Development of H_2 Safety Expert Groups and due diligence tools for public awareness and trust in hydrogen technologies and applications

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1. Executive summary

This document is a guide for the execution of Work Package 3 (WP3), *Data Gathering and Mirror Groups*, and Work Package 4 (WP4), *Preparedness Mapping, Assessment, Recommendations*, of the H_2Trust Project. It indicates and assures how to perform the research and analysis in a uniform manner as the teams will be working in parallel.

This framework will be the starting point of the Safety Assessment due diligence methodology, and also the key part of the set-up of the safety assessment task of WP4 as well as the tool development of Work Package 5 (WP5), *Dissemination*. The safety issues are addressed based on a common reference framework.

FCH stakeholder model and dimensions of analysis presented here have been defined based on standard industry practices, taking into account the full range of Fuel Cell Hydrogen (FCH) application areas and the life cycle stages of each area, applying both health and environmental safety criteria. FCH stakeholders and regulatory factors have been also considered in the model.

Summary of *“Hydrogen properties”*, “*Hydrogen risks*”, “*Safety issues*”, “*Types of storage for hydrogen*” and “*Hydrogen supply*” is provided in the ***Annex: General aspects of hydrogen.***

2. Data collection methods

In order to analyze the different information in future deliverables, the following different methods will be summarized on ***Table 1***, indicating their advantages and disadvantages:

1. Questionnaires, surveys, checklists.
2. Interviews.
3. Document review.
4. Observation.
5. Focus groups.
6. Case studies.

Figure 1. *Data collection methods*

In task 2.5 entitled *“Develop info gathering process and questionnaires”*, will be developed a uniform data gathering process comprised of questionnaires, interviews, analysis of publications and surveys. In that task will be included the information gathering process and the number of questionnaires required, posterior analysis, etc.

***Table 1.** Methods comparison*

Method	Purpose	Advantages	Disadvantages
Questionnaires, Surveys, Checklists	ₒ Collecting information from people without interaction.	ₒ Low resources required. ₒ Different sample forms (paper, verbal, online, etc.). ₒ Inexpensive administration. ₒ Anonymous participation. ₒ Quick collection of data. ₒ High amount of data collected. ₒ Standardized. ₒ Easy comparison.	ₒ No multi-optional answers. ₒ Impersonal. ₒ Low quality of data. ₒ Possible misleading. ₒ Not careful feedback. ₒ Possible superficial answer.
Interviews	ₒ Gathering qualitative information. ₒ Collecting specific information. ₒ Learning more about answers in questionnaires. ₒ Understanding non-verbal and verbal communication.	ₒ Full range and depth of information. ₒ Develop relationships with stakeholders. ₒ Flexible.	ₒ High resources required. ₒ Time consuming. ₒ Complexity of the data analysis. ₒ Results not generalize. ₒ Cannot be used for a large number of people.
Document review	ₒ Collecting and analyze data from written documents. ₒ Revising a variety of existing sources (publications, applications, finances, memos, minutes, etc.). ₒ Gathering information about the state of the art.	ₒ The information is available. ₒ Quick and inexpensive data collection. ₒ Comprehensive and historical information. ₒ Do not interrupt stakeholder’s routine.	ₒ High resources required. ₒ Time investment. ₒ Incomplete information. ₒ Not 100% reliable data (importance of checking the source of information). ₒ Information may have perspective not aligned with yours.

Method	Purpose	Advantages	Disadvantages
Observation	ₒ Gathering accurate information. ₒ Knowing how a process works. ₒ Knowing how strategy operates. ₒ Tracking the related information.	ₒ Direct method. ₒ Very accurate and reliable data. ₒ Possible adapting to events as they happen. ₒ Updated knowledge.	ₒ High resources required. ₒ Categorize observations is needed. ₒ Sometimes takes lot of time. ₒ Expensive. ₒ Interpret and not influence behaviors are required. ₒ Possible misunderstanding. ₒ Sampling cannot be brought into use. ₒ Past things cannot be studied.
Focus groups	ₒ Gathering qualitative information. ₒ Exploring a specific topic. ₒ Gathering information from members. ₒ Developing or improving knowledge. ₒ Gauging public perceptions.	ₒ High depth of information. ₒ Quick and reliable. ₒ Efficient. ₒ Generation of ideas and provide wealth of information. ₒ Non-verbal information. ₒ Interaction with participants.	ₒ High resources required. ₒ Schedule and organization of a group is needed. ₒ Difficult to analyze answers. ₒ Necessity of a good facilitator. ₒ Moderator's skills might influence in responses. ₒ Small groups cannot be representatives.
Case studies	ₒ Describing intensively and analyzing a single individual or group. ₒ Fully understanding stakeholder's experiences in strategy.	ₒ Collection of detailed data. ₒ Large sample of similar cases, especially non-standard case. ₒ Opportunity for innovation.	ₒ High resources required. ₒ Large amount of time is required (necessity of organizing and describing information). ₒ Insufficient information can lead to inappropriate results. ₒ Results might not be representatives.

The dimensions of analysis are described on section 5 of this deliverable, where the limits of the different topics of the Work Packages are indicated. The stakeholder dimensions include International Regulatory, Codes and Standards (RCS) organizations, ad hoc hydrogen safety programs and work groups. The methods above will be used to study the lifecycle of hydrogen and the normative that are going to follow are:

- **Fuel Cells and Hydrogen Joint Undertaking (FCH JU)**: Unique public private partnership supporting research, technological development and demonstration activities in FCH.
- **ISO TC 197**: Hydrogen Technologies.
- **IEC TC 105**: FCH Technologies.
- **EIHP2**: European project for the global regulation of vehicles propelled by hydrogen for drive transport.
- **UN WP29**: World forum of United Nations for the Harmonization of Vehicles Regulation.
- **NFPA**: National Fire Protection Association EEUU, storage, extract, pipeline conduction, use, detection and protection.
- **Pressure equipment directive (97/23/EC)**: provides a European legislative framework for equipment subject to pressure risks.
- **Transportable pressure equipment (99/36/EC)**: improvement of pressure equipment transport security.
- **ATEX (94/9/EC)**: protection and equipment systems for uses in potential explosive atmospheres.
- **ATEX (99/92/EC)**: minimum requirements for the improvement of health and safety protection of workers in explosive atmospheres.
- **SEVESO II (96/82/EC)**: prevention of big accidents involving dangerous substances.
- **MACHINERY (98/37/EC)**: essential health and safety requirements related to design and construction of machinery and safety components.

These normative and laws are also transposed in a national level.

3. Best practices for collecting and writing data

3.1 Collection of data

In order not to miss any relevant information, the following steps must be taken into account:

1. Check the availability of any data from the own organization or from partners that can be used. Moreover, it is also important to search if there is any public data available that can be used.
2. Identify the appropriate person, who knows about the information that you need, and try contact him.
3. Schedule your time dedicated to the data collection, having adequate time to answer data providers as well as to structure the information systematically, in order to minimize time, cost and effort required.
4. Verify all the information that you receive from different people, with the aim to use only the accurate data.
5. A survey has to be as short as possible in order to assure that people do it conscientiously. Afterwards, any document has to be examined to assure that all the information received is what is required to be used in the analysis (avoiding information without interest or repeated).
6. Indicate the date or time period where the survey was done.
7. A comparative study has to be carried out in a uniform manner, by using the same analysis method. If other methods are required in the analysis, they have to be correctly justified.
8. Use standard language, avoiding abbreviations or jargon, using simple and exact terms, replacing vague quantifying words with specific numerical ranges whenever is possible.
9. Join the information in different categories which should be as concise as possible.
10. Include the literature consulted at the end of the document.

3.2 Writing data

To report information, especially when the document is a compilation of different documents provided by different authors, it is important that all team members work in a uniform manner, following the same steps in order to have a good structured and coherent document. In this sense it is important to consider the following:

1. Before writing about a topic, it is important to know and understand the relevant laws, regulations and administrative procedures that can affect to the information collected related to this topic.
2. Develop procedures to ensure that data used is accurate and consistent.
3. Ensure that the information provided in the survey is the information that was requested; if it is not, understand how and why was answered that.
4. Be on time in every survey, as not to do so, contact the other teams to let them know how late the survey is going to be and when it will be send.
5. If the data recollect is not enough to write a survey, identify the most appropriate and knowledgeable respondents and contact them, allowing, if it were necessary, enough time for the follow-up.
6. If actual data is not available but you have in possession data from a prior period which can provide a reasonable and estimate information, provide this data indicating the change.

4. H_2TRUST Framework

According with the H_2TRUST proposal, ***Figure 2*** shows the general framework of the project, where the WP leaders are included.

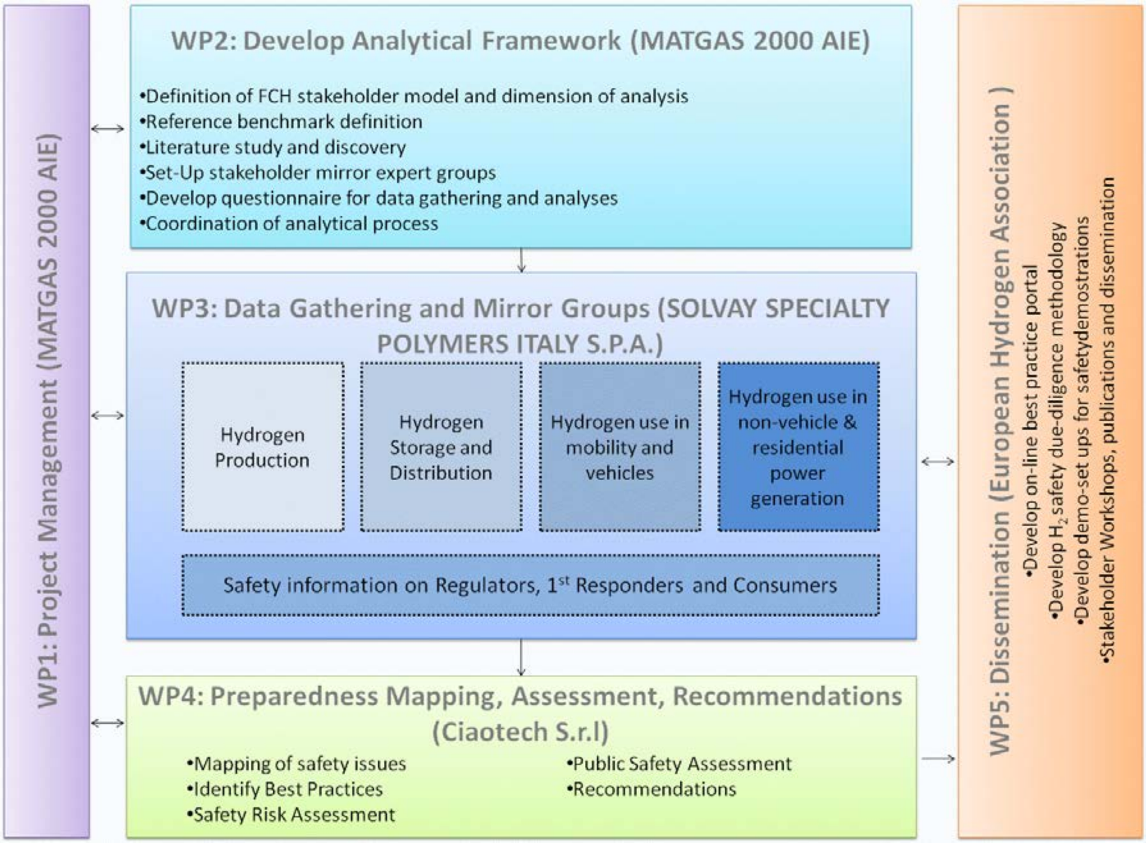

Figure 2. *H_2TRUST WPs.*

More specifically, frameworks of WP3 and WP4 are summarized in ***Figure 3*** and ***Figure 4*** respectively. In the corresponding schemes, the different development areas of each team, making emphasis at the points specified on it, are indicated.

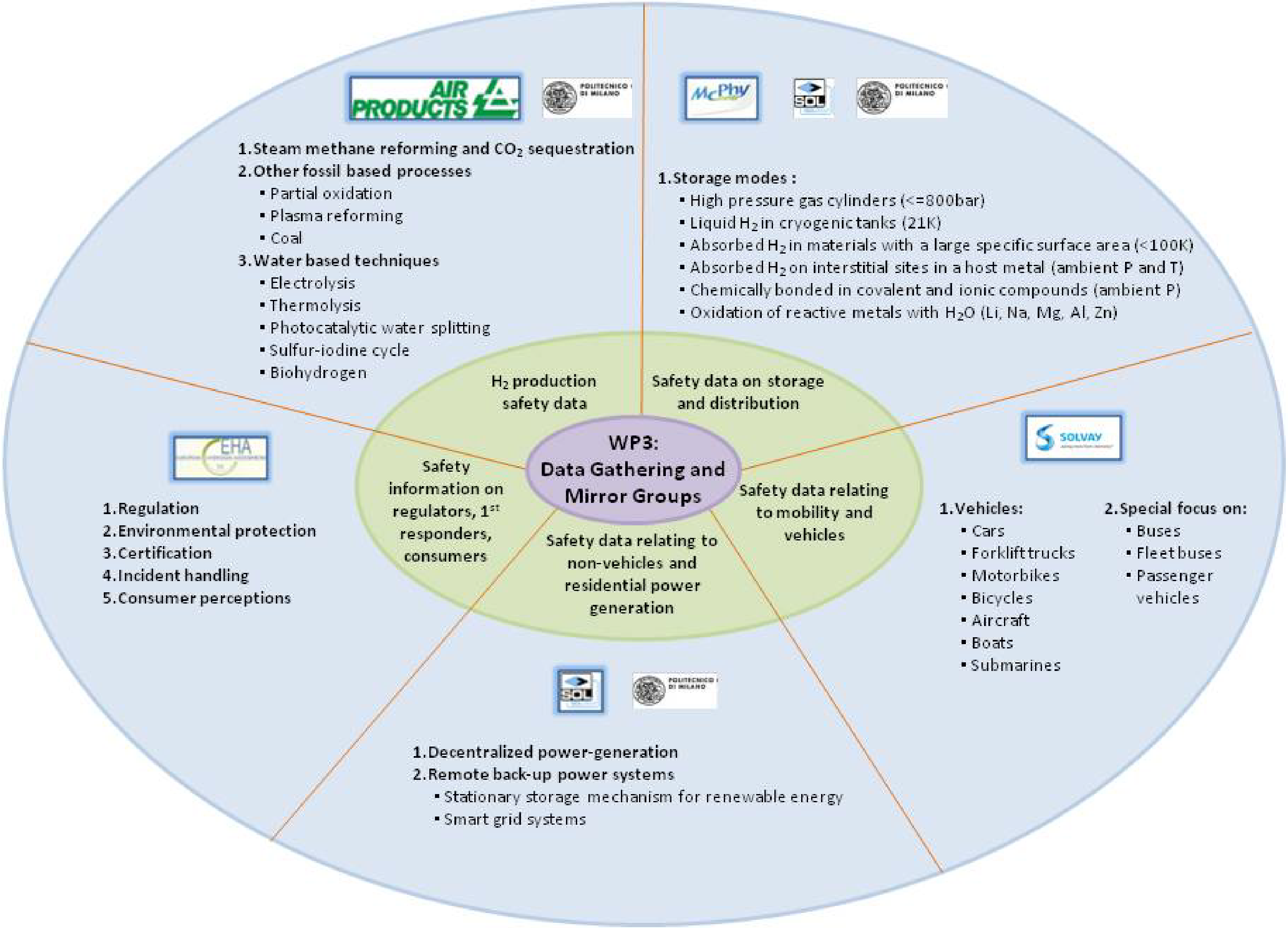

Figure 3. *WP3's framework*

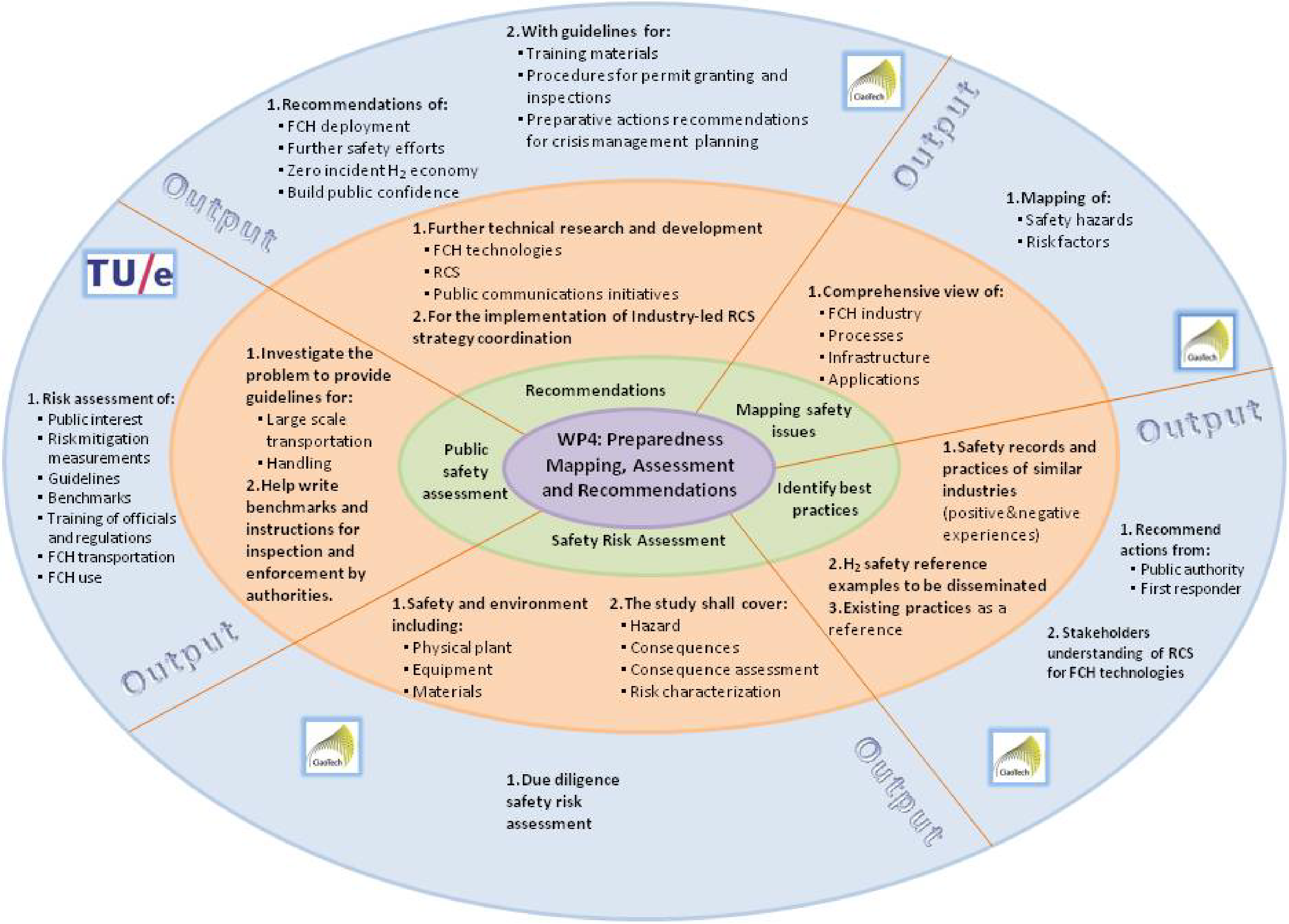

Figure 4. *WP4's framework*

5. Dimensions of analysis

The dimensions of analysis for the H_2TRUST have been developed based on the idea that they will be used to create a multi-dimensional matrix, and that each unique space in the matrix shall be examined to determine whether or not it arises a safety question to address.

The project aim is to systematically map safety issues and assess how they are addressed.

The dimensions of analysis are:

- FCH value chains and components
- FCH safety matters
- Vehicles and instruments for progress in safety
- FCH market introduction timing

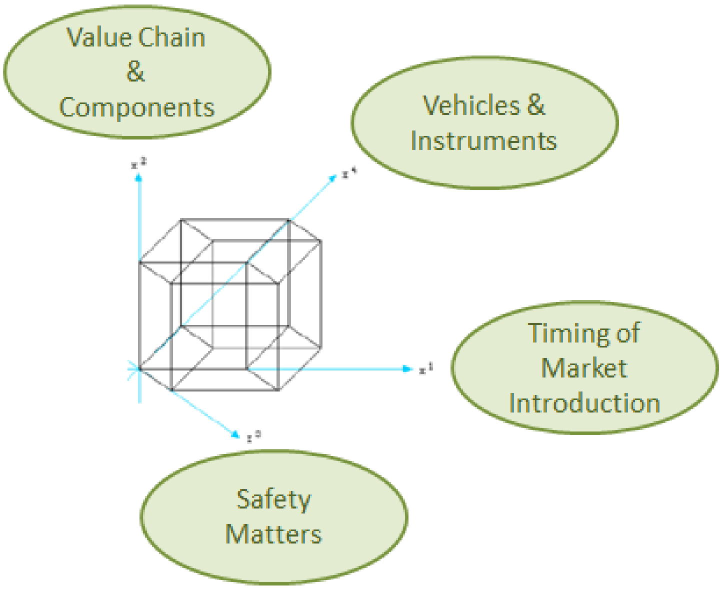

Figure 5. *Dimensions of analysis*

5.1 FCH value chains and components

In the cycle from production of hydrogen (whether from water electrolysis and renewable energy sources such as solar, wind, hydro or from surplus energy of traditional power generation plants or by steam reforming of natural gas) to the phases of storage, distribution, refueling and consumption in fuel cells, there are a number of components, technologies and processes involved. It is proposed that Task 2.2 entitled "*Definition of a reference benchmark*" creates the overall schema of reference values for WP3, the teams performing each of the tasks (covering tasks showed in ***Figure 6***) shall perform a joint work package initiation activity to validate, sketch and describe the key value chains, components and technologies involved.

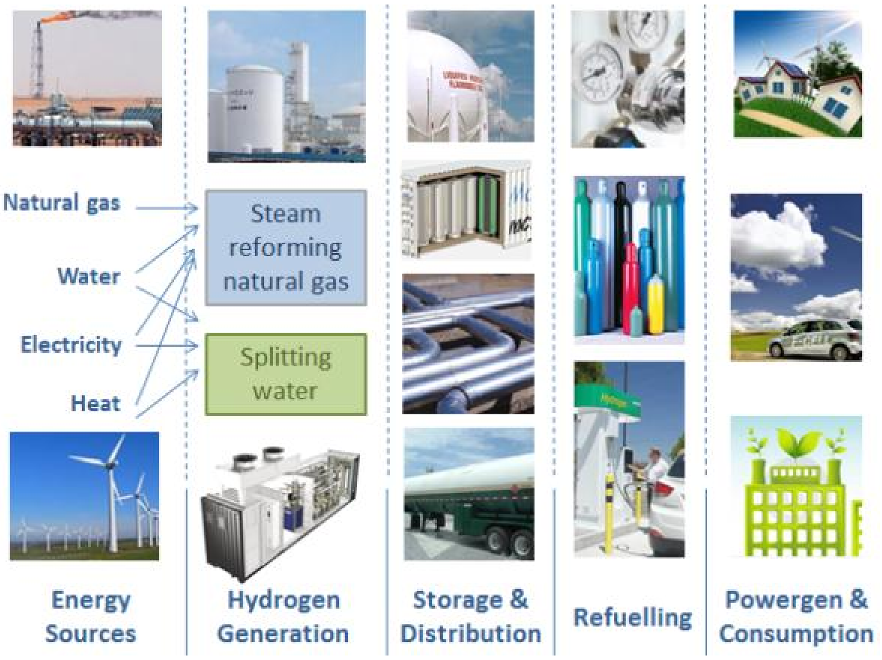

Figure 6. *WP3's tasks*

This activity will be coordinated by the lead beneficiary, and will be treated as a joint first step of the individual tasks.

The values chains which emerge will represent a more detailed version of the diagram shown across, where the components and technologies in each vertical silo are listed. Refueling of refueling stations shall be treated as "Storage and Distribution" while refueling of vehicles and of individual fuel cells from on-board or adjacent hydrogen stores or tanks shall be treated belonging to the end user application domain, i.e. mobility, vehicles, and on-site power generation. So for instance, the part covering storage and distribution shall encompass metal hydrides based storage, liquid, compressed (various regimes), in-pipe and in bulk carrier vehicle.

5.2 FCH safety matters

This dimension refers to those factors which actually have the potential to pose a safety risk and which need to be considered as potential causes of incidents when examining each of the components, technologies and processes in the FCH values chains. It is proposed that the teams performing WP3 shall work with a checklist of safety matters and Endeavour to determine which safety matters are relevant for each component or technology elements of the values chains and whether or not such matters have been already resolved, for instance, due to being a continuation of existing and proven industrial practices.

When compared to other gases and liquids, including methane for home heating or petrol for passenger vehicles, hydrogen is not an especially dangerous substance. However, it presents certain characteristics which, due to its rarity in pure form and the need to pressurize it for efficient transport and storage, give rise to the need for unique safety awareness and new precautionary measures. The key safety matters are indicated on ***Table 2*** [see ***Annex: General aspects of hydrogen*** to this document for hydrogen properties].

These safety matters shall be validated and characterized in full detail by the teams of WP3 as part of the WP initiation. In the event that team members uncover new safety matters in the core of their research later in the task, the WP leader shall evaluate need for rework across the teams to account for the new safety matter.

The most significant safety differences between hydrogen and other fuels such as natural gas or gasoline are the ease of ignition and the leakiness, both of which will require more stringent safety measures than today's fuels. Hydrogen has lower ignition energy than natural gas, where any small spark produced by static energy or tool sparks will be sufficient to ignite it. It also exhibits higher permeation rates. Additionally, the higher operating pressures of hydrogen increases the potential hazard of leaking by increasing the permeation or leakage rates. The combination of both factors requires development and reinforcement of the safety standards and regulations for avoidance of accumulation of hydrogen on closed areas.

In order to avoid accumulation of hydrogen, standards and regulations must define stringent ventilation requirements, i.e. forced ventilation (compared to the natural ventilation of existing fuels), detection and positioning of ventilation outlets to avoid high points where hydrogen can accumulate; more reducing the fuels storage around any hydrogen storage and utilization area.

Table 2. *Safety matters*

Safety matters	Main implication
Ignition when mixed with O_2	Highly flammable and explosive, though effect mitigated by tendency to rise and disperse quickly. Reducing impact on surroundings and hence considered less hazardous than petrol or methane.
Propensity to leak and flow	Building design to allow dispersion.
Ability to embrittle certain materials	During certain high temp processes such as plating and welding. Need to identify FCH applications where such conditions may arise. Can be reversed.
Invisible flame	Alerts to be introduced (e.g. through artificially coloring or other warning measures).
Very cold in liquid form (20 K)	Cold burns. Novel storage container materials required.
Highly pressurized (691 atm)	Adapt and apply techniques for pressurized systems for other gases.
Asphyxiant	Special venting needs. Can be artificially colored/flavored.
Colorless/odorless nature	Alerts to be introduced (e.g. artificial coloring/flavoring).
Association with other materials, equipment, and processes introduced into the value chain as a result of FCH market introduction	Use of potentially toxic materials, containers under pressure, extremes of temperature, new processes requiring training and awareness.

Another point to reinforce is the manufacturing and maintenance standards and regulations, defining requirements for gas tightness like leak test, welding procedures, frequency of checking and maximum time life of different elements. It is accepted that areas requiring attention are harmonization of safety distances for H_2 storage systems, H_2 refueling in non-vehicle context, installation and use of H_2 and fuel cells systems for stationary power generation in buildings, installation and use of alternative storage systems and handling/storage/use of liquid hydrogen.

Importantly, pure hydrogen is not poisonous or toxic, it disperses quickly into the atmosphere and does not leave harmful residues. H_2TRUST will examine not just H_2 the element, but also the ancillary materials, technologies and processes required as enablers for FCH applications such as the platinum alloys employed as catalysts, the new materials required for cryogenic containment or the impact of high volume transport and storage.

5.3 Vehicles and instruments for progress in safety

This dimension refers to the ecosystem of standards organizations regulatory agencies, industry and engineering bodies, policy making institutions and the standards, regulations, practices and requirements they develop and maintain.

In the course of research in WP3 the teams shall characterize, on identifying a potential safety matter, it according to which vehicles or instruments are most likely to be relevant for the resolution of such a safety matter. In this way, the H_2TRUST team shall be in a position, from an early stage, to determine which safety organizations or policy bodies can be approached subsequently for the assessment of the safety risk and the identification of pathways for resolution. Task 2.4 entitled "*Mirror Groups*", shall develop the list of vehicles and instruments in the course of its work in identifying and researching relevant stakeholders for the mirroring process.

5.4 FCH market introduction timing

In the assessment of the level of impact, urgency, effort and feasibility associated with the resolution of any given safety matter it will be valuable for the team to be aware of the timing and scale of market introduction of the components and technologies under examination and hence to be able to advise stakeholders on "when" dimension.

For each technology or component identified therefore, the team shall develop a high level view on the phases of market introduction in the period to 2030 of that element.

According to the UK H_2 Mobility project (with partner FCH-JU) in its Synopsis of Phase 1 Results (April 2013), it is described as an example how to develop a timing view in the case of fuel cell electric vehicle (FCEV). As it can be seen in ***Figure 7***, FCH technology take-up is foreseen to start making inroads 8-10 years from now and will reach significant penetration around 2030 when approximately 300 thousand (or about 15% compared to current levels) new vehicles will be FC powered and cost of ownership will have leveled with fossil energy economy.

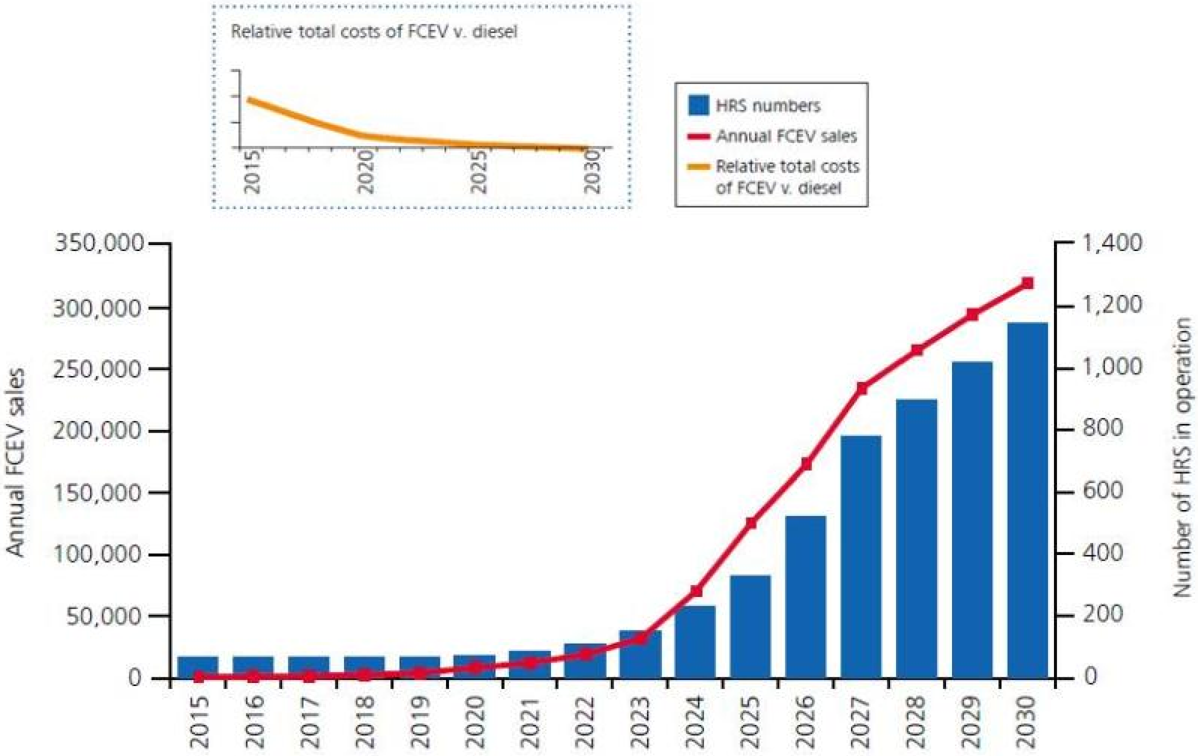

Figure 7. *FCH Technology [from UK H_2 Mobility Phase 1 Results, April 2013, p.14]*

For the purposes of the H_2TRUST project a number of different Stakeholder Populations (SP), indicated in ***Figure 8*** and ***Table 3***, can been defined based broadly on the timing relative to the forecast for FCH take-up. The total EU figures are estimated in a very general way by assuming that one in four EU/FCH vehicles are registered in the UK.

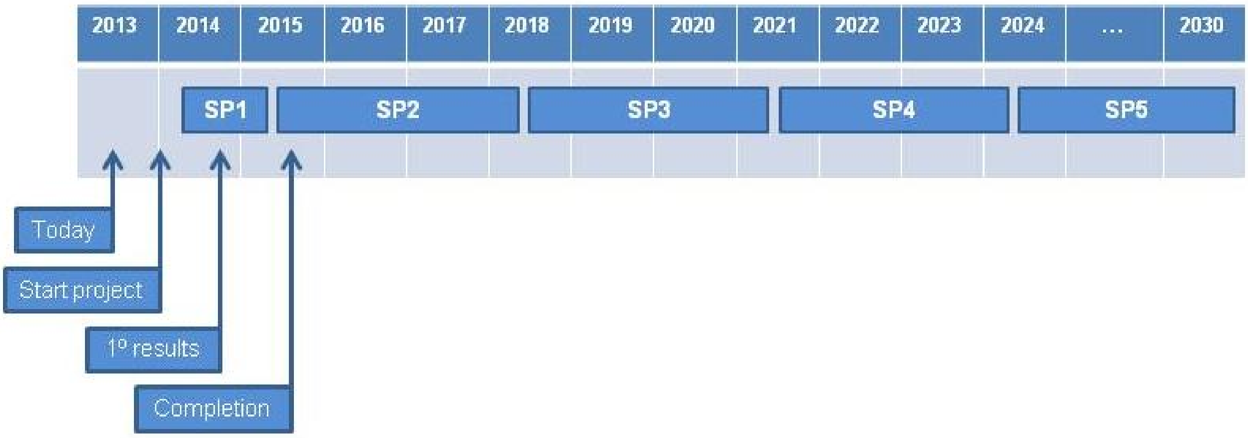

Figure 8. *Stakeholder populations*

Table 3. *Stakeholder populations*

SP	Definition
SP1	o Current set of developers, planners, educators, opinion leaders and those that are present in the lifetime of this project.
SP2	o FCH population as it develops in the three years following completion of this project. o Expected to grow up but not change in composition or requirements. o The key aim is to prepare for early adopter entry into the market.
SP3	o Comprised of the original SP2 ecosystem plus the 1st generation of early consumers, FCH technology operators and service personnel. o 30 to 60 thousand FCH vehicles in operation in Europe by the end of this period (assuming one in four vehicles is registered in the UK). o One for every 5000 vehicles present in the EU (i.e. about the same as the total number of Ferraris currently in circulation). o Enough to keep busy the equivalent of 15 dedicated refueling stations. o User/operator population might be in the order of 100 thousand people throughout Europe.
SP4	o Growing to treble in size compared to SP3 as the number of vehicles in circulation grows to well over 400 thousand and the number of refueling stations exceeds 800. o FCH car sales will grow to over 200 thousand units per year (or 1%-2% of total 2012 volumes). o Greatly overtake the likes of the current Toyota Prius which delivers just 20 thousand units per year in Europe (2012) and has a total of 200 thousand in circulation. o Critical period in the FCH commercialization process as it will see FCH vehicles and technology going mainstream.
SP5	o 6 year period from 2024 to 2030 FCH unit sales are forecast to reach 10%-20% of total vehicle sales (at 2012 levels).

Similar projections can be estimated for the other main technologies and applications in the FCH value chains, potentially grouping all timing forecasts into one unified model which matches phase (i.e. development phase, pre-commercialization, early adopter market development, early mainstream and mainstream):

- With volume (of users, of cells of hydrogen, etc. to be defined by each team of the WP3 tasks).
- With time frames (i.e. 2014-2017; 2017-2021, 2021-2030).

In this manner, the H_2TRUST team will have the knowledge enabling it to determine when new safety initiatives should be initiated and potentially ascribe phased introduction schemes for the initiatives.

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7. Annex: General aspects of hydrogen

This section covers the basics aspects related to hydrogen, with the aim to have an overview with the main topics that should be considered to carry out the work included in WP3 and WP4. Concretely, will be introduced the hydrogen properties, the risks, the safety issues, and the different types of hydrogen storage and supply.

7.1 Hydrogen properties

The phase diagram of hydrogen is shown in ***Figure 9*** , where is indicated:

- **The Triple Point:** where solid, liquid and gaseous phase coexist.
- **The Boiling Point:** where hydrogen passes from liquid to gaseous phase or viceversa.
- **The Critical Point:** where no phase boundaries exist.

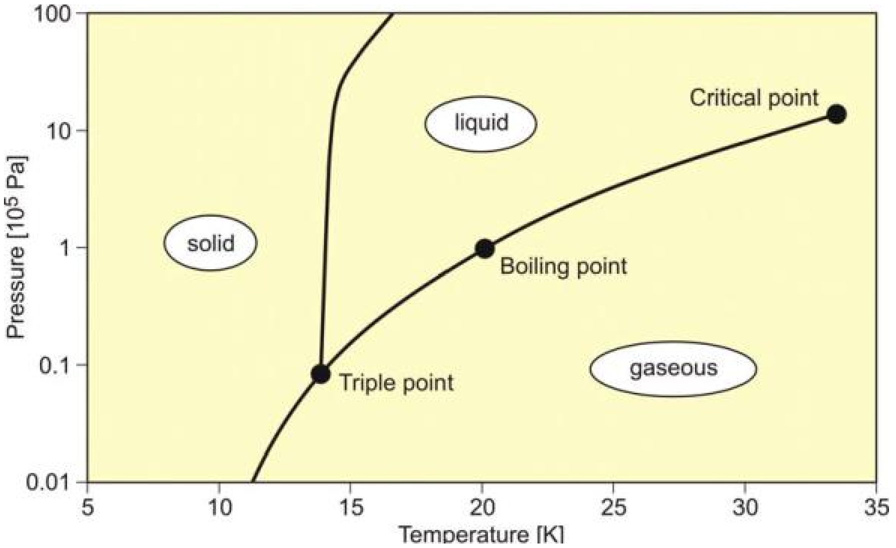

Figure 9. *Phase diagram of hydrogen [from Fundamentals of Hydrogen Safety Engineering I, Vladimir Molkov]*

7.1.1 Hydrogen gas properties

Hydrogen gas is a universal carrier, which can be produced as secondary energy from a wide variety of primary energy sources. For example, considering the energy chain from production to end-use of hydrogen when it is used in fuel cells to power transport and stationary applications, it can provide significant benefits in terms of greenhouse gas emissions and local pollutants, increasing the efficiency and having a lower rate of emission per end-use energy unit.

Density and size:

Hydrogen is the most abundant element in the universe and the lightest one. The most common hydrogen is the Protium (H), with only one atom of hydrogen. The isotope with two atoms of hydrogen is the Deuterium (H_2), which is the most stable. The free ionic hydrogen is more reactive than the molecular one. One of the most important characteristic is its low density. Over a wide temperature range and high pressures it is considered an ideal gas.

Color, odor, taste and toxicity

At standard temperature and pressure conditions (1 atm and 273 K), the hydrogen is colorless, odorless, tasteless, non-toxic, non-corrosive, and non-metallic diatomic gas. For this reason, is difficult to detect a leak with human sense of smell, according with the following range of concentrations:

- 0.13 ppm: minimal perceptible odor.
- 0.77 ppm: faint but perceptible odor.
- 4.6 ppm: moderate odor easily detectable.
- 27 ppm: strong unpleasant odor, but not intolerable.

It is important to note that odor should not be used as a warning since the gas may also induce loss of sense of smell. For solving the issues presented above, industry uses hydrogen sensors to detect the leaks, having in this way a maintained high safety record. Actually, researchers are investigating others methods that might be used for hydrogen detection like tracers sensors.

Floatability and diffusion

Hydrogen gas has high diffusivity and high buoyant velocity, the latest is proportional to the diffusion coefficient and changes with temperature. The positive buoyancy is a favorable safety effect in unconfined areas, but on the other side, it causes a hazardous situation in confined areas where the hydrogen can be accumulated.

Its small size, small molecular weight and low viscosity might cause a problem to the propensity of the gas, leaking at a molecular flow rate higher than other gases.

Parameters

Table 4 shows the values for the different hydrogen parameters that should be considered in a technical standpoint.

Table 4. *Hydrogen parameters*

Parameter	Hydrogen value
Molecular weight (g/mol)	2.01594
Stoichiometric fraction in air (vol%)	29.53
Boiling point - BP- (K)	20.268
Melting point -MP- (K)	14.01
Triple point:	
Temperature (K)	13.8
Pressure (MPa)	7.2
Critical point:	
Temperature (K)	33.25
Pressure (MPa)	1.297
Density (kg/m^3)	31.4
Electro negativity (Pauling scale)	2.20
Density:	
Gas at 273K and 101325Pa (kg/m^3)	0.08990
Liquid at BP (kg/m^3)	70.78
Solid at 4K (kg/m^3)	88.0
Specific heat at constant pressure:	
Gas at 273K and 101325Pa [kJ/(kg·K)]	14.304
Liquid at BP (kg/m^3)	9.66
Thermal conductivity:	
Gas at 293K and 101325Pa (W/m·K)	0.187
Liquid at BP (W/m·K)	0.09892
Viscosity:	
Gas at 293K and 101325Pa (µPoise)	89.48
Liquid at BP (µPoise)	132.0
Inversion temperature (K)	193
Flammability limits in the air (vol%):	
Upward propagation of flame	4.0-75.0
Downward propagation	5.3-75.0

Parameter	Hydrogen value
Detonability limits in the air (vol%):	
Weak ignition	18.3-59.0
High-energy igniter	11.6-74.9
Minimum ignition energy (J)	$1.9 \cdot 10^{-5}$
Minimum ignition energy for detonation (J)	Aprox. 10 000
Auto-ignition temperature in air (K)	793-1 023
Expansion ratio liquid/ambient	845
Diffusion coefficient at 293K and 101325Pa (m^2/s)	$0.61 \cdot 10^{-4}$
Diffusion velocity at 293K and 101325Pa (m/s)	<0.02
Buoyant velocity (m/s)	1.2-9
Surface tension at BP (N/m)	$1.93 \cdot 10^{-3}$
Heat of conversion from para to ortho (kJ/kg)	708.8
Heat of melting-fusion at MP (kJ/kg)	58.8
Heat of vaporization at BP (kJ/kg)	445.6
Vaporization index ($K \cdot cm^3/J$)	8.9
Heat of sublimation (kJ/kg)	379.6
Speed of sound (m/s):	
Gas at 293K and 101325Pa	1 294
Liquid at BP	1 093
Hot air jet ignition temperature (K)	943
Flame temperature (K)	2 318
Laminar burning velocity in air (m/s)	2.65 -3.25
Flame speed (m/s)	18.6
Deflagration pressure ratio	8.15
Quenching distance at 293K and 101325Pa (mm)	0.64
Adiabatic flame temperature (K)	2 318
Detonation velocity (m/s)	1 480 - 2 150
Detonation cell size	15
Critical tube diameter (m)	0.2
Critical explosion diameter (m)	0.16
TNT equivalent (g TNT/g)	26.5

7.1.2 Hydrogen liquid properties

Hydrogen becomes liquid below -115 K at atmospheric pressure and, as any cryogenic liquid, it can cause severe freeze burns if the liquid contact the skin. To keep hydrogen ultra-cold, liquid hydrogen containers are double-walled, vacuum-jacketed, appropriately insulated and designed to vent hydrogen safely in gaseous form if a breach of either the outer or inner wall is detected. The robust construction and redundant safety features dramatically reduce the probability for human contact.

Evaporation temperature

The liquid hydrogen evaporates at 20 K, causing two types of vapor clouds:

- Exposed surfaces at liquid hydrogen temperature can condense moisture in the surrounding air.
- A discharge of liquid hydrogen can produce a vapor cloud that is both a fire and visibility hazard.
- Both of them create a fog that reduces visibility, but is harmless.

Thermal dilation

The liquid hydrogen has an expansion coefficient 23 times higher than water, making the hydrogen to expand more than water when heat is applied. This has to be considered in the storage tanks, providing space for this expansion. In case this is not considered hydrogen can produce overpressure and the liquid entrance in the distribution and ventilation ducts.

Volume gas equivalent

Since hydrogen has a very low density, it is often transported in cylinders or by trailers at high pressures (up to 204 atm). However, it is important to note that compressed gases have to be released in a controlled manner. On the contrary, they can cause equipment damage, serious injury or death.

When hydrogen gas is dissolved in liquid at elevated temperatures and pressures (called cold hydrogen) has the advantage that it is less volatile if it is compared with ambient gas, being cleaner, having a more economic storage and its consumption is one third part of its combustion heat. However, it attacks mild steels severely causing decarburization and embrittlement.

Specific heat

The specific heat for the liquid hydrogen at constant pressure is 9.688 kJ/(kg·K), which is twice higher than water and five times higher than oxygen, as it can be seen in ***Table 5.***

Table 5. *Specific heat comparison*

Liquid hydrogen [kJ/(kg·K)]	Water [kJ/(kg·K)]	Oxygen [kJ/(kg·K)]
9.688	4.844	1.938

Condensation

Liquid hydrogen has low temperatures and, with atmospheric moisture, it produces internal condensation which may block the valves and air vent with accumulations of ice. That is why isolated pipes that transport hydrogen may trigger the liquation of the external air outside the pipe.

7.1.3 Combustion properties

Inflammability bounds

Hydrogen has a positive Thompson-Joule effect at temperatures above 193 K, where the inversion temperature takes place. The temperature of hydrogen gas increases upon depressurization, which may lead to ignition.

Hydrogen reacts with both metals and non-metals forming either ionic or covalent hydrides. It is able to chemically react with most other elements producing different results. For example, when hydrogen reacts with oxygen it turns highly flammable, so the potential risk of an explosion for hydrogen and air is very high.

Ignition energy

The auto-ignition temperature of hydrogen is 858 K, which can be decrease using catalytic surfaces. Above some critical breakdown voltage, hydrogen becomes an electrical conductor. However, it is an insulator, in normal conditions, for gaseous and liquid phase.

7.2 Hydrogen risks

Although these risks are already mentioned in section 5.2, corresponding the FCH safety matters, this section tries to provide the issues that have to be taken into account to focus the safety matters.

7.2.1 Combustion, fire and explosions

Like any flammable fuel, hydrogen can combust, but having its buoyancy, diffusivity and small molecular size as an advantage, make it difficult to contain and create a combustion situation.

Must be present at the same time the following aspects in order to have a hydrogen fire:

- Adequate concentration of hydrogen.
- Presence of an ignition source.
- Right amount of oxidizer (like oxygen).

Hydrogen has a wide flammability range (4-74% in air) and the energy required to ignite hydrogen can be very low (0.02 mJ). However, at low concentrations (below 10%) the energy required to ignite it is higher, being similar to the energy required to ignite natural gas and gasoline in their respective flammability ranges and, therefore, making hydrogen more difficult to ignite near the lower flammability limit.

An explosion cannot occur in a tank or any contained location that contains only hydrogen due to an oxidizer, such as oxygen, must be present in a concentration of at least 10% pure oxygen (or 41% air). Hydrogen can be explosive at concentrations of 18.3-59% and although the range is wide, it is important to remember that gasoline can present a more dangerous potential risk of explosion than hydrogen, since the explosion can happens at much lower concentrations (1.1-3.3%). Furthermore, there is very little probability that hydrogen will explode in open air, due to its tendency to rise quickly. This is the opposite that happen for heavier gases like propane or gasoline, which near the ground, have higher danger for explosion.

Once the ignition takes places, the standard fire-fighting response is to prevent the fire from spreading, protect surrounding equipment and let the fire burn until the hydrogen is consumed or its flow is stopped. As long as it can be done safely, the most effective way to extinguish it is to stop the flow of gas.

There are two types of combustion risks: deflagration and detonation. The detonation always carries a shock wave in the combustion process, it is propagated at a speed higher than the sound (normally between 1 500 to 2 000 m/s) and it produces high pressures. The deflagration is a flame that propagates through a fuel at a rate lower than the speed of sound. If it is produce in a tank or a pipeline, the increment of the pressure may accelerate the flame trigging into an explosion.

Gaseous detonation is a more energetic process which needs richer mixtures of hydrogen and oxidant (almost stoichometric) and more energetic ignition sources. When a detonation happens outdoors, an explosive charge is need to produce a detonation of the mix between hydrogen and air; otherwise, when a detonation happens in closed environments it is need much less energy to produce the ignition.

Detonation with liquid hydrogen, take place when this liquid is mixed with a solid oxidant, which can produce a detonation similar to a high power explosive. In this case, the ignition energy should be equivalent to the needs on a large explosive charge.

Precautions to be considered:

- Purge equipment with an inert gas before introducing hydrogen. If the air in a system is not eliminated, a flammable mixture may form.
- Provided natural or mechanical ventilation where hydrogen is used. If a hydrogen leak happens, the risk of forming flammable mixtures will reduce.
- Install the exit outside of pressure-relief devices in a safe area (i.e. from ignition sources and personnel).
- When hydrogen gas may be released or accumulate indoors, use flammable-gas detectors.
- When performing maintenance on a hydrogen system, use a portable gas detector.
- Eliminate sources of ignition from areas where hydrogen is processed, stored or used (e.g. sparks, open flames, smoking and extremely hot objects).
- Exercise caution when using or installing electrical equipment near hydrogen systems. Electrical equipment must have the classification for the NFPA 70 National Electrical Code.
- Site hydrogen systems in accordance with national codes and local regulations at appropriate distances from exposures and other hazardous materials (e.g. the NFPA 2 Hydrogen Technologies Code is one of the standard that provides direction on the proper installation of hydrogen systems).

7.2.2 Pressure release

Hydrogen in a gas phase can be compressed at very high pressures, which means the storage of a considerably potential energy. The decompression of the gas in a uncontrolled manner can produce a shock wave due to the transition from liquid to gas represents a significant increment of volume, and even more if the gas is heated to room temperature.

Precautions to be considered:

- Using pressure relief devices.
- Tanks storage must be placed at security distance from the personnel.

7.2.3 Low temperature effects

Many materials suffer a contraction, as well as ductility and specific heat loss when they reach liquid hydrogen temperatures. Moreover, the tanks and component materials can have a significant decrease of its structural solidity once they are exposed to hydrogen. That phenomenon is called *'embrittlement'* and is produced by the diffusion of the hydrogen in the material structure (see ***Figure 10)***. It can produce catastrophic damages in the tanks and, therefore, threatening the human safety.

Figure 10. *Hydrogen embrittlement [Pure Energy Systems Wiki]*

Precautions to be considered:

- It is essential that all the structural materials keep their properties at those temperatures, including security limits.

7.2.4 Hydrogen effects on human health

Hydrogen, like any other gas or combustible, is extremely toxic and irritating gas which can cause instant death.

Depending on the concentration, hydrogen can causes different effects:

- 10 ppm: eye irritation.
- 50-100 ppm: conjunctivitis respiratory irritation.
- 100 ppm: coughing, eye irritation, loss of smell sense in 2-15 minutes.
- 500-700 ppm: loss of consciousness and death in 30-60 minutes.
- 700-1000 ppm: quickly unconsciousness and cessation of respiration followed by instantly death.
- Depending of repetitions can trigger different effects:

- Repeated exposure: headache, dizziness and digestive disturbances.
- Repeated exposure to low concentrations: conjunctivitis, photophobia, tearing, pain and blurred vision.
- Repeated exposure to high concentrations: rhinitis, bronchitis and pulmonary edema.
- Chronic poisoning results in headache, inflammation of the conjunctivae and eyelids, digestive disturbances, weight loss and debility.

Asphyxia

Hydrogen, as any gas except oxygen, can cause asphyxiation. In most scenarios where the space is confined, hydrogen turns even worst because of its buoyancy and diffusivity. Asphyxia starts reducing the oxygen carrying capacity of the blood, causing respiratory failure and finishing in asphyxiation.

However, since hydrogen is flammable at a concentration of 4% in air, it is a flammable before being asphyxiate. For this reason, taking proper measures to prevent flammability will also prevent the asphyxiation hazard.

Burns

Hydrogen can cause different types of burns:

- Cold Burns: actuates blocking the oxidative process of tissue cells, depressing the nervous system.
- Hot burns: causing coughing, pain in breathing, pain in nose and throat.
- UV burns: irritating to eyes and respiratory tract, conjunctivitis, pain, lacrimation and photophobia which may persist for several days.

7.3 Safety issues

First of all, it is important to note that hydrogen is as safe as other current hydrocarbon fuels. However, as well as the other fuels, has to be understood in order to forewarn any hazard.

- To prevent any possible risk, it is important to take into account the following steps:
- Recognize, understand and prioritize the hazards.
- Identify those scenarios that generate the higher risks.
- Demonstrate the existence of a plan to manage the risks.
- Show the plan follows a suitable hierarchy.

As an example, the UK has an Explosion Protection Document which can be used for:

- Identification of the fire and explosion hazards.
- Classification of those areas where explosive atmospheres may exist.
- Evaluation of the risks.
- Specification of the measures to prevent or, if it is not possible, mitigate the effects of an ignition.

In conclusion, the most important step is to understand the phenomena and know how to prevent them.

7.3.1 Comparison with other fuels

The limitation of fossil energy resources availability as well as the climate change threat, have led to the formulation of political goals focused on the reduction of greenhouse gas emissions and on searching new energy sources, entering into a transition phase towards a post-fossil energy area. Concretely, all these issues can be solved in an efficient and sustainable way by increasing the use of renewable energy sources, and by using hydrogen through fuel cells.

As stated before, all fuels must be handled properly to prevent any possible risk. Since hydrogen is colorless, odorless, tasteless, non-toxic and non-poisonous it would be interesting to add a sulfur-containing odorant in order to detect it by human senses (as industry usually does with natural gas and propane). However, hydrogen cannot use the odorants due to its low dispersion rate. As it can be seen on ***Figure 11***, hydrogen is 57 times lighter than gasoline vapor, having the safety advantage of rising and dispersing quickly if it is released in an open environment.

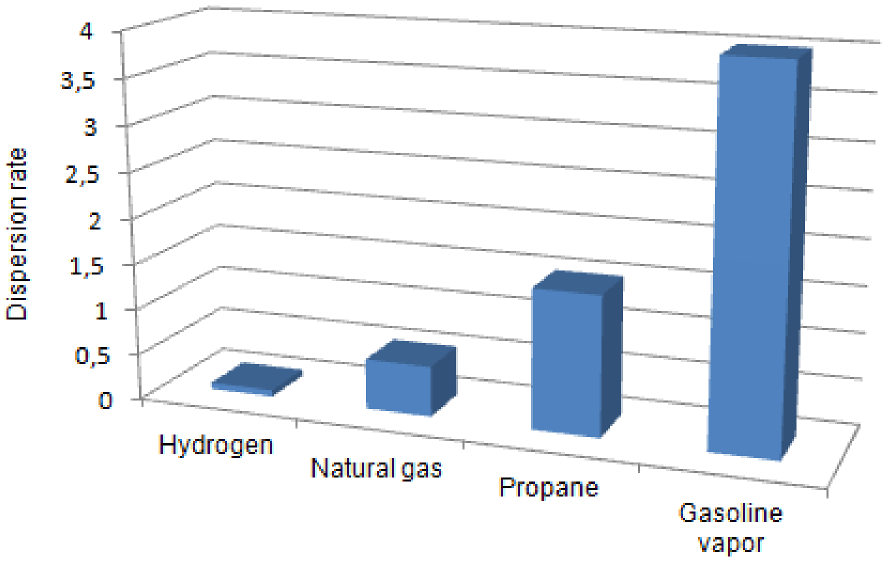

Figure 11. *Lighting fuel [from http://h2bestpractices.org, 03/07/2013]*

In ***Table 6*** is also shown a comparison between different fuels including the data related with the main hazards risks.

Table 6. *Fuel comparison*

	Hydrogen	**Gasoline vapor**	**Natural gas**
Flammability limits (in air) (%)	4-74	1.4-7.6	5.3-15
Explosion limits (in air) (%)	18.3-59.0	1.1-3.3	5.7-14
Ignition energy (mJ)	0.02	0.20	0.29
Flame temperature in air (K)	2 318	2 470	2 148
Stoichiometric mixture (most easily ignited in air) (%)	29	2	9

7.4 Types of storage for hydrogen

Depending on the requirements for the hydrogen application, the storage could be done by different ways:

- Gaseous with pressure tanks.
- Liquid in cryogenic tanks.
- Solid as gas adsorbed gas in porous systems.

7.4.1 Gaseous with pressure tank

The compressed hydrogen is stored in cylinders similar to those used for other gases (i.e. natural gas, nitrogen and oxygen).

The main advantages of this type of storage are that this is a useful method, due to its easy storage infrastructure and, the reduction of material and fabrication costs. However, the low volumetric density is a disadvantage due to the contain of hydrogen is lower.

7.4.2 Liquid in cryogenic tanks

This type of storage was developed by spatial industry, which has a big storage experience due to its special necessities. These tanks are thermally insulated at 20 K and at atmospheric pressure.

Liquid tanks require bigger energy than gas compression, requiring a 30% of H_2 energetic value. For this reason, it is necessary a special design taking into account the following requirements:

- o Insulation: reduction of conductivity, convectively and radiant heat flow.
- o Reduction heat transfer through:
  - Internal wall.
  - External wall.
  - Empty space or with insulating materials between both internal and external walls.
- o Spherical tank is the most commonly used to reduce the evaporation (taking into account that there is an inevitable evaporation: 2-3% per day for small tanks, and 0.2% per day for big tanks).

7.4.3 Solid as adsorbed gas in porous systems

Hydrogen can be storage in a solid state by using porous systems, where the gas is adsorbed. Depending of the type of adsorption, the storage would be physical or chemical.

On the one hand, the physical storage is carried out though the use of special composites, based on weak links between the gas and the elements of the composite (physical adsorption). The storage and extraction of hydrogen is controlled by heat released and absorbed respectively.

On the other hand, the chemical storage is based on chemical adsorption procedures, through the formation of alkaline or alkaline earth metals hydrides. However, has the disadvantage that the energy required for the hydrides production is even higher than the hydrogen supplied. For this reason, this method is not commonly used.

7.5 Hydrogen supply

The low density and the gaseous state make hydrogen distribution more difficult than other fuels having a higher cost for transport and suffering a significant energy loss of hydrogen. The best option for big customers is to avoid the transport stage, by building the production facilities at the point of consumption. For this reason, nowadays, the 80% of hydrogen production is for local use, and only a percentage below 20% is sold and distributed by other transports ways.

Transports can be classified as following:

- According to hydrogen state: compressed gas, liquid or solid.
- According to its transport: by truck, train, ship, or pipeline.

Depending on the application, the amount of gas required and the distance to point of consumption, the different hydrogen supply methods will be evaluated to choose the most economical one.

The most common hydrogen transportation, that covers the necessities of the different stages of hydrogen market development, are:

- Compressed gas trailers: used for small demands, avoiding the evaporation of liquid systems.
- Cryogenic liquid tanks trucks: handle big quantities, covering the demand of a growing market.
- Pipeline: transport hydrogen to high demand areas as production units.

Gas transfer processes are part of the hydrogen supply systems, therefore, its energetic performance impact have to be considered, as well as the security implications, taking into account the following:

- The decanting of liquids from one container to another can be done by gravity without adding energy.
- When a full tank communicates with another empty one, it will produce a gas flow until the pressures equalize.
- Need to use a pump to transfer the rest of the gas.
- Transferring an amount of gas between two containers, with same volume and final pressure, will result in 1% losses of the energy contained in the compressed hydrogen.

7.5.1 Supply by road

The hydrogen can be supplied by road in both gas and liquid state.

Gaseous hydrogen

This type of system involves a lower initial investment and is a good solution when a low quantity is required. The gaseous hydrogen can be transported by road in cylinders or trailers after being compressed to a very high pressure in order to maximize the capacity of the recipient.

Cylinders are built with aluminum, steel, light alloys and composites and are recommended for users with consumes lower than 5 000 Nm^3 monthly.

High pressure containers or high pressure trailers can supply to users with a range consumption from 1 000 to 56 000 Nm^3. Truck trailers can carry steel cylinders which contain from 63 to 460 kg of hydrogen with around 200-600 bar.

Liquid hydrogen

The liquid phase, which is reached by increasing energy amount per volume unit, makes easier the transport. For this reason, the important volume reduction achieved by using liquid hydrogen makes this option more attractive than the use of gaseous hydrogen, since cryogenic tanks is the most economical as it allows transporting high amounts of hydrogen.

Currently, hydrogen is liquefied by using liquid nitrogen and compressors in a complex process. However, the liquid hydrogen is evaporated at 20 K at atmospheric pressure, making the liquefaction, storage and distribution more difficult. This is the principal reason for large consumption of energy (around 30% of the hydrogen contained).

Liquid hydrogen is transported using twin shell tanks which provide insulation in order to avoid its gasification. Trucks can transport from 360 to 4 300 kg of liquid hydrogen, with an evaporation rate of 0.3 to 0.6% per day.

7.5.2 Supply by pipeline

Pipelines are the most effective system to handle large flows of hydrogen. They are more indicated for short distances because, although they have a high initial investment (0.4-1.2 M€/km), the operative costs are relatively low.

Hydrogen gas pipelines, which are currently used, have a diameter of 250-300 mm., and operates at pressure range of 10 to 20 bar, with flows of 310-8 900 kg/h. Below is indicated some examples of pipeline kilometers around the world, to provide quantitative data of their usage:

- EE.UU: 1 100 km of hydrogen pipelines.
  - The most important network is the Air Products one with a length of 480 km.
  - Pipelines concentrated in Gulf of Mexico and Great Lakes region, with a total amount of 1 000 km.
- Europe: 1 500 km.
  - The most important network is the Air Products one with a length of 20 km.
  - The oldest system is in Ruhr (Germany), with 210 km of length and transports 8 900 kg/h through a 250 mm diameter pipeline with a pressure of 20 bar.
  - The longest pipeline has 400 km and connects Amberes (Belgium) with Normandy (France).

If pipelines system use would increase, the “embrittlement” problems must be considered. The importance of the problem will depend on the type of steel, the welding used, and the pipeline pressure.

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