seals leaks of 1mm.

Table 14 presents flow hydrogen rates according to leak diameters and gas tank pressure at 700 Bar. The calculation expressions are detailed in *chapter 8.2 Theoretical Calculations*.

Table 14. Diameter of hole, hydrogen mass flow and volumetric flow in storage.

Hole Diameter (mm)	H_2 Flow (kg/s)	H_2 Flow (m3/s)
1	0.017	0.205
3	0.155	1.845
5	0.429	5.123

8 Simulation of the energy station model

In this chapter the study and analysis of the worst accidental scenario in the energy station is presented for the model of *figure 14*.

The worst scenario occurs when a large amount of gas is released in unit production area as described *chapter 7.2.1 Potential event of H2 leakage*. Analysing different types of hydrogen leakage rates will study how the gas behaves inside the unit production area.

Different cases of hydrogen leakage are simulated in CFD based on *table 14*. Different natural and forced ventilation systems are developed to compare their effectiveness.

8.1 Model definiton

The model is based on examples of energy stations and the guidelines of minimum safety distances between hydrogen and other fuel equipment. The dimensions and volume of hydrogen operations at the energy station are shown in *Table 15*:

Table 15. Locations and operations of hydrogen systems at the energy station. Area and volume of systems. (Nel manufacturer [19], [49]*).*

Location	Quantity	Area (m2)	Height (m)	Volume (m3)
Unit Production	1	190	2.5	475
Electrolyzer	1	36	1.5	54
Compressor	1	5.28	1.5	7.92
H2 Storage	1	18.2	1.4	1.79
H2 Dispenser	4	3	2	6
Free area in Unit Production	1	130.52	2.5	387.6

The electrolyzer, the compressor and the H_2 storage are in unit production. Near to the unit production area is the hydrogen line vent as is shown in *figure 14.* The quantities of hydrogen dispensing, petrol dispensing and fast charging posts are shown in *table 15*.

Figures 19 and 20 show the three-dimensional energy station modeled in CFD software. Unit production area appears without openings since it is object of study in the following chapters.

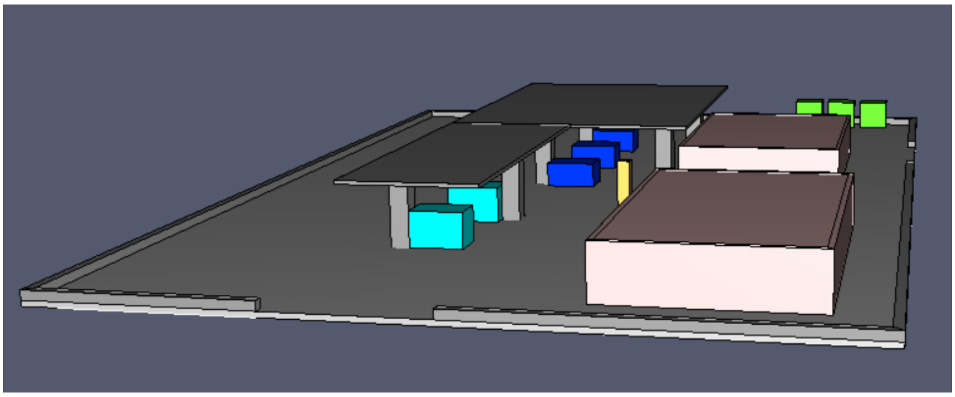


Figure 19. Energy station model in CFD.

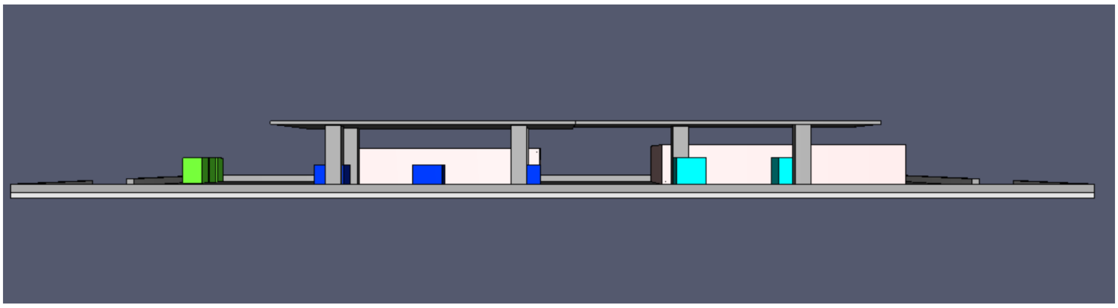


Figure 20. Profile of energy station model in CFD.

To assess the hydrogen accumulation, hydrogen concentrations and pressures in unit production are situated a pressure sensor, 5 sensors to measure volume fraction, 5 sensors to measure mass fraction and 3 sensors to measure density. Each one at a height of 2.4m above ground level. *Figure 21* shows where the sensors are located in the unit production area.

Table 16. Type of sensor and name in unit production area at the energy station.

Sensor	Name
Pressure	S1.Pressure
Density	S1.Density, S2.Density, S3.Density
Volume Fraction	S1.VF,S2.VF,S3.VF,S4.VF,S5.VF
Mass Fraction	S1.MF,S2.MF,S3.MF

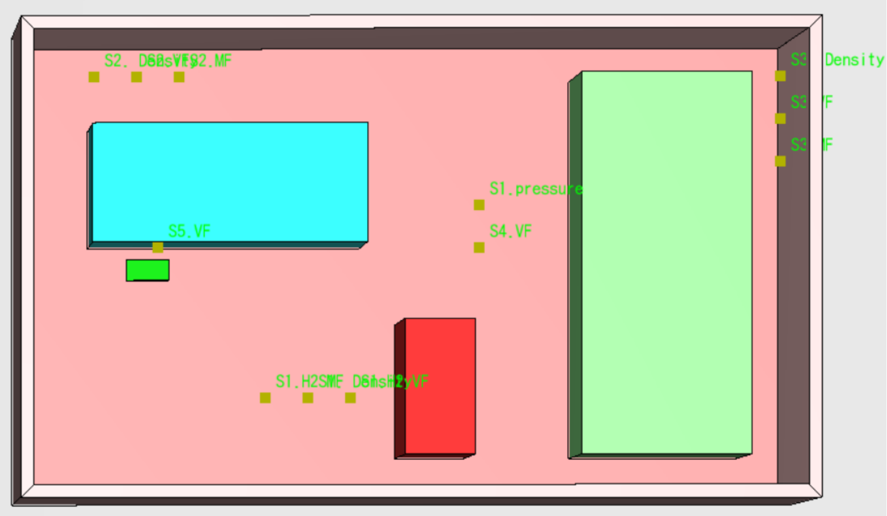


Figure 21. Location of hydrogen volume fraction, mass fraction, density and pressure sensors.

The names used to measure hydrogen outflow through the ventilation openings are shown in *figures 22 and 23*:

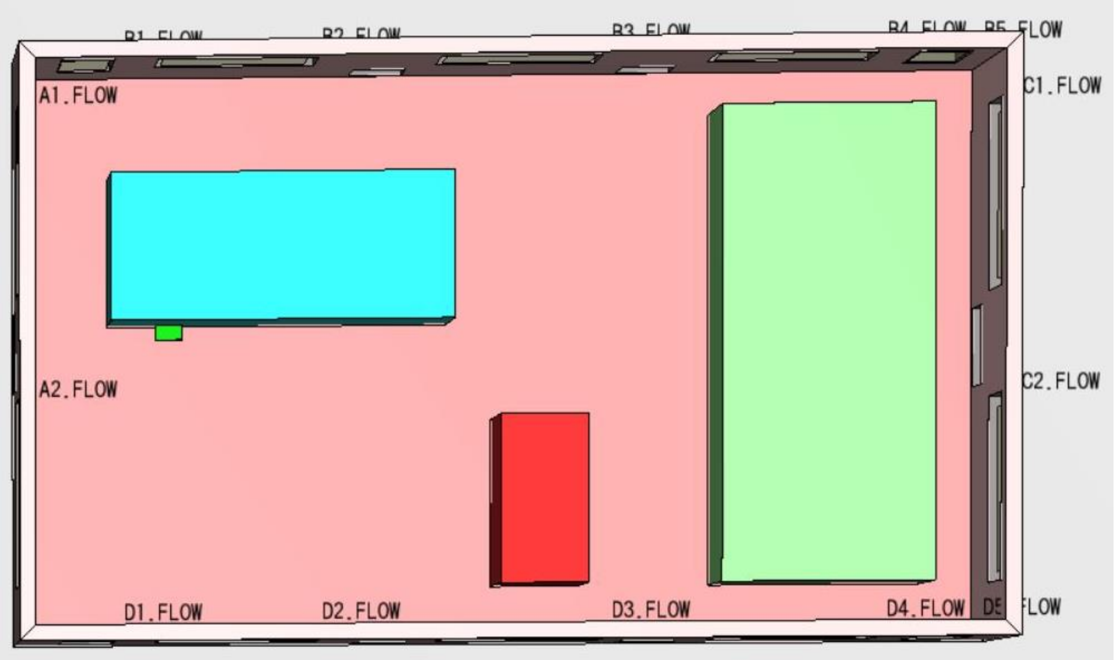


Figure 22. Sensor flow rate in openings at Test 3.

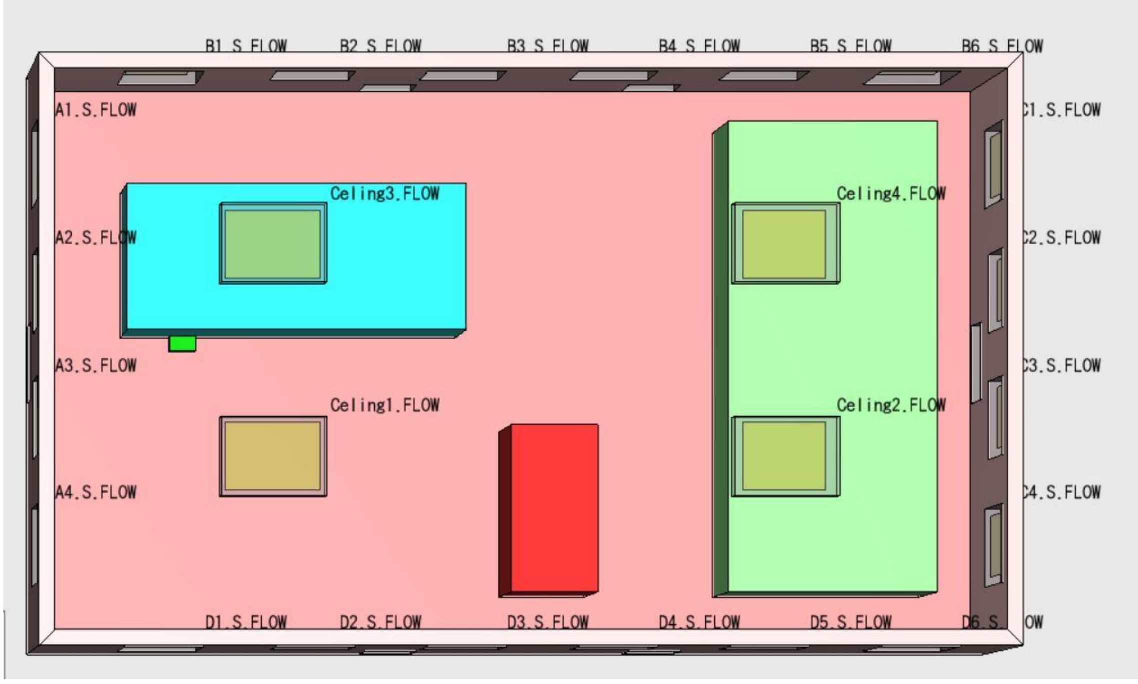


Figure 23. Sensor flow rate in openings at Test 4.

Hydrogen leaks into unit production when pressure relief valve in storage tank opens to release the high pressure. (In *figure 22*, hydrogen leakage in modelling is represented as a green rectangle located in the storage).

In approximation to a real model, it is considered that the worst leak is furthest from the walls and possible lateral vents, since the accumulations will be greater in corners and under ceilings. In relation to the direction of the flow the escape is considered in both z_out and y_out.

The leak diameters selected for the study of hydrogen leakage are 1mm, 3mm and 5mm. This information is detailed in *chapter 7.2.1.1 Hydrogen leakage rates*.

8.2 Theoretical calculations

Mass gas flow and volumetric gas flow of hydrogen for each leakage diameter is calculated to analyse hydrogen concentrations.

8.2.1 Hydrogen mass flow rate

Mass flow and volumetric flow of hydrogen leakage depend on what conditions the gas is stored. The conditions are gas density, gas pressure and gas temperature. Hydrogen is a compressible gas stored at a pressure of 70MPa and at a temperature of 25ºC.

The equation for calculating mass flow of hydrogen leakage as a function of the orifice diameter and storage blowdown time. The equation is detailed in the ***NTP 385 guide: Leakages in vessels: emission in gas phase*** [66]. The gas is considered in pressure and temperature conditions described, adiabatic process and reversible (isotropic) expansion process. The escape velocity can become supersonic when the leakage is in high pressure. However, the speed is not considered in supersonic conditions.

The mass flow as a function of time is expressed as:

$$\frac{dm}{dt} = C_D\, A\, \rho_0 \left(\left[\frac{M}{R\, T_0}\right] \Upsilon \left[\frac{2}{(\Upsilon + 1)}\right]^{\frac{(\Upsilon+1)}{(\Upsilon-1)}} \right)^{1/2} \tag{1}$$

Where;

- $dm\ (t = 0)$ initial mass flow (kg/s)
- C_D: Discharge coefficient (adimensional).
- A: Hole section area (m^2)
- ρ_0: Initial density of H_2 gas (kg/m^3)
- p_0: Initial pressure of H_2 gas (Pa)
- Υ: Ratio between the specific heats at constant pressure and volume
- M: Molecular weight of hydrogen (kg/kmol)
- R: Constant universal of gases (J/(kmol K))

Hydrogen properties and parameters to obtain the mass flow are described in *tables 17 and 18.*

Table 17. Hydrogen properties [50].

Property	**Value**	**Unit**
Molecular weight	2.016	g/mol
Boiling point	20.27	K
Melting point	14.01	K
Critical temperature	33.25	K
Critical pressure	1.297	MPa
Density of gas	0.08376	kg/m3

Table 18. Parameters to calculate hydrogen mass flow rate.

Parameters	**Value**		
D_{hole} (mm)	1	3	5
A_{hole} (m2)	7.85398E-07	7.06858E-06	1.9635E-05
C_D	0.62 (High pressure of storage)		
ρ_0	37.72 (Real density in storage)		
p_0	70000000		
Υ	1.41		
M	2.016		
R	8314		

Appendix D shows a table for calculating the density reduction as a function of the compressibility factor. *Table 19* shows the result of the mass and volumetric flow for each leak.

Table 19. Diameter hole, hydrogen mass and volumetric flow rate.

Diameter hole (mm)	**H2 Flow (kg/s)**	**H2 Flow (m3/s)**
1	0.017	0.205
3	0.155	1.845
5	0.429	5.123

8.2.2 Storage blowdown time for a leak size

The hydrogen tank is composed of 4 racks of 250 kg where each rack contains 62.5 kg (1.7 m3). Knowing the mass flow of hydrogen leakage, it is possible to calculate at what instant a tank rack will be emptied. In this study, a rack is considered since in case of leakage the rest of racks will have safety valves and emergency shut-off preventing their emptying.

Table 20 presents the blowdown time calculation obtained for the storage regarding leak size:

Table 20. Storage blowndown time for a leak size.

Type of tank	Storage Pressure (MPa)	Blowdown time for a leak size		
		1mm	**3mm**	**5mm**
1 rack (62.5kg)	70	3635 seg (60 min)	400 seg (6.5 min)	140 seg (2.3 min)

8.2.3 Hydrogen concentration

Different theoretical models described in chapter 5.4 propose methodologies to calculate the concentration of gas in a closed room when there is a vent. These proposed methods are used to have a theoretical approach to studying in CFD. The methods are the Linden model (1999) and the simple expressions developed by Cariteau and Tkatschenko (2013) described in ***Appendix 4.2 of Hyindoor Work Package 5***. These methods consider that the floating gas is in a well-mixed regime.

The flow expression that crosses the ventilation opening (m^3/s) during the filling phase is given by:

$$Q = C_D S (g'_0 h)^{1/2} \tag{2}$$

With a reduce gravity ($m.s^{-2}$):

$$g'_0 = g\left(\frac{\rho_a - \rho_0}{\rho_a}\right) \tag{3}$$

Where:

- C_D: vent discharge coefficient (constant value)
- h: vent dimension (m)
- S: vent area (m^2)
- ρ_a: air density (kg/m^3)
- ρ_0: releasing gas (H2) density (kg/m^3)

It should be noted that the molar fraction of the gas is:

$$X_f = \left(\frac{g'}{g'_0}\right) \tag{4}$$

Where g' is the reduced density of the gas in the room (hydrogen diluted with air), $m.s^{-2}$.

Then if the buoyancy conservation $g'_0 Q_0 = g'Q$ is applied, the fraction of floating gas that leads to the stable state in a room ventilated with a single vent is given as follows:

$$X_f = \left(\frac{Q_0}{C_D S (g_0' h)^{1/2}} \right)^{2/3} \quad (5)$$

Where Q_0 is the gas flow leak (m^3/s) and where C_D is recommended 0.25 for the use of the equation and determine the hydrogen concentration in stable state.

This is a simple method; it only allows the concentration in the room to be determined by means of an opening and the volumetric gas flow. If it is considered a 3x1m window and a mass flow of 0.205 m^3/s as an example, the concentration will be:

Table 21. Parameters to calculate hydrogen concentration.

Parameter	Unit	Value
C_D	constant	0.25
h	m	1
S	m^2	3
ρ_a	kg/m^3	1.19
ρ_0	kg/m^3	0.0838
g	m.s^{-2}	9.81
g_0'	m.s^{-2}	9.11
Q	m^3/s	2.26
$\boldsymbol{X_f}$	**adimensional**	**0.20**

The concentration would be around 20% in order to the enclosure has a 3m^2 window. Very high value that would generate an explosive atmosphere in a few seconds.

Logically, after this result, to study in detail the ventilation of the enclosure is an indispensable requirement. However, the inverse calculation can be performed. Total area of ventilation needed could be get from percentage of concentration about 4%.

Table 22. Minimum opening area required.

Parameter	Unit	Value
X_f	adimensional	0.04
Q_0	m^3/s	0.205
Q	m^3/s	25.625
h	m	1
$\boldsymbol{S}$	**m^2**	**33.95**

If each window is 1x3m^2 it would result in a total of 12 vents. This does not imply that the level of concentration is reduced to the calculated value, but it approximates how much ventilation it should dispose. Different configurations should be studied to determine which is the most effective.

8.2.4 Ventilation

Different configurations should be examined to reduce levels in enclosed spaces as described in *chapter 5.4 Ventilation*. The main start will be to have passive ventilation. These vents are preferable to place them at different heights, compared to a ventilation located only at the top. In addition, the result would improve if the vents are distributed on all sides of the enclosure since the wind would provide greater displacement of the gas.

Lateral vents are advisable to use before the roof vents. However, if new configurations do not improve the results it will be necessary to apply forced ventilation.

Forced ventilation will be calculated in basis of the expressions of Molkov et al. (2014) given for uniform mixtures.

8.2.4.1 Mechanical/forced ventilation by extraction

For a case of uniform concentration of hydrogen in the enclosure, the required flow rate can be calculated as:

$$Q_{FS} = \frac{Q_{H2}}{X} \tag{6}$$

For exhaust forced of hydrogen-air mixture, where X is the maximum volume fraction of target hydrogen, Q_{H2} is the rate of release of hydrogen and Q_{FS} is the required extraction rate (m^3/s).

8.2.4.2 Mechanical/forced ventilation by blow-in

For a case of uniform concentration of hydrogen in the enclosure, the required flow rate can be calculated as:

$$Q_{FB} = \frac{Q_{H2}}{X}\,(1 - X) \tag{7}$$

For the supply forced of fresh air to dilute the mixture of air and hydrogen, where X is the maximum volume fraction of hydrogen target, Q_{H2} is hydrogen flow rate and Q_{FB} is the required blow flow rate (m^3/s). In addition, if there are open vents to the atmosphere will function as an air outlet.

8.2.4.3 Unit Production: Forced ventilation by extraction

For example, exhaust forced ventilation can be calculated based on the parameters described above:

Table 23. Example of exhaust forced ventilation.

Parameter	Unit	Value
Q_{H2}	m^3/s	0.205
X	adimensional	0.04
Q_{FS}	m^3/s	5.12

This results in at least one extractor of 5.12 m^3/s, or two extractors of 2.56 m^3/s. If the same case is evaluated for a Q_{H2} of 1.84 m^3/s, for X of 0.1, this provides a Q_{FS} extractor of 18.4 m^3/s, or two extractors of 9.2 m^3/s. These values are used in forced ventilation tests performed in CFD.

8.3 Simulation strategy

In this chapter CFD is used to evaluate hydrogen dispersion gas due to a leakage of the pressure relief valve in storage as described in 2.6 CFD.

With the systematic approach used by CFD modelling in hydrogen dispersion, the concentration profile of a flammable hydrogen mixture is developed for three leak diameters described in 2.6.3 and table 19. The effects of natural and mechanical ventilation also are studied, with the aim of investigating different configurations and trying to reduce the concentration of hydrogen.

8.3.1 Scenario definition

To assess the requirements of the ventilation openings, eighteen cases were made for a hydrogen leakage rate of 1.84 m3 / s (3mm hole diameter) as described in *2.6.3*. These tests include one test without ventilation, five tests with natural ventilation and twelve tests with natural and forced ventilation.
Each test is evaluated in chain as shown in *Figure 24*. Based on the methodology of *Figure 1*, the simulation of a test is performed, the parameters of the hydrogen concentration level, the internal pressure of the compartment are evaluated and an attempt is made to reduce the level of concentration through subsequent tests.

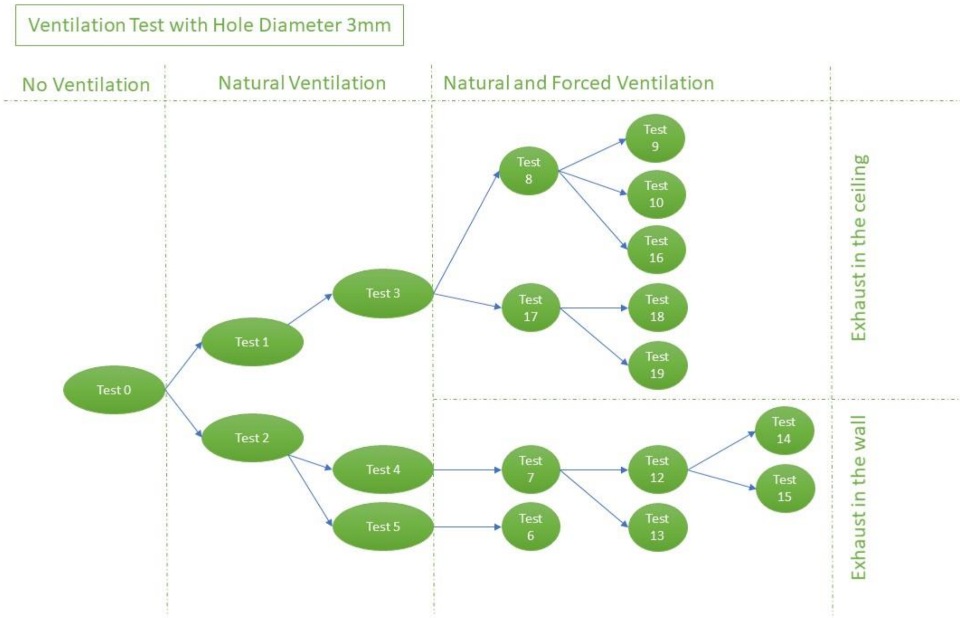


Figure 24. Test chain for different ventilation settings in hydrogen production unit with 3mm diameter hole. (Autor)

For a hole diameter of **3mm**, a leakage rate of **1.84 m^3/s** and a simulation time of **400 seconds**, the following tests are carried out:

- **Release of hydrogen without ventilation (Test 0):** in this simulation, the concentration profile of the hydrogen gas in the compartment is developed. It is analysed for a leakage rate direction in z_out and y_out. The results were used to perform the simulation of Tests 1 and 2 and evaluate the effects of ventilation.

- **Release of hydrogen considering natural ventilation:** Test 1, Test 2, Test 3, Test 4 and Test 5 are carried out to investigate the reduction of flammable fuel throughout the compartment. The size and configuration of the openings is presented in *table 24*. According to the test and the concentration in each configuration, these openings are located both in the walls and in the ceiling.

- **Hydrogen release considering natural and forced ventilation in walls:** due to the need to reduce the concentration level, Test 4 is modelled with several combined ventilation systems (natural and mechanical) to improve the ventilation condition, these are Test 6, Test 7, Test 12, Test 13, Test 14 and Test 15.

- **Hydrogen release considering natural and forced roof ventilation:** Test 3 is modelled with several combined ventilation systems (natural and mechanical) to improve the ventilation condition, these are Test 8, Test 9, Test 10, Test 16, Test 17, Test 18 and Test 19.

Figures 25 and 26 show the ventilation configuration (a x b = Length x Height) in the different tests. *Table 24* shows the definition of the configuration of each test:

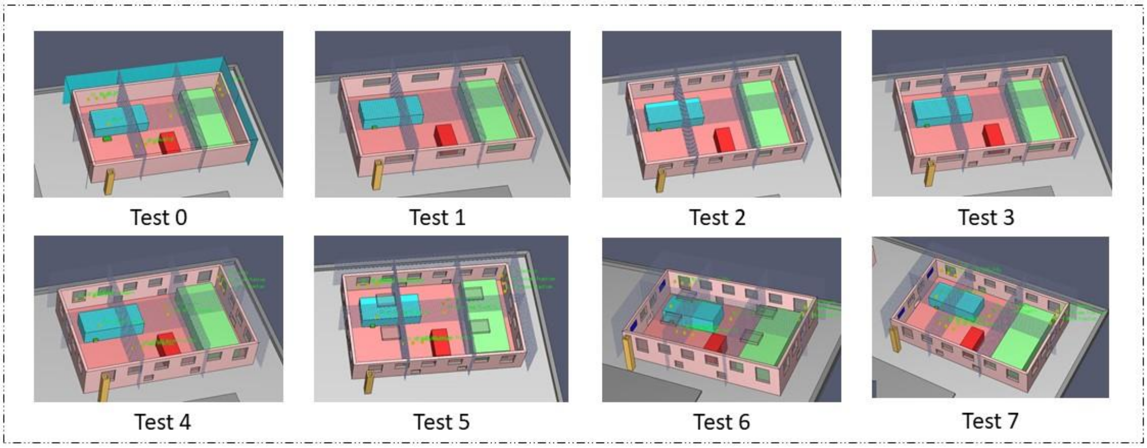

Test 0
Test 1
Test 2
Test 3
Test 4
Test 5
Test 6
Test 7

Figure 25. Ventilation configuration tests Part 1 D.3mm.

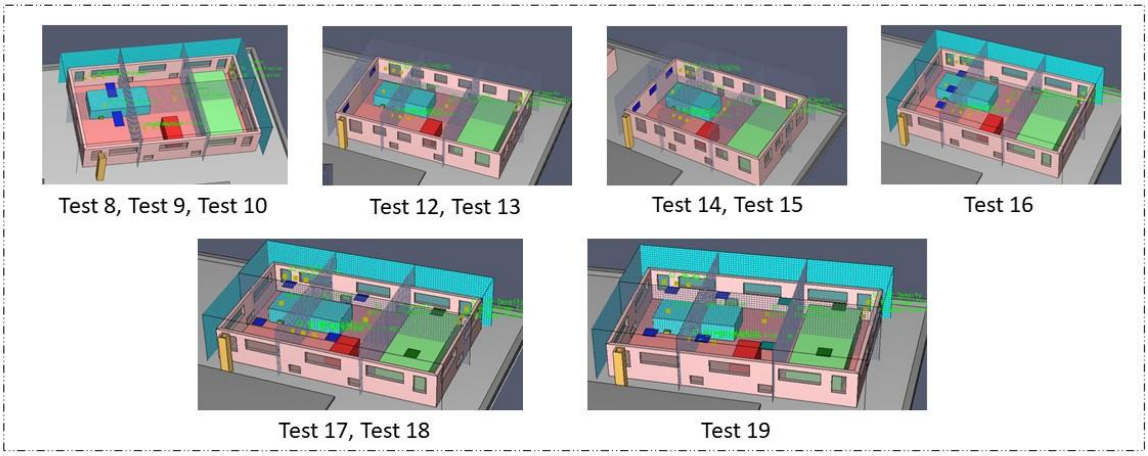

Test 8, Test 9, Test 10
Test 12, Test 13
Test 14, Test 15
Test 16
Test 17, Test 18
Test 19

Figure 26. Ventilation configuration tests Part2 D.3mm. (Autor)

Table 24. Ventilation Tests description.

Test D.3mm	Description*
Test 0	Without ventilation.
Test 1	Natural Ventilation. 10 openings 3x1m^2 placing in walls at same height.
Test 2	Natural Ventilation. 20 openings 1.5x1m^2 placing in walls at same height.
Test 3	Test 1 is added 4 openings 1.5x1.5m^2 and 2 lower openings 1x0.7m^2 on north and south sides.
Test 4	Test 2 is extended 4 openings at 1.5x1.5m^2, 2 lower openings 1x0.7m^2 on north and south sides and 1 lower opening 1x0.7m^2 on east and west sides.
Test 5	Test 4 with 4 openings 2x1m^2.
Test 6	Test 5 with forced lateral ventilation. 2 Exhaust of 5.12 m^3/s each of them.
Test 7	Test 4 with forced lateral ventilation. 2 Exhaust of 2.56 m^3/s each of them.
Test 8	Test 3 with forced roof ventilation. 2 Exhaust of 2.56 m^3/s each of them.
Test 9	Test 3 with forced roof ventilation. 2 Exhaust of 9.2 m^3/s each of them.
Test 10	Test 3 with forced roof ventilation. 2 Exhaust of 4.61 m^3/s each of them.
Test 12	Test 4 with forced lateral ventilation. 2 Exhaust of 4.61 m^3/s each of them.

Test 13	Test 4 with forced lateral ventilation. 2 Exhaust of 9.2 m^3/s each of them.
Test 14	Test 4 with forced lateral ventilation. 3 Exhaust of 2.56 m^3/s each of them.
Test 15	Test 4 with forced lateral ventilation. 3 Exhaust of 9.2 m^3/s each of them.
Test 16	Test 3 with forced roof ventilation. 3 Exhaust of 4.61 m^3/s each of them.
Test 17	Test 3 with forced roof ventilation. 4 Exhaust of 2.56 m^3/s and 2 Exhaust of 0.5 m^3/s.
Test 18	Test 3 with forced roof ventilation. 2 Exhaust of 3.5 m^3/s, 2 Exhaust of 1 m^3/s and 2 Exhaust of 0.5 m^3/s .
Test 19	Test 3 with forced roof ventilation. 4 Exhaust of 2.56 m^3/s, 2 Exhaust of 1 m^3/s and 2 Exhaust of 0.5 m^3/s .

* Exhaust values described in section 8.2.4.3 Unit Production: Forced ventilation by extraction.

The tests that show the greatest reduction in the concentration level are selected and compared for leak diameters of 1mm and 5mm as described in *chapter 8.4.2*. Test 3, 4, 5, 14, 15, 18 and 19 are evaluated with 1mm and 5mm in diameter, corresponding to simulation times of 4000 sec and 143 sec.

Due to the highly flammable nature of the hydrogen, it was assumed that the mechanical ventilation system was fireproof and electric. Therefore, the temperature inside the compartment is maintained at room temperature (20ºC) to avoid auto ignition of the released gas [67].

8.4 Results

Hydrogen mass flow within the compartment is observed for each test. This parameter performs an important role in hydrogen dispersion and concentration, since it is directly related to the risk of ignition. The effects of ventilation, hydrogen pressure and hydrogen concentration level are measured through different sensors located at unit production area.

8.4.1 Effect of venting in unit production when hydrogen is released from a 3mm diameter hole

1. Release of hydrogen inside unit production without ventilation in y_out and z_out direction (Test 0).

When a hydrogen leakage is produced the concentration of fuel is very high. According to *figure 27*, higher concentrations are observed under the ceiling where the vanishing point is located and in the upper left corner where the S2VF sensor is located. Hydrogen is accumulated in the upper area of the enclosure due to the fact that it is lighter than the air and has a strong buoyancy effect. The pressure and density in the compartment will increase putting the structure at risk.

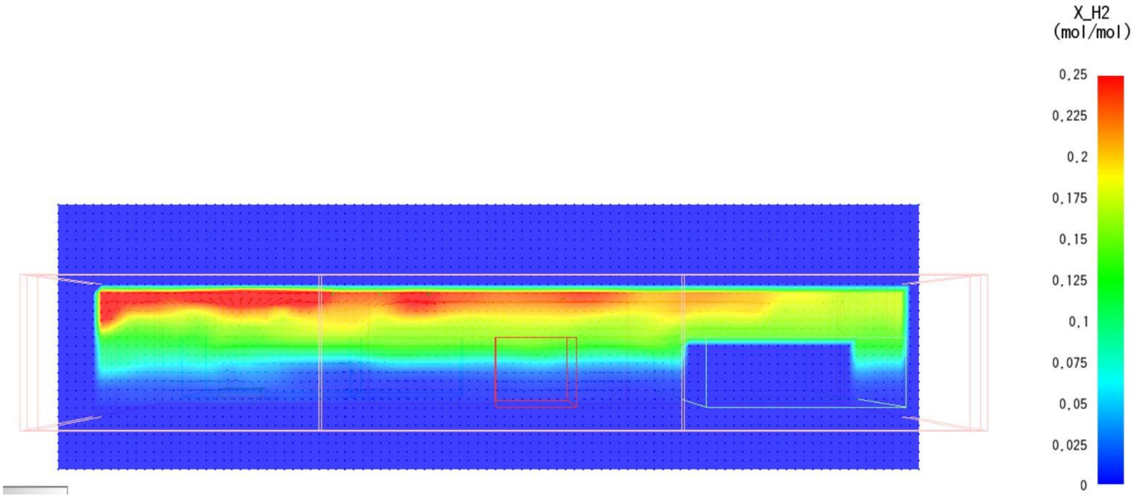


Figure 27. Hydrogen concentration profile with no opening in unit production area. Test 0. Time 70 sec.

The results indicate that the entire compartment is at risk of ignition since the concentration is higher than the lower flammability limit. The areas where electronic components are found such as in the electrolyser, compressor and storage. On the other hand, the electric bulbs under the ceiling can perform the role of sources of ignition. Therefore, ventilation will be necessary in order to mitigate the concentration.

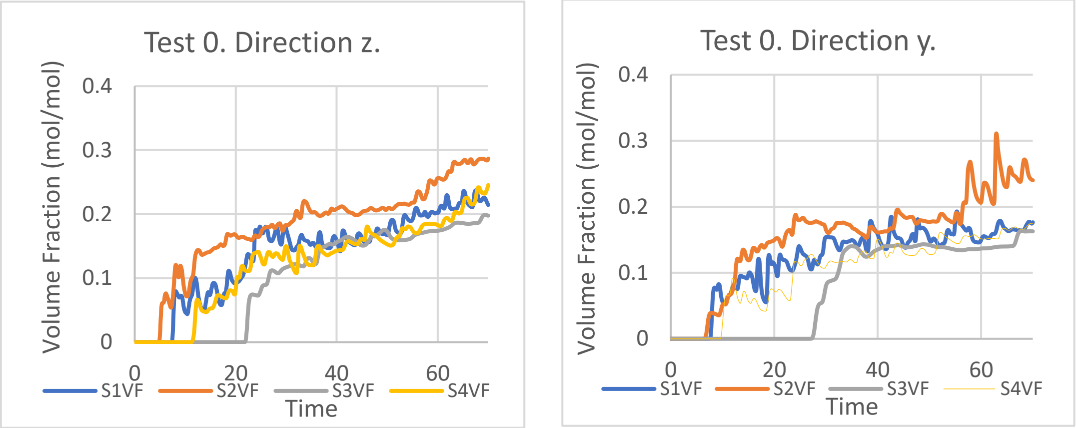


Figure 28. Test 0. Hydrogen concentration when the leakage is delivered in z direction and y direction at unit production.

In *figure 28,* it is observed that the leakage in z direction will accumulate hydrogen faster than y direction in the roof. Thus, the leakage in z direction is considered in the following tests.

2. Release of hydrogen inside unit production with different tests of natural ventilation.

Different ventilation configurations are installed to study the effect of window position and to reduce the concentration. *Figure 29* shows the concentration of hydrogen for five tests with different ventilation positions and sizes. While *figure 30* shows the interior pressure for each test at the compartment.

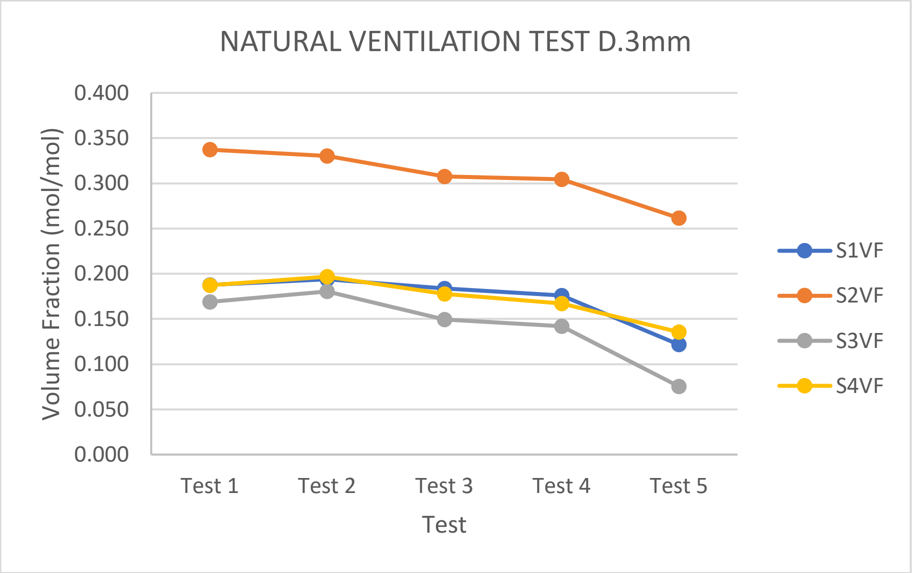


Figure 29. Hydrogen concentration in natural ventilation test at unit production. D.3mm.

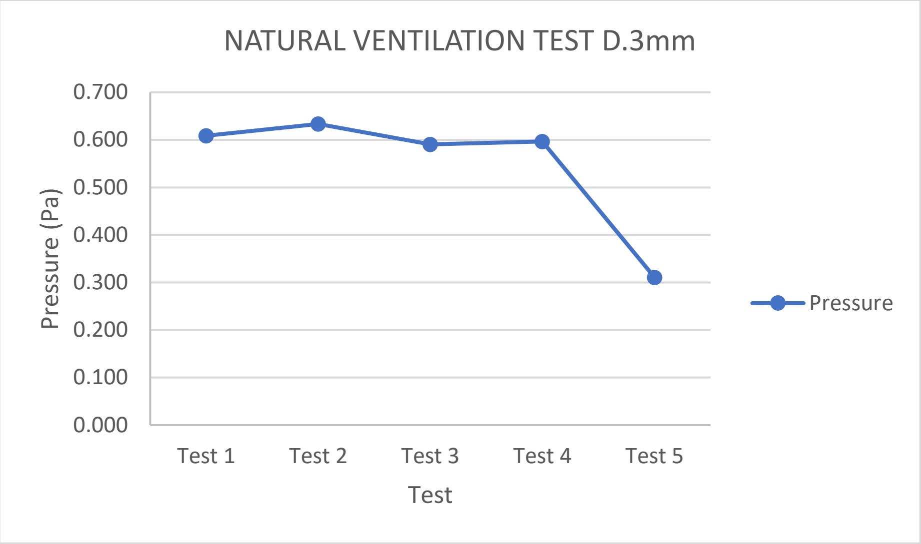


Figure 30. Pressure in natural ventilation test at unit production. D.3mm.

Test 1 and Test 2 are cases of ventilation positions located with the same height and opening area. These tests show very similar concentration values. However, these tests are slightly showing a higher concentration of hydrogen than the cross-ventilation configurations, such as Test 3 and Test 4, where the side openings are placed at different heights.

The average concentration in sensor 2, S2VF is 33.7 v/v% at Test 1, 33 v/v% at Test 2, 30 v/v % at Test 3 and 30 v/v% at Test 4. The results in these tests do not greatly improve the concentration level and are still very high in the area where the S2VF sensor is located. This is due to the fact that to hydrogen gas continues accumulating in the upper left corner (*Figure 31*). In addition, S1VF and S4VF sensors show similar concentration values between 19 and 16 v/v%, while S3VF sensor, located farthest from the source, shows lower values between 18 and 14 v/v%.

Figure 30 shows that none of the tests will present interior negative pressures and neither dangerous for the structure and equipment.

Figure 31 shows hydrogen strong buoyancy effect, which rises at the top and is vented through ventilation openings in higher walls. In this way, test 5 composed of roof openings is proposed like is shown in figure 32 and 33. *Figure 29* shows an improvement in hydrogen concentration in S2VF at 26 v/v%, S1VF and S4VF at 12 v/v%, S3VF at 7.5%. While in *figure 32* a greater dispersion of the hydrogen is observed. However, this model is insufficient since the area is at risk of ignition, therefore, it will be necessary to consider the combination of natural and mechanical ventilation.

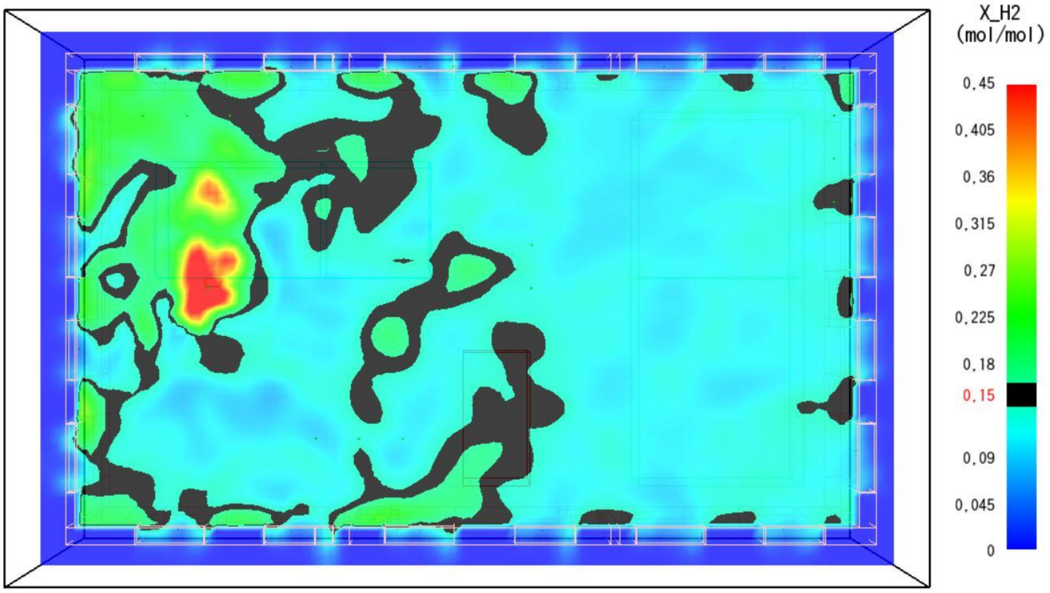


Figure 31. 2D Slide z=2.4m. Hydrogen accumulation in Test 4 at unit production. D.3mm. Time 200 sec.

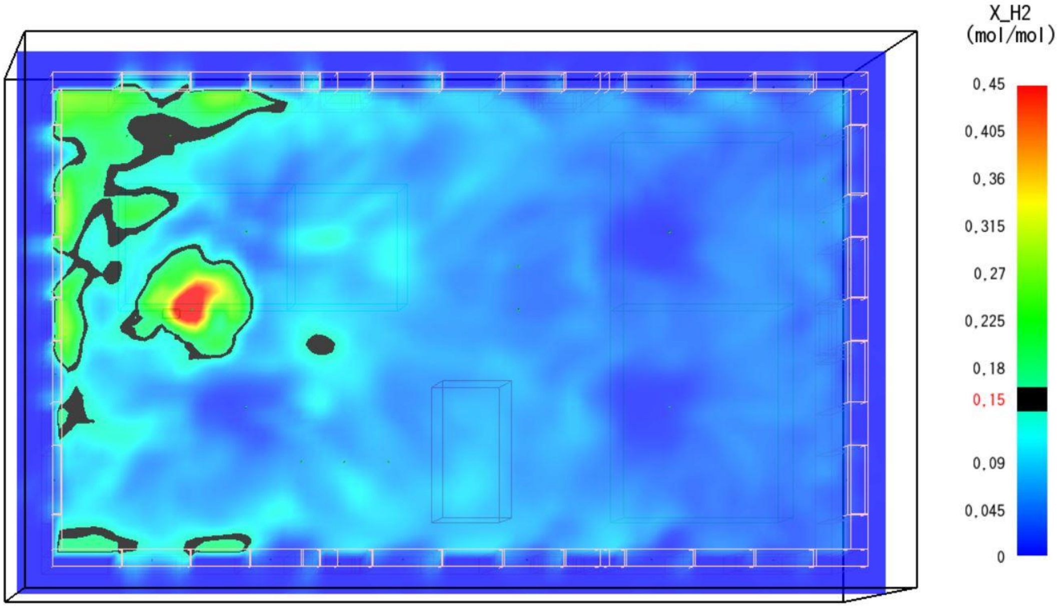


Figure 32. 2D Slide z=2.4m. Hydrogen accumulation in Test 5 at unit production. D.3mm. Time 200 sec.

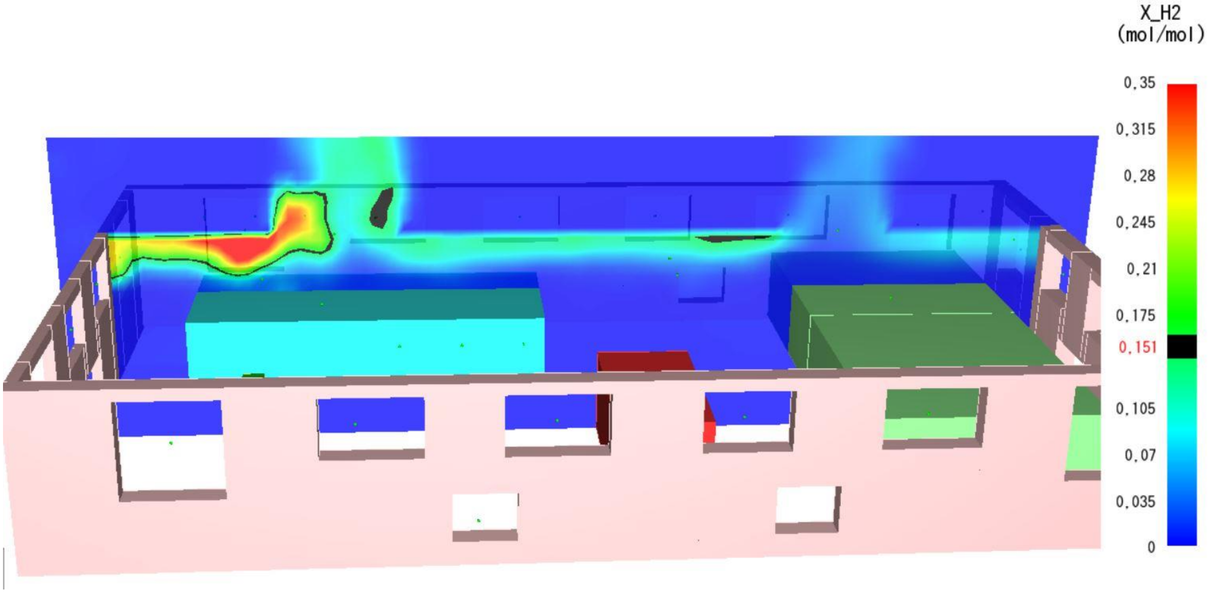


Figure 33. Effect of roof natural ventilation in Test 5 at unit production. D.3mm. Time 200 sec.

3. Release of hydrogen inside unit production considering natural and mechanical ventilation.

Different ventilation configurations are installed to study the effect of disposing lateral extraction and to reduce the concentration.

1) **Natural and mechanical ventilation with lateral extraction:**

Figure 34 shows the interior pressure at the compartment for six tests with different number of extractors and ventilation flow rates. *Figure 36* shows hydrogen concentration for positive pressure tests, including Test 15. Test 15 is included because it recovers the depression as shows *Figure 35*.

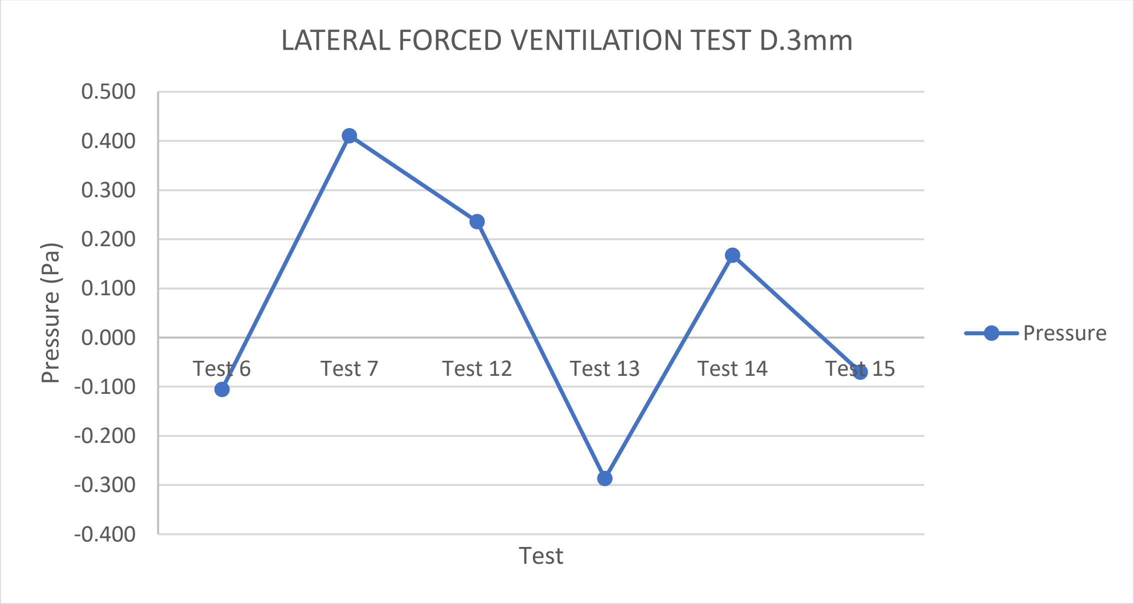


Figure 34. Pressure in lateral forced ventilation test at unit production. D.3mm.

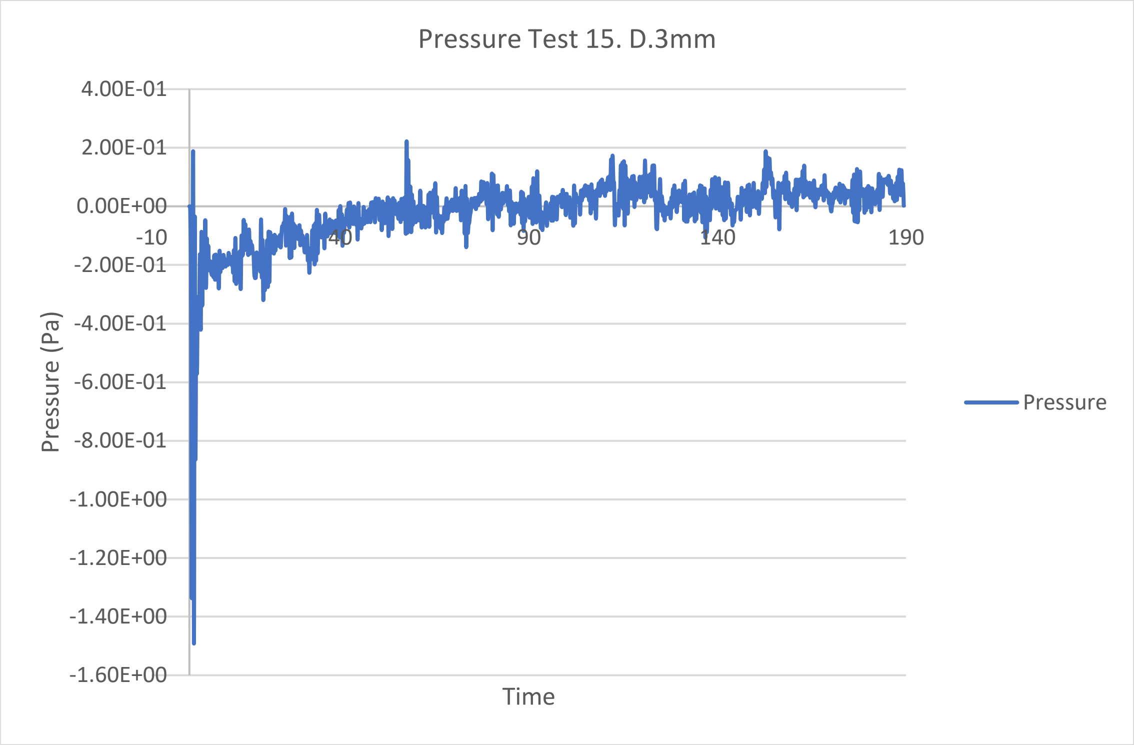


Figure 35. Pressure Test 15 at unit production. D.3mm.

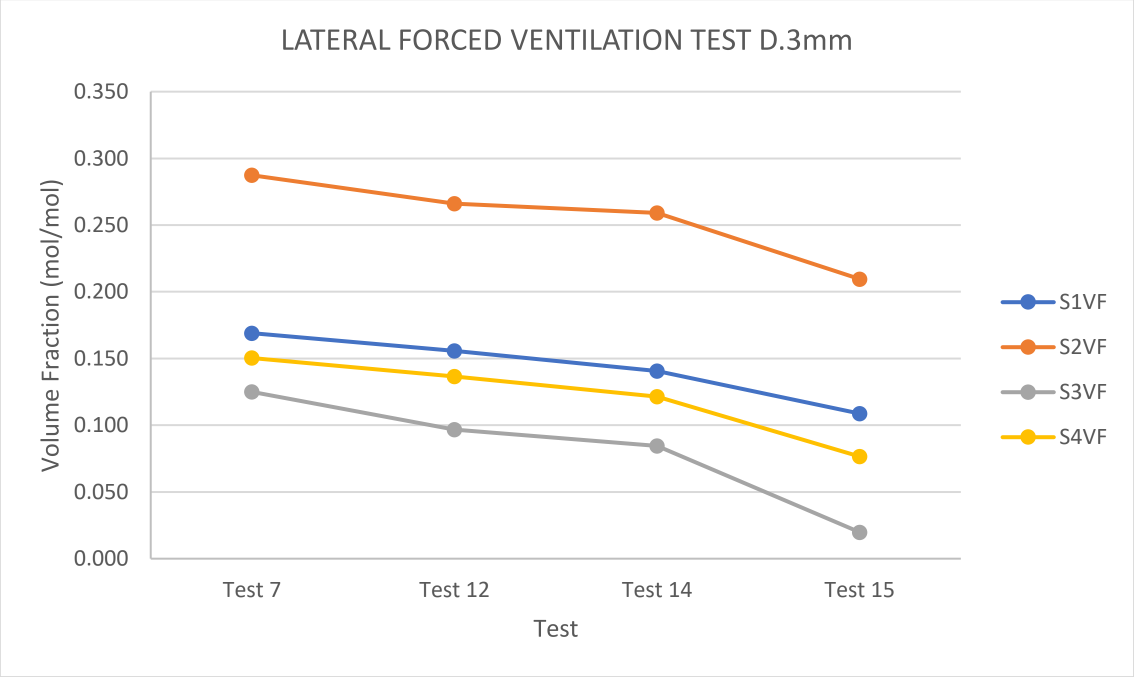


Figure 36. Hydrogen concentration in lateral forced ventilation test at unit production. D.3mm.

Test 6 and Test 7 are composed of two lateral extractors. The difference between them is that test 6 comes from Test 5 (openings in the roof) and has a higher extraction flow than test 7, as *table 24* describes. These two tests were studied to verify that the effect of mechanical ventilation with natural ceiling is not a good solution.

Figure 37, which belongs to Test 5, shows that all roof openings are expelling hydrogen to the atmosphere.

Figure 38 shows that two openings in the roof will create suction when mechanical ventilation is incorporated (Test 6). This test will present negative pressures at the compartment. This effect can be observed in hydrogen movement vector in *figures 39 and 40*.

Test 7 is an example without a roof opening and a lower extraction value is used to compensate the lower air entrance.

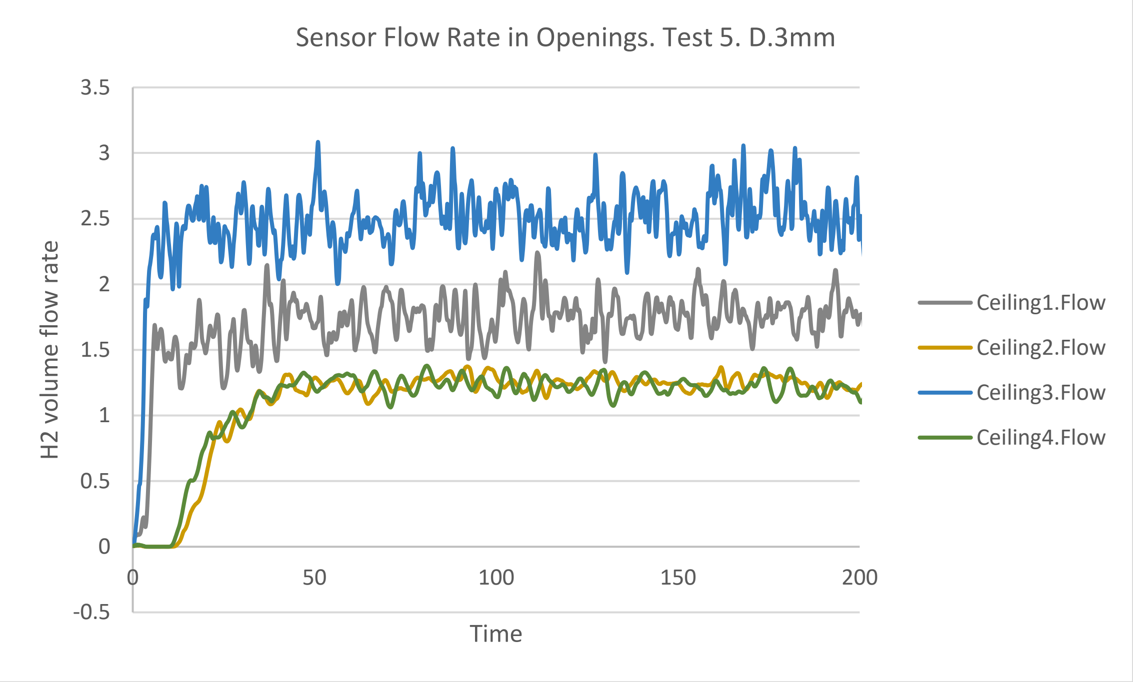


Figure 37. Flow rate sensor in ceiling opening at test 5.

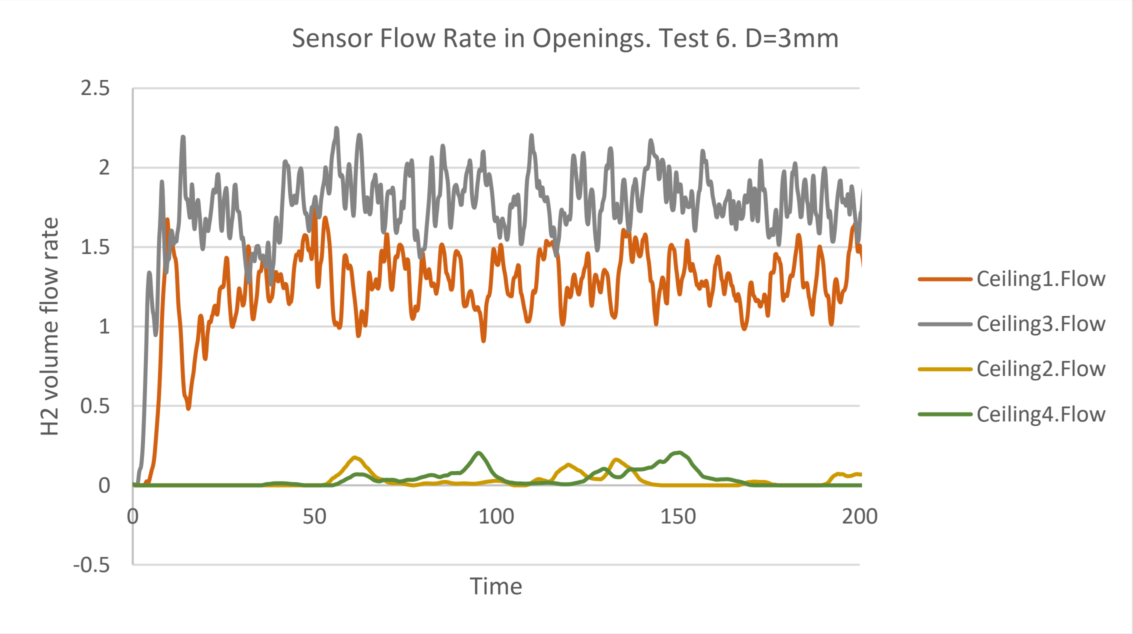


Figure 38. Flow rate sensor in ceiling opening at test 6.

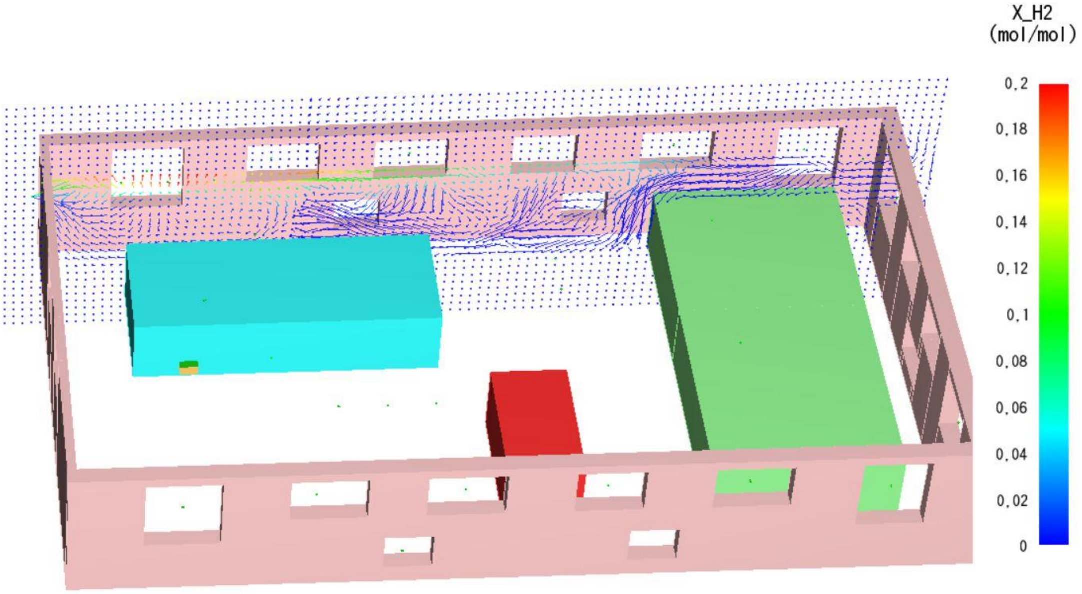


Figure 39. Effect of roof natural ventilation and lateral mechanical ventilation in Test 6 at unit production. D.3mm. Time 200 sec. Part 1.

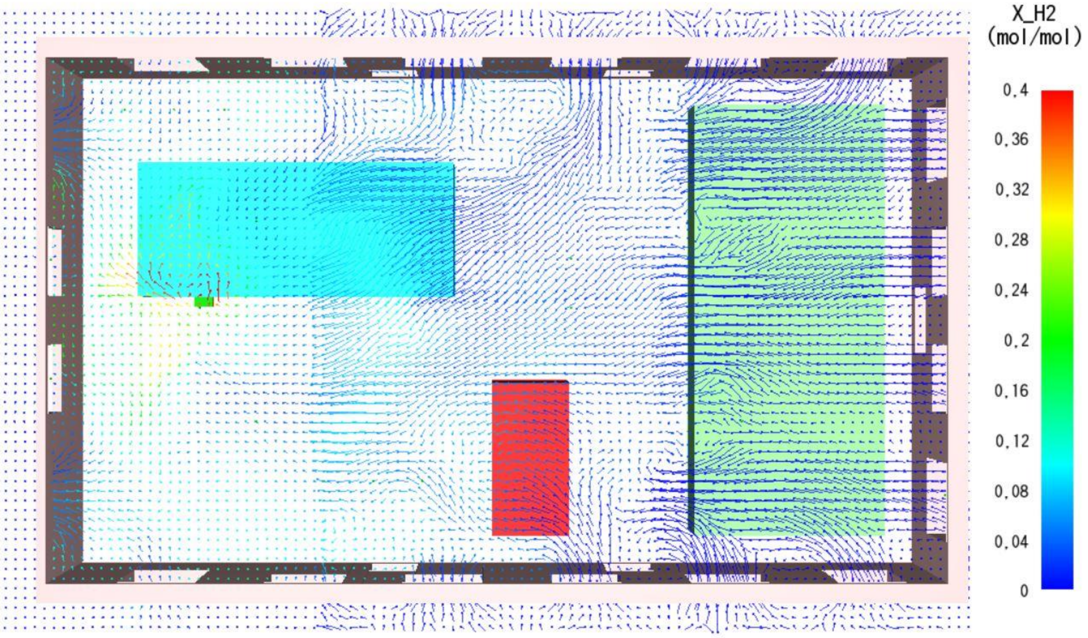


Figure 40. 2D Slide z=2.4m. Effect of roof natural ventilation and lateral mechanical ventilation in Test 6 at unit production. D.3mm. Time 200 sec. Part 2.

Test 7, Test 12 and Test 13 are comparable between them. Two lateral extractors are located with different extraction rates as it is described in *table 24*. These three tests were studied to check which extraction flow does not cause negative pressures in the inside of the enclosure for the same natural ventilation arrangement.

Figure 34 shows that test 13 presents negative pressures, since extraction flow rate is very high. On the other hand, Test 14 and Test 15 are also comparable. Three lateral extractors are located with the same extraction flow rates for Test 7 and Test 12.

Figure 36 shows the average concentration for Test 7, 12, 14 and 15. In sensor 2, S2VF, this average concentration is 28 v/v% at Test 7, 26 v/v% at Test 12, 25 v/v% at Test 14, and at 21 v/v% at Test 15. The concentration of Test 4 is improved by 33% from Test 15 as indicated in *Table 25*. These tests improve hydrogen gas accumulation in S2VF as shown in *figures 41 and 42*.

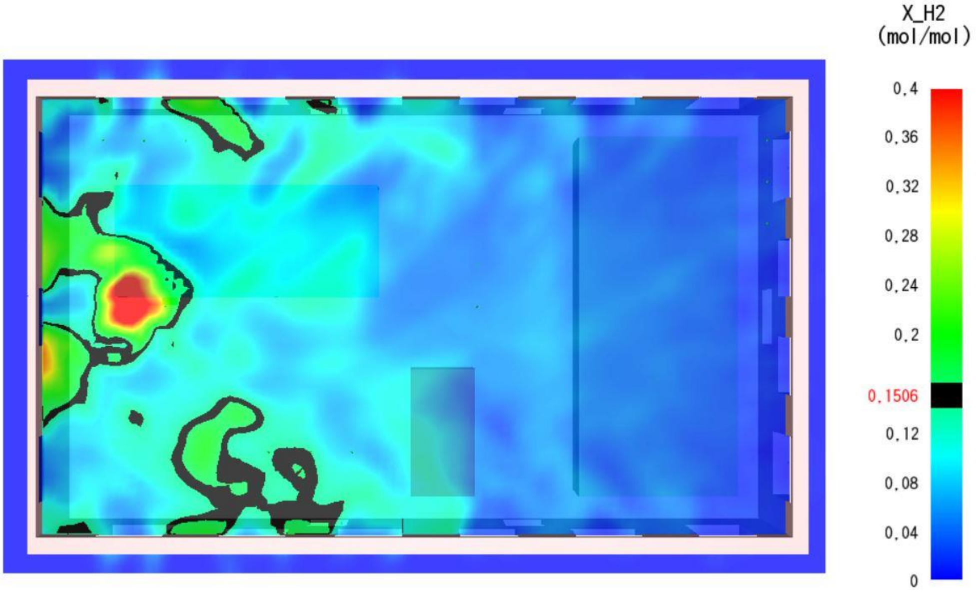


Figure 41. 2D Slide z=2.4m. Hydrogen accumulation in Test 15 at unit production. D.3mm. Time 200 sec.

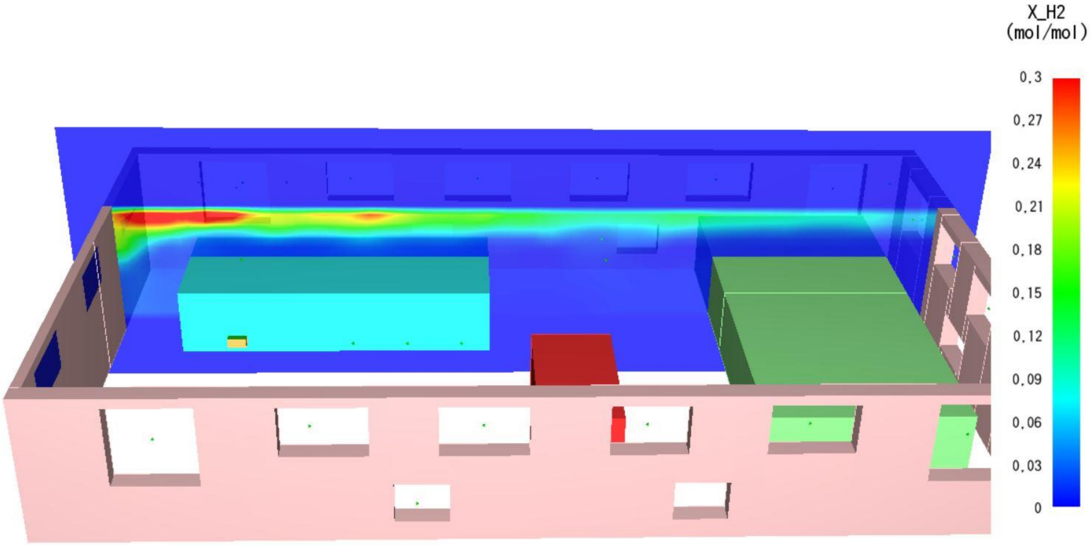


Figure 42. Profile of hydrogen accumulation in Test 15 at unit production. D.3mm. Time 200 sec.

Table 25. Improve hydrogen concentration in Test 4 when is include forced lateral ventilation. Lecture of S2VF.

Ventilation Test	Max. Fuel concentration (v/v %)	Improvement (%)	Acceptable
Test 4	31	N/A	No
Test 7	28	9.67	No
Test 12	26	16.12	No
Test 14	25	19.35	No
Test 15	21	33	No

If the rest of the sensors (S1VF, S3VF and S4VF) are compared with respect to Test 4, the reduction of hydrogen concentration in percentage is greater for Test 15. S1VF sensor shows concentration values of 10 v/v%, S4VF values of 7 v/v%, while sensor S3VF shows values lower than 2 v/v%.

As a result, this model continues to be insufficient since the area is at risk of ignition, therefore, the combination of natural and mechanical ventilation with ceiling extraction is analyzed.

2) Natural and mechanical ventilation with roof extraction:

Figure 43 shows the interior pressure at the compartment for seven tests with different number of extractors and different extraction flow located in the ceiling. While *figure 44* shows hydrogen concentration for normal pressure tests at the compartment.

Test 8, Test 9, Test 10 are comparable tests. Two extractors are located on the roof with different extraction flows, as it is described in *table 24*. These three tests were studied to check which extraction flow does not cause under pressures inside the compartment when a configuration of natural ventilation is defined, like in Test 3.

Figure 43 showing test 9 and test 16 present under pressures at the compartment, since the extraction flow rate is very high.

Test 17 and Test 18 are also comparable tests. There are six extractors distributed in the ceiling, varying their extraction flow rates. Test 19 is presented to improve Test 18.

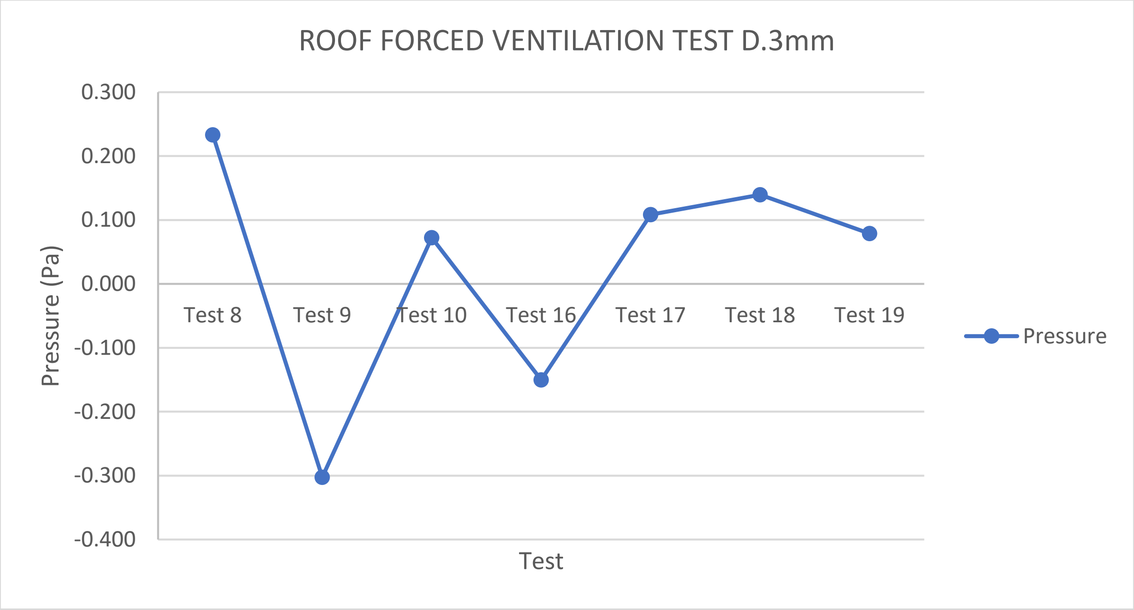


Figure 43. Pressure in roof forced ventilation test at unit production. D.3mm.

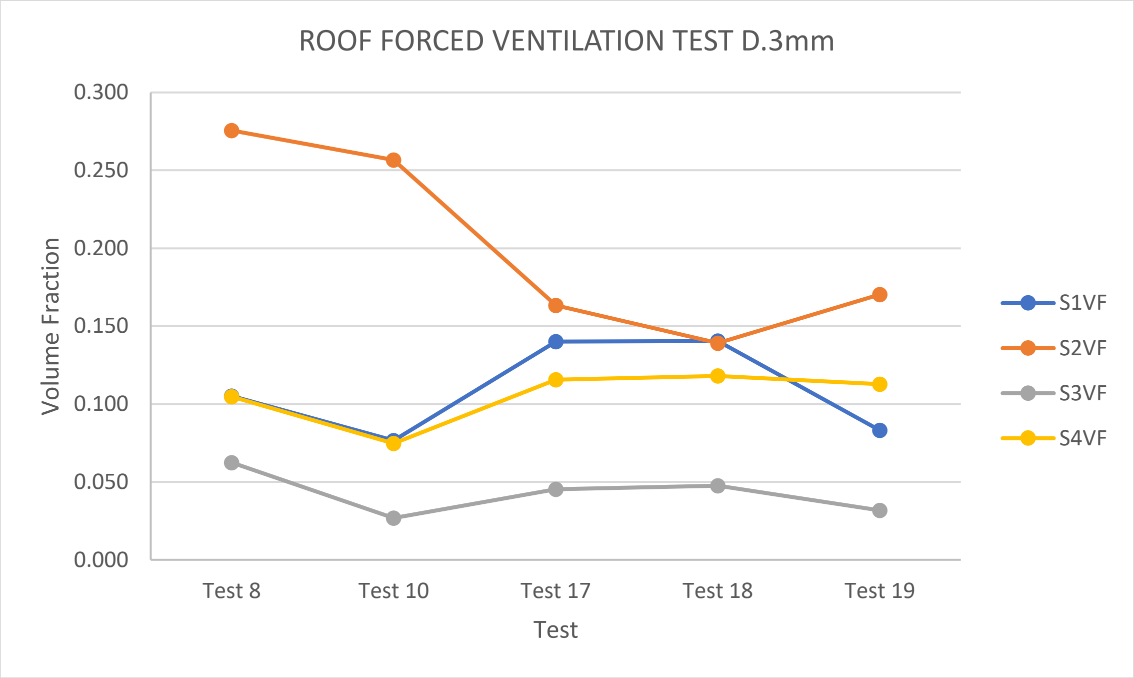


Figure 44. Hydrogen concentration in roof forced ventilation test at unit production. D.3mm.

Figure 43 shows the average concentration for Test 8, 10, 17, 18 and 19. In sensor 2, S2VF, this average concentration is 27 v/v% at Test 8, 25 v/v% at Test 10, 16 v/v% at Test 17, 13 v/v% at Test 18 and 16 v/v% at Test 19. The concentration of Test 3 is improved by 57% from sensor S2VF of Test 18 as indicated *Table 26*. This can be seen in *Figures 45 and 46* where hydrogen concentration in the upper left corner and in the rest of the compartment is reduced.

Table 26. Improve hydrogen concentration in Test 3 when is include roof lateral ventilation. Lecture of S2VF.

Ventilation Test	Max. Fuel concentration (v/v %)	Improvement (%)	Acceptable
Test 3	30	N/A	No
Test 8	27	10	No
Test 10	25	17	No
Test 17	16	47	No
Test 18	13	57	No
Test 19	17	44	No

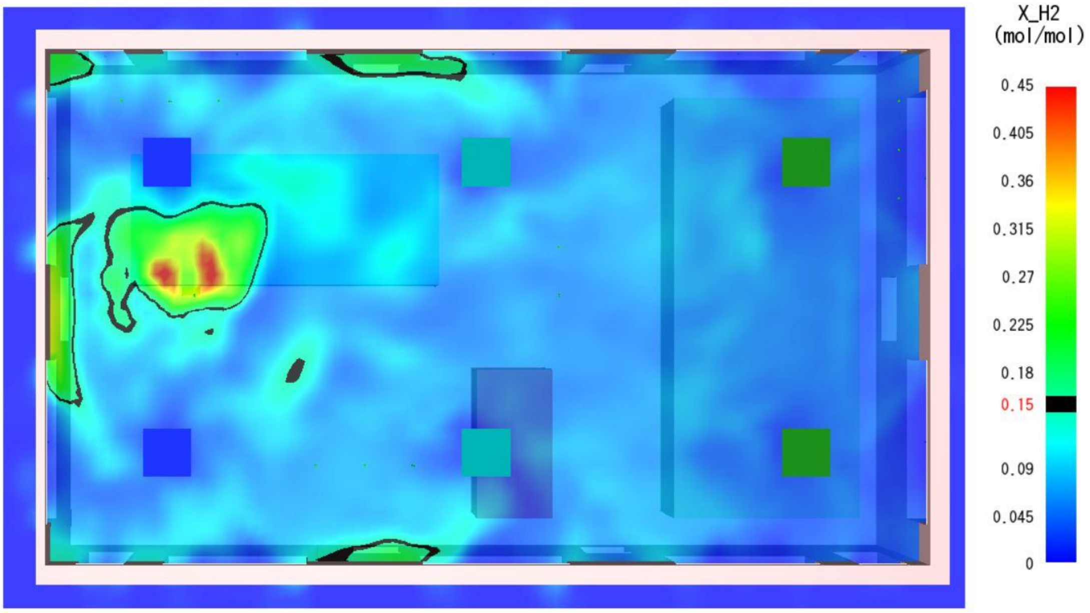


Figure 45. 2D Slide z=2.4m. Hydrogen accumulation in Test 18 at unit production. D.3mm. Time 200 sec.

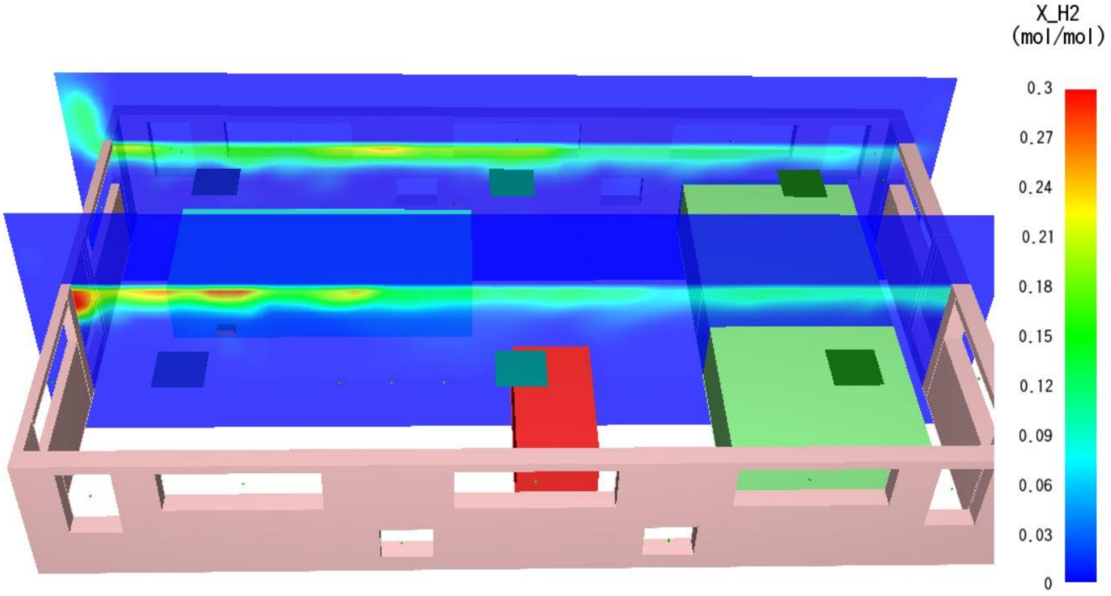


Figure 46. Profile of hydrogen accumulation in Test 18 at unit production. D.3mm. Time 200 sec.

If the rest of the sensors are analysed, a greater reduction in hydrogen concentration is obtained in the reading of sensors S1VF, S3VF and S4VF for test 10. This means a reduction of gas dispersion towards the compressor and electrolyser.

Test 19 provides values like Test 10 in SV3F at 3 v/v% and SV1F at 8.3 v/v%. However, Test 8 will provide a more even gas dispersion in SV2F compared to Test 9 and Test 10.

According to whether the system is composed of natural ventilation or mechanical ventilation, the most efficient ventilation configuration will be in Test 5, in Test 15 and in Test 18 for constant hydrogen flow rate of 1.82 m^3/s.

8.4.2 Comparison of ventilation tests in different hydrogen leakage rates

The most efficient tests described in *chapter 8.4.1* are selected to be studied with two different leakage ratios. In addition to these tests are considered Test 3, Test 4, Test 14 and Test 19. This is because forced ventilation tests will not be suitable for small leaks of D.1mm, meanwhile the forced ventilation developed will not be enough to reduce the concentration of large leaks of D.5mm. *Table 27* shows the different tests in comparison with different levels of hydrogen leakage.

Table 27. Ventilation test in different hydrogen leakage rates. Parameters: flow rate, release time, hole diameter and pressure.

Test	H_2 Flow (m^3/s)	Type of Ventilation	Release Time (s)	Hole diameter (mm)	Pressure	Analysis
3	0.204	Natural	4000	1	+	Yes
	1.82		400	3	+	Yes
	5.12		143	5	+	Yes
4	0.204	Natural	4000	1	+	Yes
	1.82		400	3	+	Yes
	5.12		143	5	+	Yes
5	0.204	Natural	4000	1	+	Yes
	1.82		400	3	+	Yes
	5.12		143	5	+	Yes
14	0.204	Natural + Lateral Forced	4000	1	-	No
	1.82		400	3	+	Yes
	5.12		143	5	+	Yes
15	0.204	Natural + Lateral Forced	4000	1	-	No
	1.82		400	3	+ o -	Yes
	5.12		143	5	+	Yes
18	0.204	Natural + Roof Forced	4000	1	-	No
	1.82		400	3	+	Yes
	5.12		143	5	+	Yes
19	0.204	Natural + Roof Forced	4000	1	-	No
	1.82		400	3	+	Yes
	5.12		143	5	+	Yes

1) **Comparison of Test 3, 4 and 5 for different leakage rates:**

Figure 47 shows a positive pressure for each test since no suctions are generated inside the compartment. In *Figure 48 and 49*, Test 3 and Test 4 for small leaks (D.1mm) present similar values of hydrogen concentration, in the same way as in medium leaks (D.3mm). In Test 3 and in test 4, sensor S2VF shows for 1mm 5.5-6 v/v% and 3mm 30 v/v%.

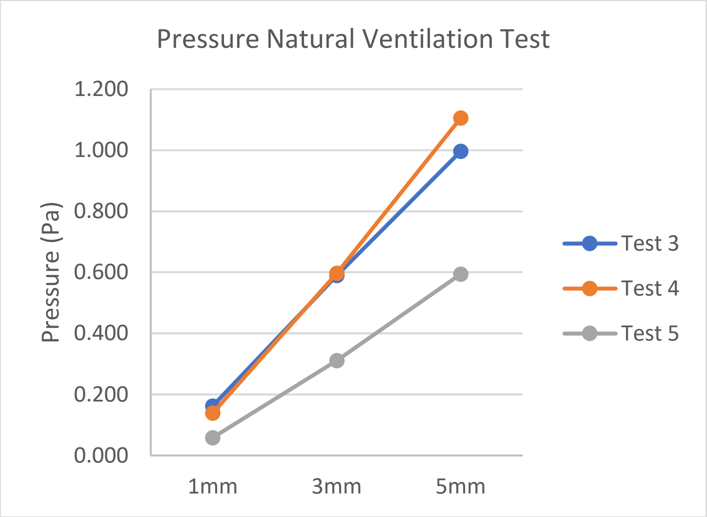


Figure 47. Pressure natural ventilation test.

In contrast, the reading of the sensors for Test 3 and Test 4 for D.5mm shows significant differences. In Test 3 sensor S2VF shows a 44 v/v% and in Test 4 a 35 v/v%. This difference can also be observed in the rest of the sensors for Test 3, the average of concentrations shows in S1VF a 30 v/v%, S3VF a 23 v/v% and S4VF a 26 v/v%, while for Test 4, S1VF shows a 23 v/v%, S3VF a 18 v/v% and S4VF a 20 v/v%.

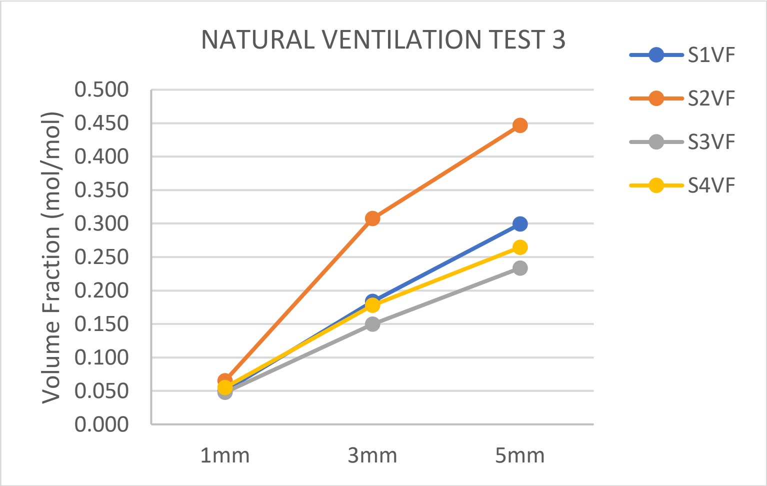


Figure 48. Volume Fraction Test 3. D: 1,3 y 5mm.

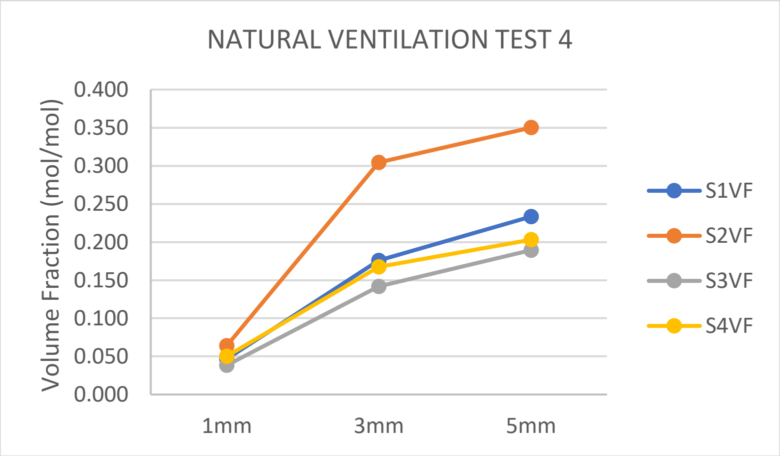


Figure 49. Volume Fraction Test 4. D: 1,3 y 5mm.

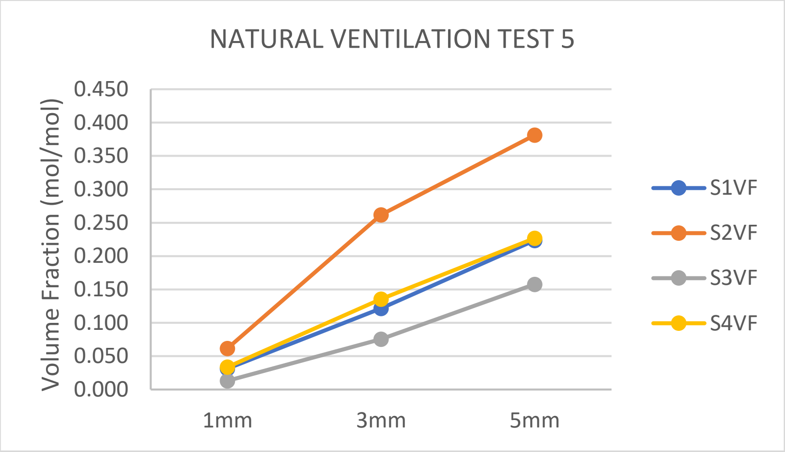


Figure 50. Volume Fraction Test 5. D: 1,3 y 5mm.

In the same way, Test 5 is compared for different leakage values. As it is described in *chapter 8.4.1*, Test 5 proposed an improvement of Test 4, thus reduces concentration by providing an opening in the ceiling, as shown in *figures 49 and 50*. On the one hand, if it is analysed for D.1mm both tests do not show differences in concentration. On the other hand, the roof openings of Test 5 do not reduce the concentration of Test 4 when the leaks are from D.5mm.

As a conclusion, for small leaks (1mm) the tests have similar concentrations around 5 v/v%, values close to hydrogen lower flammability limit. For medium leaks (3mm) distribute the same total window area, but more windows at different heights slightly reduces the concentrations (Test 3 and Test 4), while placing openings in the ceiling (Test 5) reduces the concentration. For large leaks (5mm) distribute a greater number of windows at different heights with the same total area (Test 4), it does reduce the concentrations, but incorporating roof openings will not reduce hydrogen levels.

2) Comparison of Test 14, 15, 18 and 19 for different hydrogen leakage rates:

Figure 51 shows the pressures for each test inside the compartment. Negative interior pressures will be present for D.1mm, so it is deduced that these forced ventilation tests are not solutions for small leaks.

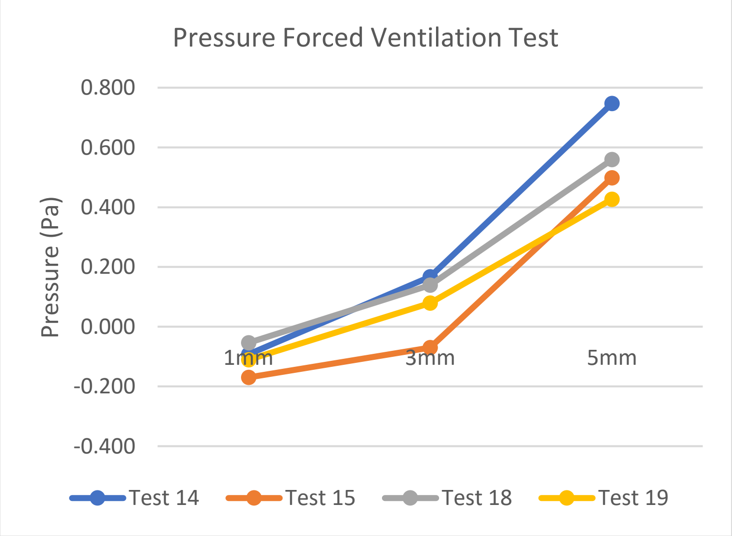


Figure 51. Pressure forced ventilation test.

In *Figure 51*, Test 14 and 15 are shown for medium and large leaks. These tests are comparable, same configuration of mechanical ventilation with variation in the volumetric flow of each extractor. As a result, lower hydrogen concentrations for leaks from D.3mm and D.5mm are observed at Test 15 compared to Test 14.

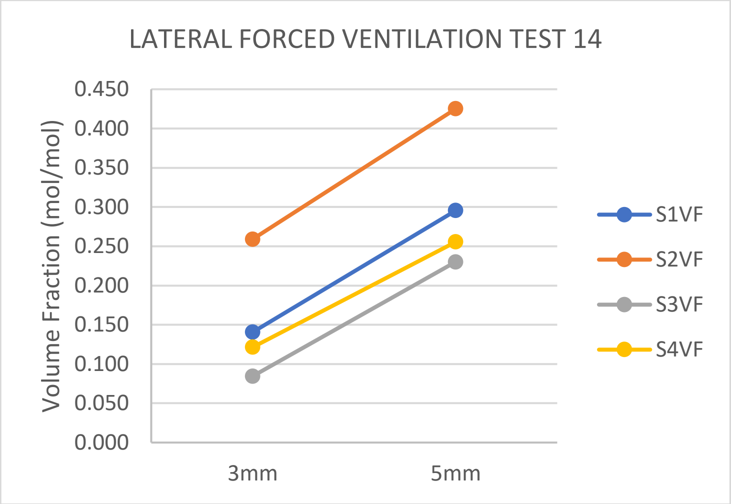


Figure 52. Volume Fraction Test 14. D: 1,3 y 5mm.

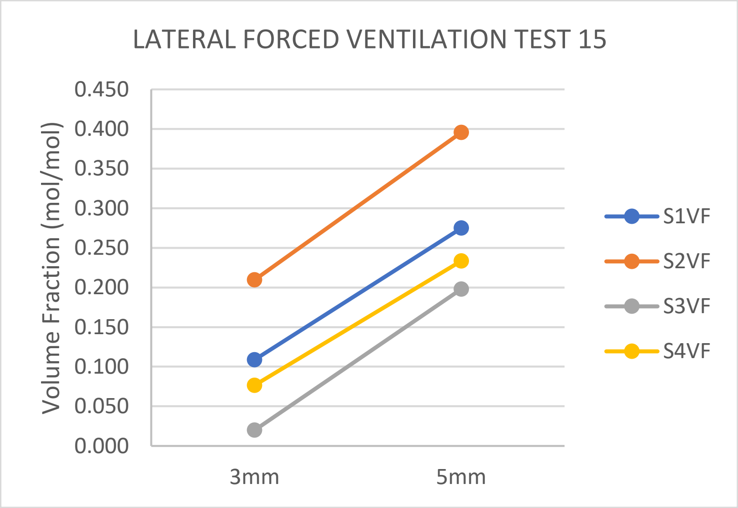


Figure 53. Volume Fraction Test 15. D: 1,3 y 5mm.

In figures 52 and 53 are shown Test 18 and Test 19. These tests have different number of extractors in the ceiling but with the same total extracted volume. Test 18, composed of a smaller number of extractors, presents in sensor S2VF lower concentrations for medium leaks (D.3mm) compared to Test 19. This sensor shows percentage of concentration in Test 18 around 13.7 v/v% compared to Test 19 around 17 v/v%.

Sensor S1VF in Test 18 shows the same behaviour as S2VF for D.3mm and D.5mm of leakage. This is due to the fact that Test 18 will have a higher volumetric extraction rate.

Test 19 significantly reduces the concentration of S1VF for D.3mm and D.5mm. This is because the sensor is in the centre of the compartment, so that placing more extractors will allow the hydrogen to be dispersed evenly.

For large leaks (D.5mm), Test 18 has higher concentrations in sensors S3VF and S4VF compared to Test 19. On the other hand, for medium leaks, sensors S3VF and S4VF present slightly the same concentrations.

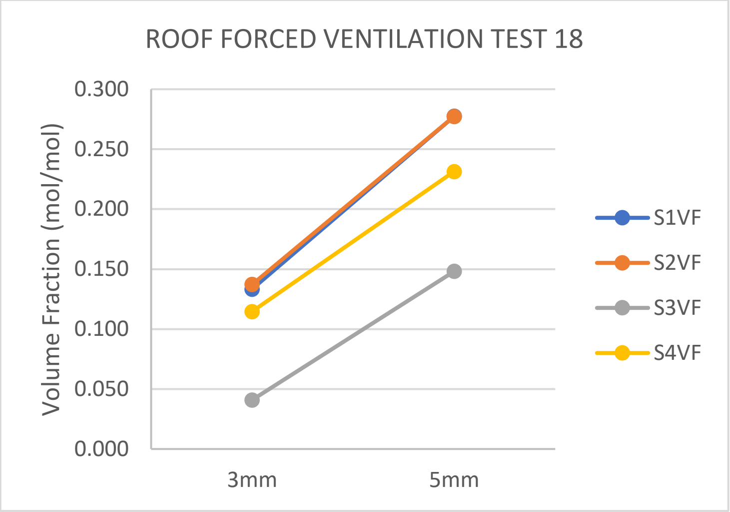


Figure 54. Volume Fraction Test 18. D: 1,3 y 5mm.

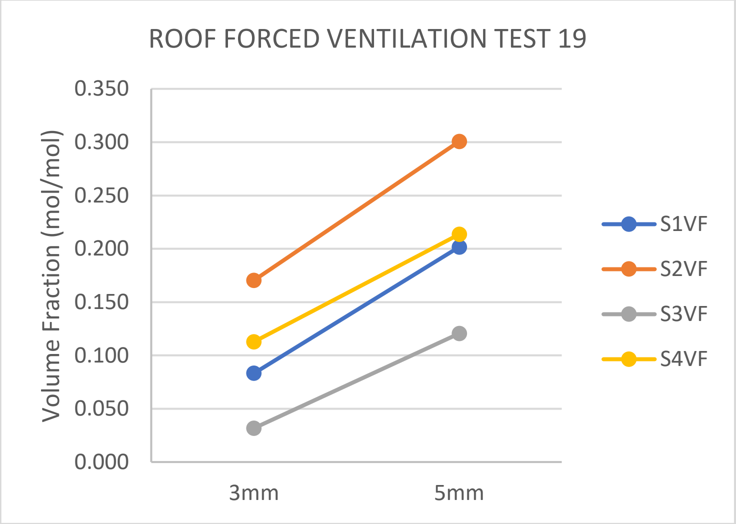


Figure 55. Volume Fraction Test 19. D: 1,3 y 5mm.

On first thought, it is difficult to know which Test is better in each case. Some sensors improve their concentration level depending on the Test and the leak diameter. For this reason, *tables 28, 29, 30 and 31* show the improvement of the sensors for each Test for D.3mm and D.5mm.

Table 28. Improvement of hydrogen concentration in Test 3 when is include roof forced ventilation. D.3 and 5mm. Lecture of S2VF.

Ventilation Test	**D_H**	**Max. Fuel concentration (v/v %)**	**Improvement (%)**
Test 3	3	30	N/A
Test 18	3	13	57
Test 19	3	17	44
Test 3	5	44	N/A
Test 18	5	27	39
Test 19	5	30	32

Table 29. Improvement of hydrogen concentration in Test 3 when is include roof forced ventilation. D.3 and 5mm. Lecture of S1VF.

Ventilation Test	D_H	Max. Fuel concentration (v/v %)	Improvement (%)
Test 3	3	17	N/A
Test 18	3	13	24
Test 19	3	8.3	52
Test 3	5	29	N/A
Test 18	5	27	7
Test 19	5	21	28

Table 30. Improvement of hydrogen concentration in Test 3 when is include roof forced ventilation. D.3 and 5mm. Lecture of S3VF.

Ventilation Test	D_H	Max. Fuel concentration (v/v %)	Improvement (%)
Test 3	3	15	N/A
Test 18	3	4.1	73
Test 19	3	3.2	79
Test 3	5	23	N/A
Test 18	5	14.8	36
Test 19	5	12.1	48

Table 31. Improvement of hydrogen concentration in Test 3 when is include roof forced ventilation. D.3 and 5mm. Lecture of S4VF.

Ventilation Test	D_H	Max. Fuel concentration (v/v %)	Improvement (%)
Test 3	3	18	N/A
Test 18	3	11.5	36
Test 19	3	11.3	37
Test 3	5	26	N/A
Test 18	5	23.1	11
Test 19	5	21.4	18

Test 18 with D.3mm has a lower concentration of hydrogen in sensor 2, while sensors 1, 3 and 4 have a lower concentration in test 19. For D.5mm of leakage the result is the same. Test 18 provides a more equal distribution of concentration in production area for medium-sized leaks against large leaks.

As a result, small leaks (1mm) in forced ventilation tests is not a good solution. On the other hand, in medium (3mm) and large (5mm) leaks, a greater number of extractors with different extraction flow rates will have lower concentrations in the compartment.

9 Discussion

9.1 Hydrogen refuelling systems and safety guidelines

The use of hydrogen in vehicles has developed the growth of hydrogen refuelling stations in recent years and most of these stations are included in traditional service stations.

In this project, an example of an energy station was presented based on found manuals (**HyApproval, HyResponse and E4tch), InterReg Project** and current stations. Hydrogen is produced in the station and is supplied to vehicles in a gaseous state as most stations operate in Europe. Based on preliminary studies [17] it was decided that hydrogen will not be transported due to the disadvantage it presents in terms of energy in liquid state and in terms of volume in gaseous state. Studies about on-site hydrogen production [15], [16] show that reforming (Gas-mix, Biogas-mix or LNG) produces higher greenhouse gas emissions than electrolysis when electrolysis is produced by renewable energy like solar panels. The electrolysis process considered is alkaline because it achieves higher efficiencies than PEM and the circulating liquid electrolyte (KOH) has a freezing temperature lower than -40ºC, allowing start-up under sub-freezing conditions which requires less maintenance compared to PEM [14], [17].

Another important aspect is the space available at the station to incorporate all hydrogen equipment. The dimensions of the storage will vary depending on the number of vehicles that supply daily. The dimensions will also be affected by the fact of being located in large spaces, rural areas or in urban areas. Greater safety distances should be taken into account and this could affect the decision to produce hydrogen at the station or transport it.

Currently, there is no standard on safe distances between hydrogen systems and other fuels located in the station. This is due to the lack of consensus between countries to adopt a complete standard. Most guides or best practices are compiled in ***ISO / TS 19880-1: 2016*** as described in *3.6.1. Guides* such as the **SW** (Swedish distances) have greater safety distances compared to **NFPA** (US) and **BGPA** (UK).

Previous studies [43] show the guidelines used in hydrogen refuelling stations and compare the risk control measures of each one with respect to technical barriers, human barriers, preventive barriers, protective barriers and safety distances. Among these guides, we can highlight the international standard (ISO), European applications such as **HyApproval WP2** and **EIGA IGC Doc 15/06**, American applications such as **NFPA 55** and **SAE J 2600** and national applications such as **UK Cop E**.

It is concluded that the minimum safety distances are based on risk assessments of hydrogen leakage sizes and their probability of leakage. In addition, some guides use different leak rates [44]. When it comes to deciding which type of guide to follow, the most appropriate would be to carry out a risk assessment study in hydrogen leakage with probability of explosion as presented in the following documents [46], [47], [48].

9.2 Discussion of methods

9.2.1 Risk assessment methods

Risk assessment methods help to detect undesirable events in all equipment and operations. Preliminary studies on qualitative and quantitative risk assessment in hydrogen refuelling stations were based on combinations of PHA, HAZOP, FMEA or FTA.

- [27] performs a risk assessment in the electrolysis process using HAZOP, followed by FMEA. It analyzes faults in safety valves, vent line leaks and failures in pressure relief valves.
- [28] determines the frequency of occurrence of accidental scenarios by means of FMEA in both the compressor and storage, selects two deviating variables (hydrogen flow rate and storage pressure) and analyzes them in a HAZOP by detecting two tops events (hydrogen leakage and

overpressure of the storage). Finally, it performs an FTA describing the case of overpressure in storage during the filling phase. It concludes that the worst scenarios are due to a failure of the pressure relief valves both in storage (PRD) and in the compressor (PRD1).

- FTA is used in [63] to evaluate possible events of hydrogen leakage in storage.
- [48] evaluates the risk of locating a station in urban areas using the HAZOP methodology by means of failure frequencies in accidental scenarios in storage and dispensers. From these failures, it studies the frequency and probability of death due to overpressures and structural failure in each scenario when jet fire occurs due to a hydrogen leak.

In most of the studies, the frequency of occurrence was evaluated by means of a failure database, while the consequence of occurrence was analyzed by means of equations in terms of impact of body (from overpressure and heat flux) and impact of structure. Knowing this information allows us to initially study the higher frequencies and consequences through FMEA and analyze them in the HAZOP methodology as authors [28], [47], [48] develop.

During the realization of the project there was not a quantitative study of fault frequencies, so it was decided to develop a very detailed PHA, followed by a HAZOP and an FMEA. Other methodologies such as SWIFT were discarded since it did not provide more information to the analysis. In addition, FMEA based the study of the level of risk (high, moderate, low) in a preliminary project of a station [7], [20].

In this project, on the one hand, the PHA included all the possible dangers and risks that may occur throughout the power station. The large amount of information on risk assessment [10], [34], [35] found at traditional service stations helped to develop which hazards may occur in pipes and in hydrogen dispensing area [11]. The rest of the risks in systems (electrolyser, compressor and storage) were documented in HIAD database on past accidents in hydrogen refueling station, in specialized manuals [50] and studies described in [1], [27], [28], [63]. On the other hand, with the help of HAZOP the focus was transferred to the hydrogen installation and deviations were developed in the hydrogen systems to detect its cause and consequence. Each deviation was evaluated based on two criteria: production of hydrogen leaks and risk of fire and / or explosion (such as an explosion due to overpressure or external fire) as it is claimed [28], [62]. Finally, their selection was studied in FMEA and failure modes were evaluated in safety valves, pressure relief valves, normal valve operations, and anomalies in hydrogen production systems with the criterion of hydrogen leakage and overpressure in equipment.

9.2.2 CFD modeling

In this thesis CFD was used as a tool to study the dispersion of hydrogen, analyse its accumulation and concentration in a closed space. This is in agreement with authors [67] who use the software to study hydrogen releases in large-scale facilities. In contrast, [69] use CFD to measure concentrations, to compare with the lower limit of flammability and estimate the overpressure in case of ignition followed by explosion of the hydrogen leak.

The method of analysis in CFD is comparable with experimental tests in the dispersion study when simulated at an intermediate scale with mesh resolutions of 0.1m as stated [67], [69]. The studies also explain that a finer mesh in large-scale enclosures requires a very high computational calculation. Due to the expected time to perform the simulations, a mesh resolution of 0.2m was used, confirming that a higher gas release rate implies a higher computational calculation.

9.3 Risk assessment in hydrogen refuelling at the energy station in relation to fire and/or explosion: accidental scenarios

The risk is defined by the consequences of a dangerous event and the probability that this danger will occur. When studying and evaluating the hazards related to fire and/or explosion at the power station it was important to distinguish between different scenarios that could arise. This project focused on describing all accidental events by means of the HAZOP methodology of *chapter 6.1.2* and the FMEA methodology of *chapter 6.1.3.* These scenarios were also the basis for risk assessments conducted by other sources. On the one hand, these scenarios were the dangers of hydrogen leakage with the possibility of explosion, and, on the other hand, overpressure and explosion in systems containing hydrogen.

A leak of hydrogen gas with the possibility of explosion is an event that can occur with greater probability in the compressor, in the storage or in the dispensing area. In these cases, it will occur because of the high pressure of the gas. The pressure relief valve will open to release that high pressure (PRD). It will also occur in the dispenser when there is a rupture of the hose. The gas will mix with the air in the enclosure and may ignite when its concentration level is at its lower flammability limit (4 v/v%) [50] and an ignition source is present.

High pressure and explosion in systems containing hydrogen (storage and dispenser) is a scenario that can occur when these tanks have been subjected to a strong heat stress (external fire) or when there is a failure in pressure relief valve (PRD). In this case, an explosion will occur and emit dangerous overpressures. Other studies [56], [70] qualify this scenario as unlikely, because the tank is locally heated since it is fireproof and the fire extinguishing devices act to extinguish the fire. This means that its probability is very small, since several events should happen before the tank breaks. Thus, the most serious case that can occur is the PRD opening accidentally, releasing the stored hydrogen content in a matter of seconds.

Previous studies analyse releases of hydrogen leaks in the electrolyser, in the connection pipes and in the dispenser, but greater potential damages will occur in case of leakage of hydrogen in storage. The storage is at pressures of 70MPa, in a closed area and close to the production of hydrogen. Further consequences will occur when the release happens at high pressure. This was determined by performing the theoretical calculations in *chapter 8.2*. The calculations show that higher pressures will cause higher flow volumetric flow rates, shorter tank emptying time and higher concentrations. High hydrogen concentration in closed area will produce explosion if hydrogen is ignited. Large overpressures will occur when the concentration exceeds 10% [56], [57] and will affect the equipment, the structure and people close to the station.

In general, the accumulation with possible explosion in case of hydrogen leakage will be influenced by a series of factors:

- The discharge speed will depend on the pressure of the tank and the diameter of the PRD.
- The amount of gas released will depend on the tank and how much is left inside it.
- The concentration of hydrogen gas at the compartment will be higher when the leakage rate is higher.
- Higher concentrations will be more likely to ignite and explode.
- The concentration will be higher when the size of the enclosure is smaller.
- The ventilation settings will affect the concentrations (natural or mechanical).

9.4 CFD simulation results

The scenario analysed in CFD was the leakage of hydrogen in a closed space such as the production area. A factor that is not considered in the analysis is the gas explosion, it is simply considered that it will be dangerous if it exceeds the lower flammability limit of hydrogen (4 v/v%) and the lower explosive limit (18.3 v/v%).

This scenario allows to investigate the concentration of gas inside the compartment by means of different leakage ratios. It is important to note that a station will be safe if the hydrogen concentration does not exceed 50% of the LFL (2 v/v%) [37]. The results of the simulations of each test proposed in this thesis show that reaching such low concentrations in large rooms with high leakage ratios is not possible with natural ventilation alone.

In this project, three hydrogen leakage ratios were studied. Obtained based on small leaks in the joints of facilities with an equivalent diameter of 1mm and based on the diameter of valves for relief of pressure characteristic in tanks such as 3mm and 5mm. It may be borne in mind that there is a considerable discrepancy between the leakage ratios used in this project compared to other projects. On the one hand, it can be caused by the fact that the pressure in the storage in previous studies is less than 70MPa. On the other hand, leaks are analysed in the dispensers based on the diameter of the hose [71] or they analyse small leaks based on the pressure in the electrolyser [72], [73].

Different ventilation configurations were presented in the production area to study the concentration level for the three 1mm, 3mm and 5mm leak diameters with a volumetric flow rate of 0.204 m^3/s, 1.82 m^3/s and 5.12 m^3/s. Unventilated simulations showed that hydrogen accumulates in the ceiling of the enclosure area because it is lighter than air and has a strong buoyancy effect, as well as increasing the density and pressure in the compartment.

On the one hand, the previous paragraph is confirmed in [67] as presented in *chapter 8.4*; having different configurations natural ventilation affects the dispersion and concentration of hydrogen gas in the compartment. On the other hand, the claim of [72], [73] is confirmed; natural ventilation will not be enough in medium and large leaks so it must be complemented with forced ventilation.

The results showed in the natural ventilation study described in *chapter 8.4.2* show that for small leaks (D.1mm) the tests have similar concentrations around 5 v/v%. For medium-sized leaks (D.3mm), distributing a larger number of openings in walls with the same total area and at different heights improves the concentrations slightly, while placing openings in the ceiling is more efficient and reduces the concentration level. In contrast, for large leaks (D.5mm) it is more efficient to distribute openings in walls compared to placing them in the roof.

The results in the forced ventilation study showed that for small leaks (D.1mm) there are no improvement in concentration compared to natural ventilation. On the other hand, for medium (D.3mm) and large (D.5mm) leaks, distributing a larger number of extractors with different extraction flow rates will lead to lower concentrations in the compartment.

Although the purpose was to reduce the level of concentration below the LFL in the compartment, this solution could not be obtained with the time predicted in this thesis. Each simulated test had better purpose than the previous one as presented in *chapter 8.3.1*, but it came to a state where new simulations in forced ventilation did not introduce improvements.

9.5 Implementation of the results at the energy station

The risk assessment models have allowed to analyse hazards and accidental situations in hydrogen refuelling systems and operations. The result is accidental scenarios regarding hydrogen leakage with possible explosion. The complete preliminary study will help future projects to study in more detail the failures in hydrogen operations that produce serious leaks. These models confirm that leaks must be controlled through adequate safety systems. If it is not controlled, there will be consequences such as gas explosion and overpressure in the room. The study of this event is essential since the potential damage could be seriously affecting the equipment, the structure and the people.
The guides found during the project serve as a basis to unify all the existing information about hydrogen refuelling stations. The guide ***ISO / TS 19880-1: 2016*** is recommended as it shows some existing guides on minimum safety distances. However, it would be more realistic to carry out a risk assessment study of the station together with CFD to study the safety distances in case of a jet fire or explosion for different leakage rates.

The simulation tests show hydrogen leakage concentrations in the compartment of hydrogen production unit. These tests showed that for a small leakage rate, the concentration of 10 v/v% is exceeded when the hydrogen gas is stored at high pressures. Concentrations of this percentage will cause high overpressures if ignition and explosion occur.

The natural ventilation systems in walls show that for small leaks the concentrations in unit production area will not reach LFL. This is possible thanks to openings that work by introducing an amount of air equivalent or higher than hydrogen leakage rate. Introducing openings in the roof improves concentrations for medium leaks but this opening does not reduce concentrations for large leaks. This result shows why most of the current hydrogen stations are designed without a roof. For large leaks, having a roof is a problem because hydrogen gas will quickly accumulate inside the enclosure.

Natural ventilation systems are insufficient for medium and large leaks. Forced ventilation is a solution to reduce concentration levels. The gas will be dispersed in the enclosure in more equal concentrations when there is a greater number of extractors distributed in the roof and with less volumetric flow of extraction. It should be noted that the forced ventilation study carried out did not reach values of concentrations close to LFL, but it will be the basis for future projects. This project will help in new research to study the utility of forced ventilation by extraction with high leakage rates. It will also have to be studied if this equipment could act as sources of ignition.

In general, the project develops a wide information about the risks when working with hydrogen in an energy station. The problems of accumulation of hydrogen in closed spaces were analysed for a real case, however, the explosion in the compartment will be the starting point in future investigations.

9.6 Suggestions for future work

The literature lists several areas where more knowledge is needed. An important area is the evaluation of risk models. The models used for risk analysis are important to be validated so that they describe more real accidental scenarios. Another area where more study is needed is the validation of safety distances at the energy stations. The distances between the equipment of the energy station could be validated in CFD modelling when accidental leak and explosion scenarios occur.

Another remarkable work would be the study of the probabilities of accidental scenarios. This would be possible with information from previous accidents compiled in the database or by contacting specialists in the area. So that it can be determined if the risk of having hydrogen recharge in urban areas is acceptable.

The CFD study was conducted based on concentration levels in a closed area. New modelling would allow to have a vision of the behaviour of the gas in case of ignition and explosion. In addition, they would allow to analyse situations where hydrogen leakage produces steam clouds, fire blast or explosion fire.

The simulations have evaluated the leakage of hydrogen in the compartment where the hydrogen storage is located. These have helped to evaluate how the type of ventilation and how the location of different aperture configurations reduces gas concentrations in enclosed spaces. In contrast, the dispensing area would be an area of the station with a risk of leakage that should be investigated in future projects. The gas could be trapped in the roof of the dispensing area with difficulty in evacuation and serious consequences.

These would be some of the most important suggestions if the completion of this master thesis was the beginning of the development of a PhD. Other suggestions could be:

- Investigate why levels of hydrogen concentration have not been obtained in the production area below LFL.
- Analyse the concentrations when the forced ventilation system is by blow-in.
- Analyse whether hydrogen leak rates can occur in real situations.
- Analyse in case of ignition in closed areas the possible explosion and overpressure. Determine up to what levels the damages would affect the systems, the structure and the customers.
- What effects would it have if other fuels in the power station affected the hydrogen facilities (e.g. fire gas pool is produced near hydrogen dispensers).

10 Conclusion

In this literature study, the hazards and accidental situations related to fire and explosion at the energy station model have been examined. Risk analysis models (PHA, HAZOP and FMEA) describe the consequences of faults in the operations of hydrogen equipment at the station. The consequences are related to hydrogen leakage with possible explosion, where hydrogen leaks are due to the opening of the pressure relief valve when there is overpressure inside the storage tank.

This consequence was the basis for studying by means of CFD the concentration of hydrogen in a closed space such as the hydrogen production unit. In this space the leakage rate was considered based on valves diameter and on the pressure of 70MPa in the storage. Due to the high pressure of stored gas, small leaks in a closed area will cause high concentrations, higher than 10 v/v% and the gas will be dispersed in the area, accumulating under the ceiling creating hydrogen pockets. This effect will increase the probability of ignition and explosion occurring and high overpressures could occur.

To reduce the concentrations to a level lower than 4 v/v% both a natural and a mechanical ventilation system are needed. The tests performed with different ventilation configurations showed that for small leaks a natural ventilation system would be enough not to reach concentrations higher than the LFL. However, the same tests for medium and high leaks described the need for mechanical ventilation. In addition, these tests confirmed that good results for small and medium leaks are not good solutions for large leaks. It must be reminded that no solutions were reached below the LFL in the medium and large leak tests.

The risk analysis shows that more safety measures should be implemented in hydrogen facilities to reduce the risk of explosion when a leak occurs. This involves studying the safety distances, controlling the operation of the valves, having equipment resistant to high pressures, good ventilation system, leak detectors, studying fire protection and controlling of the sources of ignition. In conclusion, the hydrogen facilities will be as safe as the gasoline and diesel facilities if a complete risk analysis is studied and all the necessary safety measures are implemented.

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Appendices

A Preliminary hazard analysis (PHA) description

Element	Nº	Hazard	Hazardous event	Cause	Consequences	Risk-reducing measure
1. Transformer	**1.1**	Electrical heat energy	1.1.1 Resistance heating in electrical equipment	1. High resistance joints 2. Overloading 3. Bad cooling	1. Internal arcing 2. High temperature 3. Gas generation 4. Internal Pressure increase 5. Failure relief valves 6. Tank rupture 7. Flammable gases in atmosphere 8. Ignition 9. Fire	• Prevention measure of tank rupture and uncontrol release of oil and arcing gases. • Indoor installation avoiding oil and arcing gases encountering oxygen.
			1.1.2 Induction heating	High currents in conductors		
			1.1.3 Dielectric materials heating	Properties deteriorates		
			1.1.4 Heating from arcing	Dielectric material stress		
			1.1.5 Heating from lighting strikes	Overvoltage		
2. Hydrogen Production Unit	**2.1**	Electrical circuit	2.1.1 High voltage exposed	Transformer voltage failure	Stop electrolysis Employee injury	
	2.2	Interruption electrolysis	2.2.1 Impurity water supply	Filter water failure	Electrolysis damage Release toxic gases Maintenance: Human skin irritation	• Maintain and replace water filters
	2.3	Interruption hydrogen flow	2.3.1 Hydrogen Leakage	1. Overpressure in Electrolyser 2. Open pressure relief valve	1. Leakage 2. Flammable gas in atmosphere 3. Ignition source	• Control the concentrations inside the electrolyser. • Enough ventilation and unconfined area. • Prevent release of hydrogen with sensors and emergency shutdown.

				Connections and seals	4. Ignition 5. Explosion	
				Low maintenance		
			2.3.2 Heating	High concentration levels of oxygen	1. Flammable gas 2. Auto-ignition	
				External fire	1. Overpressure 2. Close pressure relief valve 3. Explosion	
3. Compressor	**3.1**	Interruption hydrogen flow	3.1.1 Hydrogen leakage	Bad cooling generates overtemperature	1. Overpressure 2. Leak or possible rupture	• Check that the cooling is constant. • Pressure and temperature controls. • Continuous maintenance. • Prevent release of hydrogen with sensors and emergency shutdown.
				Maintenance inadequate		
4. Pipe connections	**4.1**	Interruption hydrogen flow	4.1.1 Hydrogen leakage	Corrosive and mechanical damage Low maintenance in fittings, valves, pumps…	1. Leakage 2. Flammable gas in atmosphere 3. Ignition source 4. Ignition 5. Flash fire or jet fire	• Regularly maintain and test monitoring/leak detection systems. Install a leak prevention and detection systems and use non-corrodible or double skin pipework. • Visual examination of accessible parts, maintain and replace where is necessary.
5. Storage	**5.1**	Interruption hydrogen flow	5.1.1 Hydrogen leakage	1. Overpressure in tank 2. Open pressure relief valve	1. Leakage 2. Flammable gas in atmosphere 3. Ignition source 4. Ignition 5. Explosion	• Install a suitable leak prevention or detection system and regularly maintain it. Carry out regular visual inspections of the tanks and its fittings for signs of corrosion or damage.
				Connections and seals		
				Low maintenance		
			5.1.2 Heating	External fire	1. Overtemperature 2. Overpressure	• Protect tank with an insulating material, provide additional fire protection measures such as automatic fire detection equipment

					3. Close pressure relief valve 4. Explosion	and ensure that there is adequate separation between tanks and other features
			5.1.3 Car collision	Human error collision in the storage	1. Leakage	• Locate or re-locate tank away from normal site traffic route and provide physical protection such as bollards or fencing.
6. Dispenser	6.1	Interruption hydrogen flow	6.1.1 Hydrogen leakage	Dispenser damage (nozzle and hose) Inappropriate joint Failure in safety valves	1. Leakage 2. Flammable gas in atmosphere 3. Ignition source 4. Ignition 5. Flash fire	• The vehicles must have a clear route and enough lighting in the station. The dispenser a fixed barrier to protect it and prevent collisions. Supervision of the forecourt during dispensing. Stop fuelling operation when the valve safety or detection system detect leak. Use dispenser with volume or time limited cut-offs, limiting devices and shear valves.
			6.1.2 Heating	External fire		
			6.1.3 Car collision	Dispenser damage (nozzle and hose)	1. Leakage	

B Hazard and Operability (HAZOP) description

General Process

Nº	**Guide Word**	**Variable**	**Deviation**	**Causes**	**Consequences**	**H2 Leakage**	**Fire/Explosion Risks**	**Selected to FMEA study**
G.1	More	Voltage (Tension)	High voltage electrical circuit	Transformer voltage failure. Human error in maintenance.	Cables no support high voltage and high temperature. Cables degrade.	NO	YES, fire in cables.	NO
G.2	More	Static electricity	Accumulation of static electricity than expected	Bad earth grounding. Circulation of H2, O2 gas in the valves or possible turbulence inside pipes and equipment.	Overheating in cables. Jumping arcs in electronic systems. Short circuit. Production of electrostatic sparks.	NO	It is an Ignition Source.	NO

Hydrogen Production Process: Water Electrolysis								
Nº	**Guide Word**	**Variable**	**Deviation**	**Causes**	**Consequences**	**H2 Leakage**	**Fire/Explosion Risks**	**Selected to FMEA Study**
P.1.1	More	Level	More water level than expected in electrolyser	Safety water valve failure. Demineralizer failure (Saturated).	High accumulation of water in electrolyser. Sludge water minerals.	NO	NO	NO
P.1.2			More oxygen level than expected in electrolyser	Safety oxygen valve failure. Shut-off oxygen valve failure.	High oxygen level in electrolysis gas. Oxygen leak.	NO	YES	YES
P.1.3				Deteriorate of sealing in cell due to corrosion, fatigue or defect in joints.	High temperature in catalytic purifier	NO	YES	YES
P.1.4			More hydrogen level than expected in production	Pressure relief hydrogen valve failure. Shut-off hydrogen valve failure.	Hydrogen leak. Overpressure.	YES	YES	YES
P.2	Less	Purifier	Reduction of hydrogen purification in tank	Catalytic purifier h2 failure	Fouling. High oxygen concentration in hydrogen product Ingress air particles in compressor.	NO	YES	YES
P.3	More	Level of Moisture	High moisture in hydrogen dryer	Mechanical failure in dryer	High moisture in hydrogen production, corrosion or hydrogen embrittlement of downstream equipment.	NO	NO	NO
P.4	No	Cooling	Reduction of hydrogen cooling after compression	Aftercooler catalytic purifier failure	Leak of hydrogen into cooling system	YES	YES	YES

Hydrogen Production Process: Hydrogen compression								
Nº	**Guide Word**	**Variable**	**Deviation**	**Causes**	**Consequences**	**H2 Leakage**	**Fire/Explosion Risks**	**Selected to FMEA Study**
C.1.1	More	Flow	High quantity of hydrogen flow	Overpressure of H2 in compression suction line.	Heating by high-pressure.	YES	YES	YES
C.1.2				Compressor over-run. (Mechanical failure)	Filter overload, disorder. Compressor overload. Break of pipe.	YES	YES	YES
C.2	Less	Flow	Low quantity of hydrogen flow	Short inflow of H2. H2 leakage at pipe. Compressor reduce operation. Break or damage of pipe.	Rough H2 filling. Leakage of H2.	YES	YES	YES
C.3	None	Flow	No hydrogen flow	No inflow of H2. Malfunction in valves. Broken compressor.	Impossible to fill H2. Overload of compressor.	NO	NO	NO
C.4	Other	Flow	Other flow	Supply of gas other than H2.	Damage by filling of other gas.	NO	NO	NO
C.5.1	More	Pressure	High pressure of hydrogen	Failure of pressure relief compressor valve (PRD)	Overpressure and rupture pipe. Overpressure in compressor. Leak of hydrogen.	YES	YES	YES
C.5.2				Failure of pressure switch compressor valve (PS). Compressor continue working when the storage is full.	Overpressure and rupture pipe. Overpressure in storage. Leak of hydrogen.	YES	YES	YES

Hydrogen Production Process: Hydrogen filling of storage at high, medium, and low pressure.

Nº	**Guide Word**	**Variable**	**Deviation**	**Causes**	**Consequences**	**H2 Leakage**	**Fire/Explosion Risks**	**Selected to FMEA Study**
S.1.1	None	Hydrogen flow	No exist hydrogen flow	Compressor Failure.	Pressure vessel filling interruption.	NO	NO	NO
S.1.2				Isolation valve (Iv) in compression line closed.	Compression line pressure increase.	NO	NO	NO
S.2.1	More		High quantity of hydrogen flow	Pressure switch (PS) compressor valve failure when the pressure is higher than the storage set point.	Overpressure in storage. Leakage of hydrogen.	YES	YES	YES
S.2.2				Compressor gas high flow and (PR) pressure regulator fails	Pressure increase and possible storage vessel overpressure.	YES	YES	YES
S.3.1	Less		Low quantity of hydrogen flow	PS compressor valve failure at pressure lower than the storage set point.	No complete vessel filling	NO	NO	NO
S.3.2				PR pressure regulator fails.	Delay in storage vessel filling	NO	NO	NO
S.3.3				Hydrogen leak at pipe.	Loss the hydrogen	YES	YES	YES
S4.1	More	Storage pressure	High pressure of hydrogen	PS compressor valve failure at pressure higher than the storage set point.	Overpressure in storage.	YES	YES	YES
S.4.2				Compressor gas high flow and PR pressure regulator fails.	Pressure increase and possible storage vessel over pressurization.	YES	YES	YES
S.4.3				Failure of pressure relief tank valve (PRD)	Overpressure in storage. Leak of hydrogen.	YES	YES	YES
S.5.1	Less		Low pressure of hydrogen	PS compressor valve failure at pressure lower than the storage set point.	No complete vessel filling	NO	NO	NO
S.5.2				PR pressure regulator fails.	Delay in storage vessel filling	NO	NO	NO

Hydrogen Production Process: Hydrogen Dispensing.

Nº	Guide Word	Variable	Deviation	Causes	Consequences	H2 Leakage	Fire/Explosion Risks	Selected to FMEA Study
D.1	More	Hydrogen flow	High quantity of hydrogen flow	Safety dispenser valve failure (PRD) when at pressure higher than the nozzle set point.	Overpressure in dispenser. Leak of hydrogen.	YES	YES	YES
D.2.1	Less		Low quantity of hydrogen flow	Safety dispenser valve failure (PRD) when at pressure lower than the nozzle set point.	No complete dispensing.	NO	NO	NO
D.2.2				Leak of hydrogen in hose or pipeline Brake or damage of pipe.	Loss of hydrogen	YES	YES	YES
D.3	None			No inflow of H2. Break or damage of pipe. Malfunction in valves.	Impossible to fill H2	NO	NO	NO
D.4.1	More	Dispenser pressure	High pressure of hydrogen	Safety dispenser valve failure (PRD) when at pressure higher than the nozzle set point. Shut-off dispenser valve failure.	Overpressure in dispenser. Leak of hydrogen.	YES	YES	YES
D.4.2				Depressurize dispenser valve failure.	Overpressure in dispenser	YES	YES	YES
D.5	Less		Low pressure of hydrogen	Safety dispenser valve failure (PRD) when at pressure lower than the nozzle set point.	No complete dispensing.	NO	NO	NO

C Failure modes and effects analysis (FMEA) description

Nº	**Process**	**Study Section**	**Hazard**	**Failure Mode**	**Cause**	**Effects in the system**	**F**	**C**	**Risk**
1	**Electrolysis**	**Water Electrolysis Hydrogen Generation**							
1.1			Potential Fire and/or explosion	Cell seal/demister failure	Corrosion, fatigue, defect or loosening of threaded joints	1. High oxygen level in electrolysis gas 2. High temperature in catalytic purifier 3. Auto-ignition 4. Potential internal fire or explosion	L	H	Moderate
1.2				Purification H2: Catalytic purifier failure	Fouling	1. High oxygen concentration in product hydrogen 2. Ingress air in the compressor 3. Potential explosion in compressor	L	H	Moderate
1.3				Oxygen leak	- Vent line oxygen safety valve failure - Shut-off oxygen valve failure	1. Higher concentration of oxygen 2.Potential fire hazard	L	L	Low
1.4			Hydrogen Leakage	Hydrogen gas leak	- Pressure relief valve is closed when should be opened - Shut-off valve failure	1. Overpressure in Electrolyser 2. Explosion	M	H	High
					- Pressure relief valve is opened to liberate pressure	1. Leakage 2. Flammable gas in the area 3. Ignition source presented 4. Ignition 5. Explosion	M	H	High
1.5				Cooling system failure	Catalytic purifier aftercooler failure	1. Leak of hydrogen into cooling system 2. Flammable gas in the area 3. Ignition source presented 4. Ignition 5. Potential fire or explosion in surge tank	L	M	Moderate

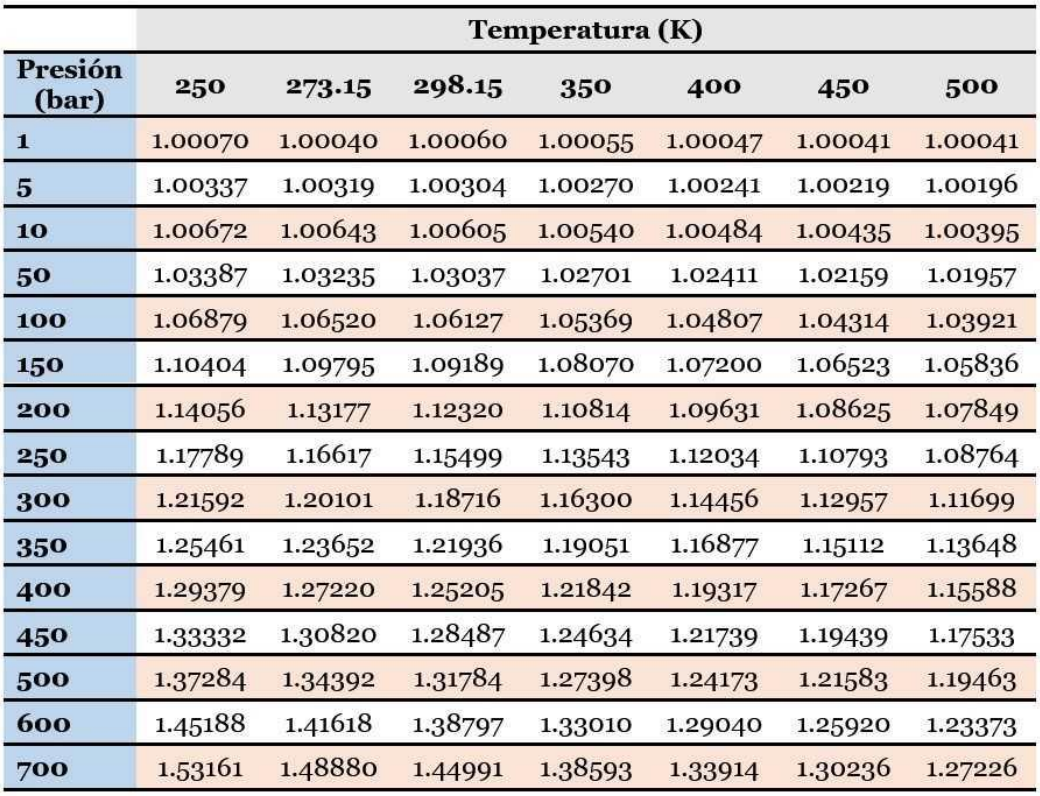
№	Process	Study Section	Hazard	Failure Mode	Cause	Effects in the system	F	C	Risk
2	**Electrolysis**	**Hydrogen compression**							
2.1			Hydrogen Leakage	Compression suction line failure (pipe damage)	Mechanical failure of pipe, line or fitting	Release of hydrogen and potential fire and explosion	L	H	Moderate
2.2				Lubrication system failure	Loss of fluid	1. Compressor failure 2. Hydrogen leak 3. Potential fire or explosion	L	H	Moderate
2.3				Seal failure	Mechanical failure	1. Release hydrogen 2.potential fire or explosion	L	H	Moderate
2.4				Pressure relief valve in compressor failure (PRD)	- Pressure relief valve (PRD) is closed when should be opened	1.Overpressure compressor 2. Rupture line 3. Explosion	M	H	High
					- Pressure relief valve (PRD) is opened to liberate pressure	1. Leakage 2. Flammable gas in the area 3. Ignition source presented 4. Ignition 5. Explosion	M	H	High
2.5				Pressure switch valve in compressor failure (PS)	- Pressure switch valve (PS) is not in off state at pressure higher than the storage set point	1. Overpressure in storage 2. Rupture the pipe and leakage. 4. Ignition 5. Explosion	M	H	High

Nº	**Process**	**Study Section**	**Hazard**	**Failure Mode**	**Cause**	**Effects in the system**	**F**	**C**	**Risk**
3	**Electrolysis**	**3.1 Hydrogen storage**							
3.1			Hydrogen Leakage	Overpressure in tank	Fill storage tank on cold day Heat stored gas during day	1.Overpressure tank 2. Rupture tank 3. Potential fire or explosion	M	M	Low moderate
					Pressure relief tank valve failure (PRD) is closed when should be opened.		M	H	High
					External fire due to large spill of gasoline from delivery truck and Pressure relief tank valve failure (PRD) is closed		L	H	Moderate
					Pressure switch (PS) compressor valve switch off when the pressure is higher than the storage set point.		M	H	High
					Compressor gas high flow and (PR) pressure regulator fails		L	H	Moderate
3.2				Pressure relief tank valve failure (PRD)	Pressure relief valve (PRD) is opened to liberate pressure.	1. Leakage 2. Flammable gas in the area 3. Ignition source presented 4. Ignition 5. Explosion	M	H	High
3.3				Piping leak	Mechanical failure	1. Leakage 2. Flammable gas in the area 3. Ignition source presented 4. Ignition 5. Explosion	L	H	Moderate

№	**Process**	**Study Section**	**Hazard**	**Failure Mode**	**Cause**	**Effects in the system**	**F**	**C**	**Risk**
4	**Electrolysis**	**4.1 Hydrogen dispensing**							
4.1			Hydrogen Leakage	Piping failure	Vehicle impact to dispenser	Potential fire or explosion	L	H	Moderate
4.2				Safety valve dispenser failure	- Safety dispenser valve is closed when should be opened - Shut-off dispenser valve failure	1.Overpressure in dispenser 2. Possible hose rupture 3. Potential fire or explosion	M	H	High
					- Safety dispenser valve is opened to liberate pressure	1. Leakage 2. Flammable gas in the area 3. Ignition source presented 4. Ignition 5. Explosion	M	H	High
4.3				Vehicle pressure relief device	Mechanical failure		L	M	Moderate
4.4				Vehicle tank isolation valve leaks	Mechanical failure and leaking check valve		L	M	Moderate
4.5				Depressurize dispenser valve failure.	Depressurize dispenser valve is closed when the nozzle is used.	1.Overpressure in dispenser 2. Possible hose rupture 3. Potential fire or explosion	L	H	Moderate
4.6				Leak in connection and disconnection nozzle	Nozzle damaged	1. Leakage 2. Potential fire	M	L	High
4.7			Potential Fire and/or explosion	- Drive away while connected to dispenser - Collision in dispenser	Human error	1.Rupture hose 2. Leakage 3. Potential fire or explosion	L	M	Moderate

D Compressibility factor

The density has been calculated considering the ideal gas expression and applying the compressibility factor.



	Temperatura (K)						
Presión (bar)	**250**	**273.15**	**298.15**	**350**	**400**	**450**	**500**
1	1.00070	1.00040	1.00060	1.00055	1.00047	1.00041	1.00041
5	1.00337	1.00319	1.00304	1.00270	1.00241	1.00219	1.00196
10	1.00672	1.00643	1.00605	1.00540	1.00484	1.00435	1.00395
50	1.03387	1.03235	1.03037	1.02701	1.02411	1.02159	1.01957
100	1.06879	1.06520	1.06127	1.05369	1.04807	1.04314	1.03921
150	1.10404	1.09795	1.09189	1.08070	1.07200	1.06523	1.05836
200	1.14056	1.13177	1.12320	1.10814	1.09631	1.08625	1.07849
250	1.17789	1.16617	1.15499	1.13543	1.12034	1.10793	1.08764
300	1.21592	1.20101	1.18716	1.16300	1.14456	1.12957	1.11699
350	1.25461	1.23652	1.21936	1.19051	1.16877	1.15112	1.13648
400	1.29379	1.27220	1.25205	1.21842	1.19317	1.17267	1.15588
450	1.33332	1.30820	1.28487	1.24634	1.21739	1.19439	1.17533
500	1.37284	1.34392	1.31784	1.27398	1.24173	1.21583	1.19463
600	1.45188	1.41618	1.38797	1.33010	1.29040	1.25920	1.23373
700	1.53161	1.48880	1.44991	1.38593	1.33914	1.30236	1.27226

Figure 56. Compressibility factor. Temperature vs pressure [66].

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