Rising safety hazard related to hydrogen on-road applications as leave the laboratory environment

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Abstract: Despite the fact that nowadays Hydrogen is mostly considered a carbon-free energy vector, this tiniest molecule is in its artificially separated status and one of the most difficult and dangerous substances to handle on earth. The engineering community acknowledges this fact and treats hydrogen carefully, using it in the chemical industry with a respectable safety record. However, to distribute hydrogen to millions of untrained customers such as vehicle owners seems a parlous idea. Serious risks can arise due to the mass production, the cost sensitivity of which might has a negative impact on material and production quality. Further risks are posed by imprudent user behaviour, unqualified maintenance and repair, in which the unreliable quality of aftersales parts can increase the possibility of faults and equipment time-wear, may lead to additional risks. Any failure within a H_2-system may incur not only the cost of an unworkable vehicle, but the cost of human lives.

Keywords: Hydrogen, Pressure Vessel, Fuel-Cell Vehicles, Refuelling infrastructure, Cryogenic, Pressure equipment, CFRP, Cracking, Vehicle Stock, Service Workshop, Vehicle registration

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Content

Introduction

The current global carbon reduction fever putting the hydrogen into spotlight. Despite the fact, it is mentioned as a carbon-free fuel, however it is almost entirely produced from CH_4, the by-product is CO_2, and the efficiency is not even close to perfect. On top, the cost related to production, storage, distribution and at the end of the supply chain the sales are high. Nevertheless the hydrogen fuelling with fuel-cell applications has a long baby born stadium, the GM was already [1] delivered a running experimental vehicle 55 years ago. The only one ever built General Motors Electrovan has survived to this day and on display at GM Heritage Collection. The original development goal was a challenge from Kennedy, to send man to moon and less interesting target was to find alternative to the cheap and abundant petrol. Later, as learned the first oil crises, this idea was developed towards. A few other manufacturers were also getting in charge, especially as the performance of Ballard's cells became acceptable. As I was spending my time in the University (around early '90s), it was already obviously mentioned, that Mercedes-Benz – which had the NECAR 1 proto on road in '93 on followed by 2, 3, and 4, in different versions as well a bus for the public transportation – will offer the hydrogen vehicle for sale around the millennium, if not earlier. Daimler along with Ford made a generous investment in Ballard in 1997. But we did not get closer for a production car.

Fig.1.: GM Electrovan research vehicle from 1966, [photo: GM]

Some producers drove millions of kilometres with their prototypes, demo vehicles, a few hundred vehicle manufactured for testing until 2010, without having the wide-scale testing in mind. In the last decade the continues effort and billions of investments (connected mainly to supporting funds) led to an elevated appetite for patent applications and as average ~7000 patents were issued for FCs per year [2]. Despite all of this, till today not more than 4 personal vehicle manufacturer could report vehicle manufacturing in (very small) serial. In the same time, the earlier try-outs for hydrogen fuelling in internal combustion engines were completely stopped. Comparably to the fuel-cell vehicles (FCEV) the (only) battery electric vehicle (BEV), as well the plug-in hybrid vehicle (PHEV) developments are on the natural automotive development time-line curve, and their market entries – which grandiosely supported by subventions – show positive sales results, especially in 2020. Many skin-deep observer can believe, soon we will have no other type of vehicles on road as electric, what is actually far from the reality and rationality.

Despite all the surrounding hype, it should be clear that battery technology does not present a useable solution to all transport needs – the almost 100 million vehicles manufactured globally per year cannot rely only on batteries. Political pressure to reduce CO_2 emissions, which was initiated more than a decade ago and which concentrates only on tailpipe emission has not rectified. Car manufacturers are left with no better option but to sell as many locally emission-free vehicles as possible, at the cost of their business interests and partly the expectations of their customers. This problem circle creates another basis for the push towards FCEV development, which is also known as "zero emission", despite the known issues related to local emission and hydrogen production. Beside, these generously obscured information comes as a tough nut to crack: the cost of hydrogen which one is well distributable in the chemical industry but not in the energy sector, including the fuelling [3], but also the weakly available infrastructure network.

Of course, the fuelling network could grow up to a useful scale if provided that (a) the price of the hydrogen fuel allow for (b) a positive business case together with (c) the hydrogen powered vehicle penetration growth – and provided that all could be realized within (d) an acceptable industrial risk level within the hydrogen infrastructure network.

This paper is intend to provide a knowledge basis and an overview on the problems: ensure the long term safety related to the (c) hydrogen powered vehicle penetration growth and (d) the hydrogen infrastructure network which together combine serious hazards. Until now, numerous papers have been presented on vehicle safety on topic ranging from pressure equipment through crash worthiness to analysis of the behaviour of the hydrogen, attempting to obtain conclusions from the different parties in the industry and scientific world as well governmental funding supported experiments. However, the reality of the consumers – vehicle owners, out of brand services, life-long usage behaviours – has not been analysed or at least no report on results related to this topic has been confirmed.

Under the regular industrial standards, a holistic overview of hazard identification (HAZID) should have been done, and upon realized level of qualitative and quantitative risks, should take a conclusion. Based on the understanding that not possible to finalize a HAZOP assessment with an acceptable result, the implementation of the hydrogen fuel needs to be categorized as a currently not implementable solution.

1. The Hydrogen molecule

Despite of everyone who reads this paper learned about the great atom and molecule, which one starts the Mendeleev table (or might called as the periodic table of elements), need to pay a little attention to summarize the physical properties of this particular element. This will serve as basis of the paper.

1.1. Atomic and molecule structure

The Hydrogen is the most abundant and simplest atom in the universe. As atom consists of a single proton and neutron and a tiny electron forming a surrounding cloud. The atomic arrangement of a single electron orbiting a nucleus is highly reactive. Because of, the atoms are naturally pairing into a molecular form: H_2.

> *„To further complicate things, each proton in a hydrogen pair has a field associated with it that can be visualized and described mathematically as a "spin". Molecules in which both protons have the same spin are known as "orthohydrogen". Molecules in which the protons have opposite spins are known as "parahydrogen". Over 75% of normal hydrogen at room temperature is orthohydrogen. This difference becomes important at very low temperatures since orthohydrogen becomes unstable and changes to the more stable parahydrogen arrangement, releasing heat in the process. This heat can complicate low temperature hydrogen processes, particularly liquefaction."* [4]

Not like the atomic or molecule form, the hydrogen is abundantly present on the earth with combination of carbon as well as combined with oxygen (known primarily as water) or connected to both two elements. The wide variation of hydrocarbons are available, the lightest ones are gases, the longer, more combined chains are liquid in atmospheric pressure and ambient temperature range. The hydrogen is widely produced from the smallest and commonly available hydrocarbon, the methane. In the same time, the hydrogen is widely used in the industrial scale for upgrade longer hydrocarbons at the refinery process. In a magnitude lower quantity is produced from water by known electrolysis, while the costs are significantly higher as the methane steam reforming. This – artificially – produced (separated) hydrogen molecule has some extreme feature, which often ignored as considering the hydrogen deployment as an energy vector for the close future.

The size of the hydrogen atom is extremely small, the radius is 25 pm, or $2.5x10^{-11}$ m. However, the atom is very reactive and rapidly build up connection to many other molecules. The dihydrogen molecule is mentioned as a quite stable molecule, in it's lowest energy state the bond length is declared as 74 pm (0.74 Angstrom). Based on this small size, many of the materials mentioned as gas tight, not sufficiently structured against the hydrogen diffusion.

1.2. The hydrogen gas density and packaging

The Hydrogen in the ambient condition is in gaseous state, it has no odour, no colour to recognize if present. That hold serious risk, while the Hydrogen is extremely flammable at the presence of air, or even more at oxygen. The hydrogen is not only the lightest atom, but the density is also very low. Only 80.77 g/m^3 at condition of 1 bar, 300 K [5]. This represent a quite low quantity of energy. Energy content is just 11.45 MJ/m^3 (HHV, about 1/3 litre of petrol). This require a packaging to increase the density of the gas to a reasonable level.

As it is discussed later, the Hydrogen is often stored and transported in a highly compressed stage. Only that way can be used as a vehicle fuel. The compression range is in the highness of 100 MPa, occurs high physical stress for the materials.

1.3. The hydrogen gas behaviour in cryogenic state

There is another method communicated, as could be useable in the vehicle and fuelling technology. It is known as a unique large-scale industrial operation, first of all the NASA rocket propelling. The liquefaction would result an even higher energy density, about 850-times of the ambient condition, nevertheless still only 71 kg/m^3 density can be reached. The LH_2 fuel idea came from the experiences of the other cryogenic gas, the LNG, which one's large-scale capability well proved.

The Hydrogen is the second only to Helium of all substances in the lowest boiling and melting points. The melting point (T_m), what is on the equilibrium curve also mentioned as Triple point is so close to the absolute zero as 13.95 K (-259.2°C). The boiling point (T_b) – where the gaseous material reaches it's liquid phases at 1 bar – is also not far from the T_m since that is as cold as 20.27 K (-252,88°C). Even more challenging that the critical point (T_c) is right coming at 33.19 K, meaning a 13.1 bar p_c. [5]

Compare the properties of LH_2, the boiling point of LNG (T_b) is 111.7 K, where the material availability are safer. Do not need to mention, it is way more comfortable to work with a range, where the critical point (T_c) is at 190.56 K, p_c 45,9 bar. Well, to compare the not even 13°C liquid phase working range at LH_2, the LNG is offering 89°C range.

1.4. The flammability of the hydrogen

The Hydrogen is second again in term of combustion characteristics of the various fuels right after the Acetylene. The flammability range of the air-hydrogen mixture declared from 4 % (LEL) to 74.2 % (UEL) [5]. However this is the case only at the room temperature, while the range is widening by the increase of temperature, and founds at 400°C 1.4 % LEL to 87.6 % UEL limits [6], so in fact any mixture is combustible.

To make a comparison again, the flammability for natural gas (methane) is in the range of 5.3 % to 15 %, the propane-butane 2.3 % to 9.5 %, the petrol is 1.4 % to 7.6 %, the diesel fuel is 0.6 % to 5.5 %. Just to notice, another recently picked up possible alternative – which one also being superior in the toxicity – the Methanol is flammable between 6.7 % and 36 % [5].

There are further characteristics which makes Hydrogen so special: first, it's gas-air mixture can be ignited with so little energy as 0,017 mJ [6]. That is a magnitude less energy as needed to ignite the natural gas-air mixture and about 40-times less as required the gasoline-air mixture. For the comparison, people cannot feel an electrostatic shock under 1 mJ.

As second, the perfectly burning mixture has a high temperature of 2318 K, what is mostly invisible.

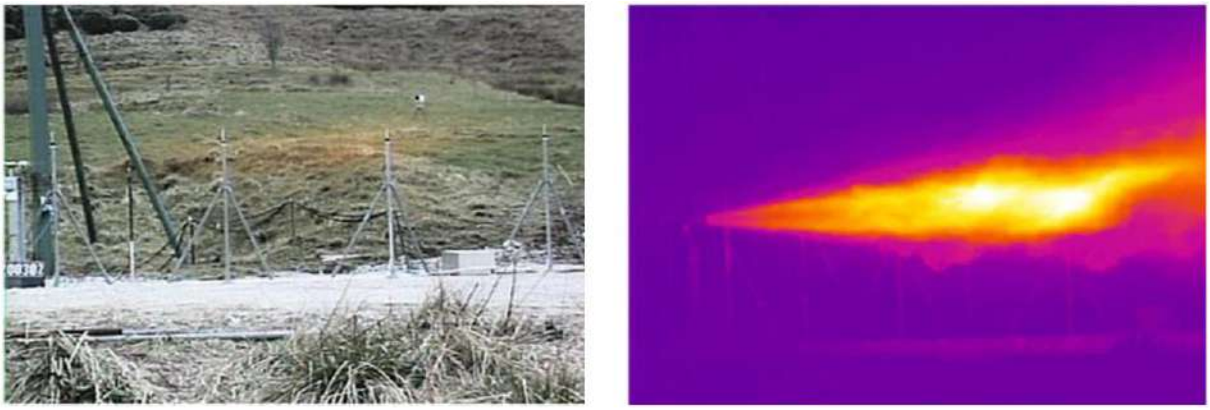

Fig.2.: Comparison between the visible flame (left) and the flame extent obtained through thermal imaging (right) (Moonis et al., 2010, taken from [8])

As third, the laminar flame propagation velocity in the air can be 2.83 m/s, which is about 6 times the speed of the frequently used hydrocarbons.

One should also be alert that the static electricity forming ignition hazard is also serious. The hydrogen is extremely prone to ignition from electrostatic discharges from insulating or non-conductive materials, and as have seen a very little energy is enough to ignite it in a wide range, close to any range of gas mixture (outer the 0 and 100 %), and hence the filling speed and other parameters need to be carefully limited. Where valves on cylinders are briefly opened direct to atmosphere, presumably to clear any debris from the cylinder, ignition has occurred [7].

Donatella Maria Chiara Cirrone mentioned in her PhD thesis [8]:

"Because of these characteristics, an unintended release of hydrogen results in a serious danger of jet ignition and accident escalation. In addition, it must be considered that the high pressure of the containment system leads to different approaches and models for the study of the effects of the storage tank failure, preventing the use of models and engineering tools obtained and employed for low-pressure releases."-

1.5. The blast wave behaviour related to hydrogen excess

The unattended pressurized hydrogen excess to air goes together with jet flow and blast wave and a short living but high temperature "hemispherical cloud" like fireball. The consideration of 35 MPa and 70 MPa systems created wave can be serious. Comparing the overpressure of 16.5 kPa may rapture the eardrum with 50 % probability, called "injury" and 100 kPa known as fatality overpressure threshold [9]. According to Donatella Maria Chiara Cirrone [8], an experimental bonfire test of a Type III and Type IV 70 MPa tanks rupture, resulting a respectively 74.3 kPa and 110.5 kPa blast wave peak at 5 m distances, a fireball diameter of ~20 m. The even more expressive information is: the fragment scattering distance was experienced as ~200 m and ~20 m. If the detonation in enclosure area the overpressure could be more significant, up to about 0.7 MPa [9].

"The speed of detonation wave depends on a composition of hydrogen-air mixture. In stoichiometric mixture it can be as high as 2000 m/s. The safety of hydrogen automotive applications and the related infrastructure, including garages, maintenance workshops, underground parking, and tunnels, is a main area of concern." [9]

As effect of the tank filling rate and the quantity of the fuel inside the tank has relevance for the blast wave it can occur. Analysing the tunnel effect, the HyTunnel-CS project was concluded the following diagram, with a burst of a 700 bar tank at the previously examined 94.5 MPa pressure level. The lines are showing the recorded maximum blast wave overpressures at 140 m distance from the experimental tank rapture. [9]

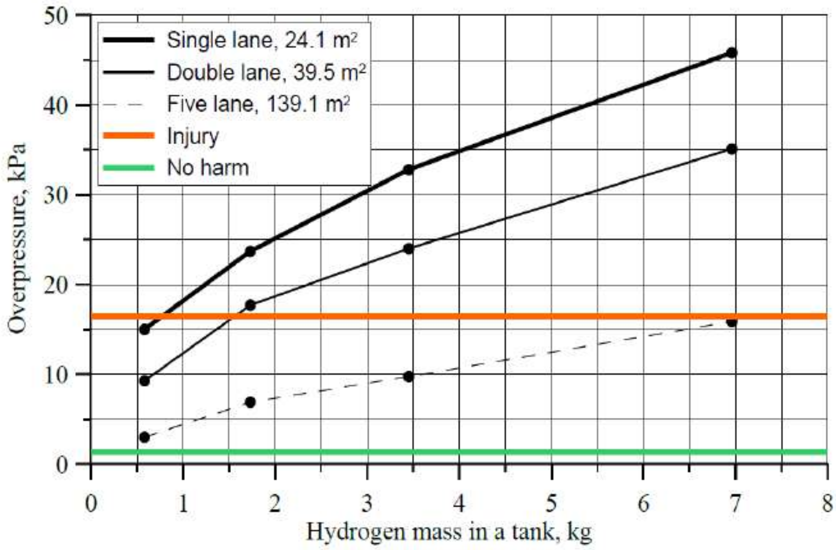

Fig.3.: Blast wave pressure in different tunnels 140 m away from the centre of the hydrogen detonation [9]

2. Diffusion, accumulation and material degradation related difficulties

Since welding and metallurgy is deeper investigated, it is known, that at elevated temperatures and significant hydrogen partial pressures, hydrogen will penetrate into carbon steel, reacting with the carbon in the steel to form methane and also tend to accumulate in the structure of the material. The pressure generated causes a loss of ductility (hydrogen embrittlement) and failure by cracking or blistering of the steel. This behaviour needs to be keep in eyes at each manufacturing procedure and the appropriate measures have to be taken. But also to aware of the phenomenon "hydrogen attack", if the material is being exposed by high temperature – above 200°C – in operation.

The removal of the carbon from the steel (decarburization) results in decreased strength. Resistance to this type of attack can be improved by alloying with molybdenum or chromium.

Hydrogen damage can also result from hydrogen generated in electrochemical corrosion reactions.

The atomic hydrogen formed on the metal surface by the corrosion reaction diffuses into the metal and forms molecular hydrogen at microvoids in the metal. The presence of hydrogen atoms in a solid metal dissolved in the metal grid and accumulated in disturbed lattice regions results in the reduction of its ductility by decreasing the energy of cohesion and consequently in the increase of its probability of brittle fracture. This is the degrading of the metal's mechanical properties, called as "hydrogen embrittlement" and later "hydrogen embrittlement cracking".

In the metal the dissolved hydrogen atoms concentrates, creates gas bubbles ("blistering"), defecting the crystal structure, while the metal ductility decreases and becomes brittle. The concentration in the metal grain boundaries potentially forms hydrates and the hydrogen and metal reaction increase the embrittlement mechanism. The propagated internal cracks is the "hydrogen induced cracking".

Fig.4.: This excised piece of a hydrogen industrial spherical container shows the hydrogen accumulation deep in the 50 mm wide steel plate, which was even able to straighten the inner side. Under heat and pressure the Hydrogen bubble created bursting force is over 100 MPa range. [Author]

The other main trouble what hydrogen can occur is at the low, cryogenic temperature effects. The so-called "cold embrittlement" can occur if the operating temperature is below the material ductile-brittle transition temperature with good probability leads to rapid material cracking. This phenomenon should be considered not only at LH_2 application, but at the pre-cooled gas filling or other events where the sudden gas-volume increase can happen.

The materials to be acceptable for hydrogen service are carefully studied and categorized in the report of Sandia National Laboratories (SNL) [10]. Nevertheless, that report is concentrating to the metals in wide range and no deep analysis provided for the non-metal materials, concluded:

> *„Relatively large amounts of hydrogen often soluble in polymer materials; therefore, exposure to high-pressure hydrogen may cause damage (blistering or swelling) of the polymer materials. This is manifest*

in high-pressure applications due to depressurization of a system (or rapid temperature changes) as hydrogen expands in free volume and at interfaces within the polymers."

The HySafe project concluded report [11], about the material consideration for hydrogen service noting:

„The reasons that cause the embrittlement of materials are still debated in the scientific community. Hydrogen embrittlement detection seems to be one of the most difficult aspects of the problem.
...
Fortunately many materials can be safely used under controlled conditions (e.g. limited stress, absence of stress raisers such as surface defects….) [here need to highlight the constrain of the statement: under controlled conditions].
...
The main knowledge gaps on this matter are concentrated on the reasons that cause the embrittlement of materials.
….
Currently this phenomenon is not completely understood and hydrogen embrittlement detection, in particular, seems to be one of the most difficult aspects of the problem."

These statements from the HySafe project – which was subsidised by the European Commission under the FP6 instrument – leaves no doubt about that even the professionals in the related subject, afraid of the significant risks at the automotive use of hydrogen.

The raised question to be discussed in the chapter 6.1, how far from the *"controlled conditions"* the real vehicle life exists? Or, as opposite: what is the risk probability that under regulated circumstances, the unattended vehicle will occur a fatal accident?

2.1. Non-metal material resilience in hydrogen environment

The still open questions about the lifetime degradation in hydrogen environment is related to each materials connected to the gas system, pipes, fittings, sealing, etc. Might the most dubious part is the composite vessel enforcement materials, the Carbon Fiber Reinforced Polymer (CFRP) and the Aramid Fibers (Fiberglass). These are widely known about their extreme tensile strength, but the durability in time not as reassuringly proven until now.

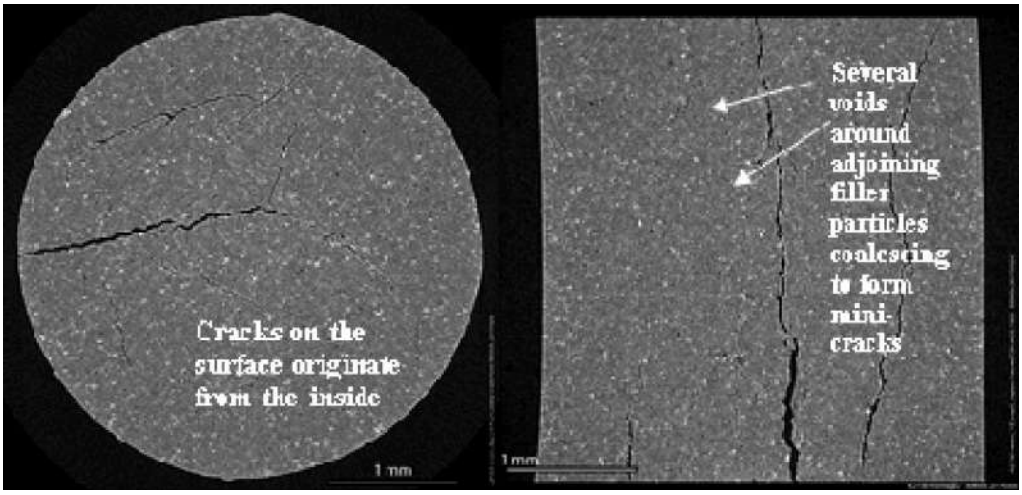

Fig.5.: SNL report [17] gave inside to hydrogen exposure related micro cracks on O-ring

The SNL gave a report [17] on the polymer materials in a scoop of application in hydrogen infrastructure and vehicles. The next excerpt sentences are relevant in the aspects of the fittings, sealing too.

"The properties of polymers depend not only on their chemical structure, by which they are typically designated, but on a variety of other factors. The most important of these are molecular weight (...) of polymer chains, and the processing history…. Processing techniques like extrusion can induce orientation

and extension of polymer chains, influencing properties…. Polymers are not subject to hydrogen embrittlement in the same ways as metals. Hydrogen absorbed by polymers exists as a diatomic molecule; it does not dissociate as it is known to do in metals. The fact that it remains chemically intact does not necessarily imply that hydrogen does not influence polymer properties…. Hydrogen is expected to be inert in the presence of most polymers, but its effects have rarely been explored at high pressures…..Temperature is likely to have a large impact on the properties of polymer materials in hydrogen infrastructure and vehicle fuel systems…However, when characterizing materials under specific conditions and failure modes relatively unique to hydrogen systems, a reassessment of the combined effects of temperature and pressure in hydrogen environments may be valuable."

The relatively recent SNL report [17] summarize some serious knowing gaps related to the polymers for apply in hydrogen environment. Some conclusions are:

- *Fracture and fatigue: The influence of high-pressure gaseous hydrogen (up to 100 MPa) on fracture and fatigue of polymers is unknown.*
- *Failure modes: The modes of failure of polymer materials in high-pressure gaseous hydrogen have been neither categorized nor characterized.*
- *Rapid gas decompression: This failure mode is widely acknowledge; however, a fundamental understanding of the failure process (and damage evolution) is lacking. Methodologies to evaluate damage evolution in polymers due to pressure cycling and establish design life are also missing.*

These statements from SNL are important to understand: the modern and highly engineered materials for these applications have not been analysed and understood well enough to be able determinate the long-term and failure-free operability, especially not for operating in such a non-industrial environment as car users.

2.2. Lifetime prediction for fibre based composite structures

The composite pressure vessel enforcement materials (describe them under Section 3.) are highly important, but not all the aspects of their behaviours are known yet. Seeking for scientifically determinate a lifetime expectancy of carbon fibre composite materials for hydrogen storage, S. Camara at Al. prepared a statistical study [16]. The authors used the stochastic properties of the fibres, determines the range of lifetimes, leading to an evaluation of failure probabilities for the vessels. The study were carry out without any reflection on possible influences as material degradation could take place based on chemicals, oxygen, UV, nor the hydrogen. The paper introduce the information as it is:

"*Carbon fibres are elastic and show no time dependent properties at room temperature. This is unlike other types of reinforcements such as glass fibres, which fail by stress corrosion. This latter process governs the long term behaviour of glass fibres and their composites and involves the gradual growth of defects at the fibre surface due to the combination of applied stress and the environment. The defect develops until it is of a sufficient size for the fibre to break under the applied stress….The structure of carbon fibres is based on the strongest atomic bond in nature, the carbon-carbon bond. Carbon fibres seem to show neither any time dependent properties, at room temperature, nor sensitivity of fatigue…As with all fibres, carbon fibres show considerable scatter in their strengths."*

The carbon-fibre strength scatter is illustrated through the probability of failure curves.

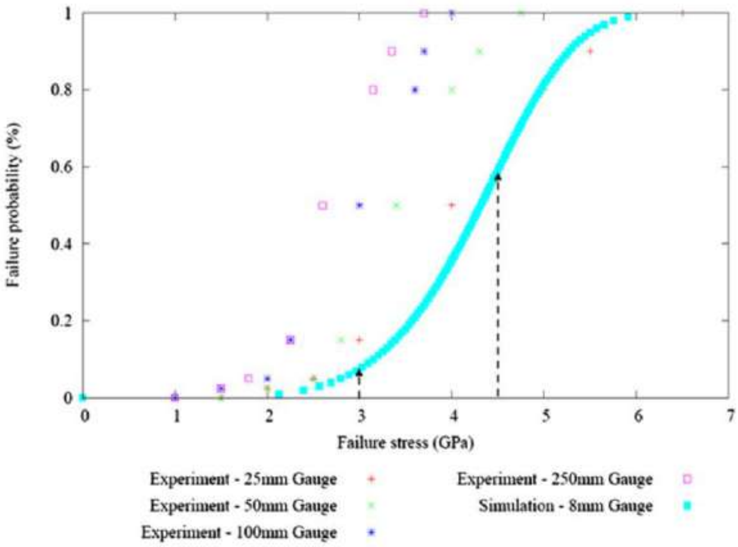

Fig.6.: Probability of failure curves for different length of carbon fibre samples and the consequence of overloading on number of broken fibres [16]

The fibre failure curve has some important aspects according to the study [16]: *"The main strength of carbon fibres depends on their length, or more correctly their volume. The strength is not an intrinsic material property but is stochastic, reflecting the distribution of defects in the body….The arrows show the effects on number of fibre breaks of overloading by fifty percent. It should be obvious that the traditional hydraulic pressure test in which a pressure vessel is subjected to one and a half times the maximum in service pressure is far from ideal for evaluating the behaviour of a composite pressure vessel and results in further damage to the structure. "*

The knowledge above might need to interpret a bit; all the produced vessels are need to be tested prior to dispatch from factory by an over pressure, according to the regulations. This event start in the carbon fibres shell a rupture progress, which one is weakening the material. That is a same avoidable treatment like testing metal cylinders with highly corrosive media.

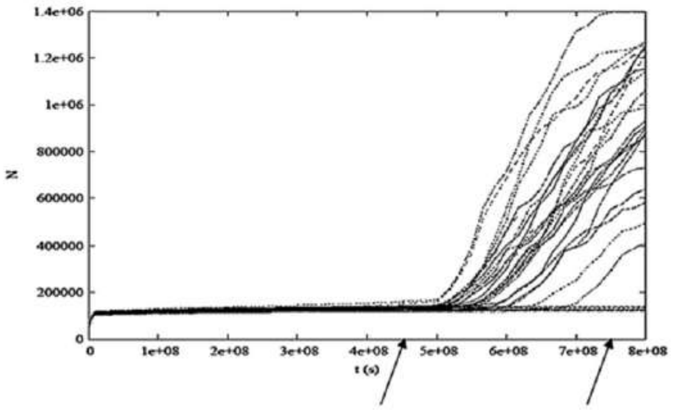

Fig.7.: Having experimental fibre break test on 30 macroscopically similar probe, quite a wide time pattern realized for rupture of the carbon fibres under a steady load of 85% to the failure strength [16]. The inflection point on the curves shows the coalescence of breaks vs. time, or means the failure of the specimen of probe. The arrows are representing 15 years and 25 years.

Assuming the statistical calculations, and the industrial standard failure target rate of one per million, result of the study for the carbon fibre life expectancy is: "*The reliability of these composites structures can only be guaranteed with a 99.9999% probability for a lifetime of just less than ten years."* [16]

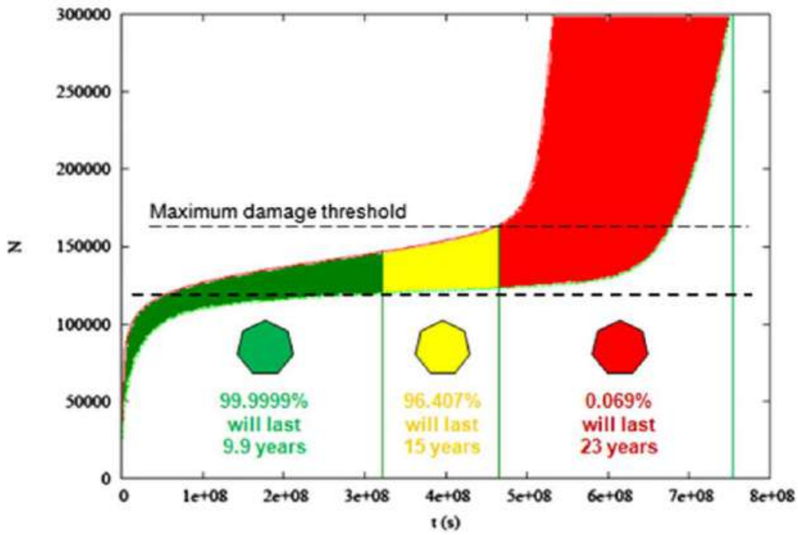

Fig.8.: Results of the carbon fibre strength test shows, only 96.4 % of the tanks will last for the designed 15 years

> *"For longer lives to be achieved, to say fifteen or twenty years, for the same failure probability, there are only three ways of achieving this; reduce the load; change the material properties or change the geometry of the composite. In the case of pressure vessels, the load, or maximum in-service pressure, is fixed, so this is not an option. Neither can the material properties be modified by a pressure vessel manufacturer;… The obvious solution is to increase the thickness of the composite in the fretting layers."*[16]

Nevertheless, the current and the future development goes only to the opposite direction. Each player of the industry but also the customers have the same interest: to reduce the cost of the tanks. All-in-all the trend is to make the wrapping weaker.

The missing factor in these strength tests are the environment, first the temperature. While no real different in the fibre rupture probes as the temperature is changed, but the epoxy polymer in which the carbon fibre or glass fibre is sitting, not heat resistant and at T_g = 115°C temperature it is finally leaving the glass-like phase. The HyCOMP Project WP2 task report [26] concluded the followings:

"The levels of ambient temperature and humidity could modify viscoelasticity property of epoxy matrix inside the composites.

- *The effect of temperature:*

When the level of ambient temperature was elevated, the molecules of epoxy matrix became active due to the absorption of heat energy and the epoxy polymer (glass state) transformed toward rubbery state. As a result, the creep process is the epoxy matrix was augmented in the composite. This means that the efficiency of load transfer mechanism at the interface of fibre and matrix declined and the effect of the existing fibre breakage in the neighbouring fibres enlarged. Consequently, more neighbouring weak fibres were likely to rupture. The (next graph) *shows that the elevation of the temperature accelerated the growth rate of fibre breakage; the increase in damage accumulation rate was increasing at a rapid rate with the elevation of the temperature toward T_g.*

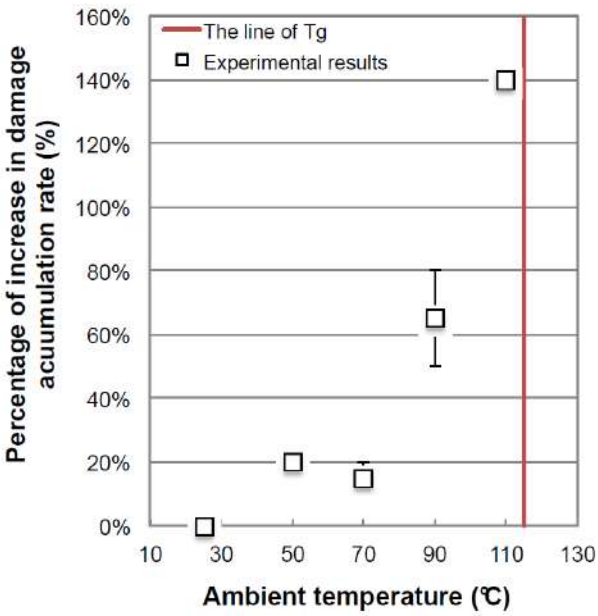

Fig.9.: *"Percentage of increase in damage accumulation rate with respect to ambient level. The test were carried out in the sustained tensile loading at 50% of average failure stress."* [26]

Moreover, the effect of elevated temperature was severe when the composites were subjected to higher level of the applied tensile load. The (next graph) *shows that the increase in damage accumulation rate was higher for the UD specimen* (carbon-epoxy probe) *tested in the 90°C environment when subjected to higher applied stress level.*

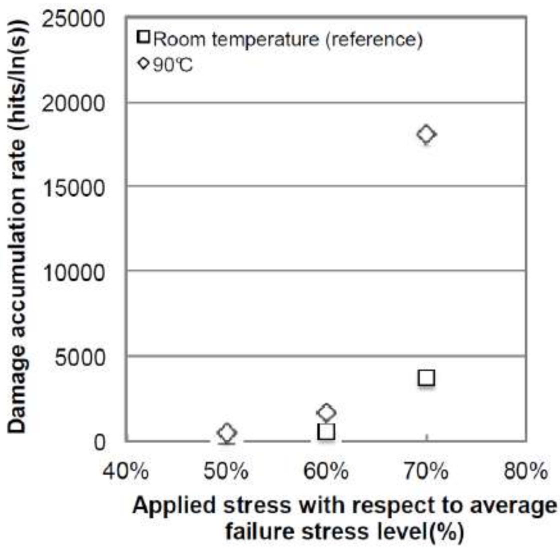

Fig.10.: *"Damage accumulation rate measured for the UD specimens subjected to sustained tensile loading test under two-stage temperature conditions: room temperature and 90°C. The applied stress levels were varied from 50%, 60%, and 70% of the average failure stress level."*[26]

As proceeding to the topic of the temperature related effects in the Section 3.6., the importance of these information becomes clear. The HyCOMP report [26] explaining the behaviour of the carbon-epoxy in the presence of humidity as well:

> *"It was determined that the water intake diffusing into the composites could cause a reduction to the glass transition temperature of the material. The modified T_g for the hygro-saturated HYCOMP composites reduced to 95 °C, which is 20°C less than the T_g for the virgin composites. This means that the damage process can accelerate in the hygro-saturated composite when subjected to lower level of temperature rising as the viscoelasticity of epoxy matrix becomes more sensitive to the temperature."*

Continuing it:

> *"As a result for the long-term operation, the increase in damage accumulation rate due to the elevation of the temperature could significantly affect the lifetime of the composites. It was calculated that the lifetime for the composites subjected to creep test at 70% of the average failure stress decreased from $2e^{+27}$ years to 0.2 year when the ambient temperature changed from the room temperature to 90 °C."*

3. On board storage solutions selected nowadays

First need to declare against the mainstream marketing, the FCEV vehicle is in correct form would mention as a Hydrogen Gas Fuel-cell Generator Electric Propelled Vehicle, and the shorter term could be the Hydrogen Fuelled Vehicle. Where the Hydrogen Gas itself is so determinative as the petrol or diesel.

For automotive application 5 different hydrogen storage solution found so far, of which 2 became ready for the pilot operations and small scale manufacturing level of todays. These are:

- the mature Compressed Hydrogen Storage System (CHSS) or as also called it, Compressed Gas Hydrogen (CGH_2) tank systems on two different pressure rates,
- the prototype levelled Liquefied Gas Hydrogen system (LH_2),
- the even less advanced stage of Cryo-compressed Hydrogen (CcH_2),
- and only embryonic research phase status of the solid storage, where the hydrogen is absorbed in a carrier material.

In the following, it is worth to spend intention to the CHSS systems and beside of, to the LH_2 solution because of recent marketing communications mention an arrival of a long haulage vehicle with cryogenic on-board tank.

3.1. Compressed 350 bar

The compressed gas fuel tank solution is since long available in the vehicle industry. Today, about 20 million vehicles are running with it. The filled in fuel is fossil or renewable natural gas, so primarily methane. The nominal working pressure mostly 200 bar, a few (solely) closed consumer area runs on 250 bar system, but this is good for footnote only. The entire chain of the CNG vehicles and fuelling infrastructure is built up on very cautious way and this was until now crowned with only a small number of incidents. Even so, there is more than enough examples served for systematic safety review.

There are 4 different technical solution is used worldwide for CNG tanks and additionally some other – non cylinder form type – unique solutions are under research. The produced solutions are:

- Type 1 - are thick wall steel cylinders, cast iron, seamless products, what makes it especially heavy.

  The condition of the painted steel can be easily analysed and recognize if any injury on corrosion protection or corrosion started to reduce the material stiffness. As it was a serious issue at the earlier vehicle types, some corrosion resulted by the not reliable protection of the vessels which were mounted under the vehicles exposed to the harsh environment of every days use. That can be detected at the regular inspection and if problem founds, the change of the vessels can be prescribed.

Fig.11.: At the inspection as “not usable” determined Type 1 cylinder under a CNG vehicle, because of the material corrosion. This type of failure can be detected well, if the vehicle inspection is regular and serious. In 2017 there was a wave to recall most of the VW CNG vehicles to check their bottles and had been replaced a large number of them. [Author]

The lifetime is, allowed by the regulation 20 years as maximum, producers can restrict for a shorter time. The cylinder Type 1 used also for gas storages, up to 300 bar pressure level, mentioned as nominal working pressure (MAWP), what does mean, at product tests the 450 pressure must not burst it, while the vehicle tank needs to be stable at 300 bar during each product test.

- Type 2 – steel cylinders with somewhat thinner wall and an overwrap enforcement by carbon fibre or fiberglass on the vessel's cylindrical sidewall, but the whole shape is not entirely covered.
  The solution is just a little lighter as the Type 1, nevertheless some markets are not accepting it by regulation, questioning the uncertain long-term reliability.

- Type 3 – a vessel has a metal (mainly light alloy) liner over which it is overwrapped with enforcement structure such as carbon fibre (CFRP) or fiberglass (aramid fibre), the wraps are in epoxy resin. This material mixture called composite cylinder. Comparing to the Type 2, here the wrapping covers the full cylinder, including the dome and neck.

Fig.12.: Type 3 vessel cross section at the neck part [photo: Dynatek]

The Type 3 version is intend to be a far lighter container as the Type 1. The stiffness of the structure primarily can be weakened by any means of injury on the wrapping. Any surface scratches that deeper as 1.5 mm should not be considered to operable any more. It need to send back to the producer for analysis and repair, if that found as possible. Nevertheless, the test procedure of the type approval require a sequential pressure test for tube, which one scratched over the limit. This is a so tiny surface damage that not easy to recognize, and can be traced back for any mishandling action. Widely understood that based on the wrapping liner quantity, the Type 3 cylinders can be made to allow way higher pressure ranges as the CNG would require.

- Type 4 – it is also composite with carbon fibre or fiberglass full wrapping, but the inner shell layer (called it liner) is made from non-metallic material, means plastic, High Density Polyethylene (HDPE). The Type 4 is sometimes referred as all-composite cylinder. Where the end Boss part is made from metal to make available the joining with the fitting parts. ´

Fig.13.: Type 4 vessel cross section at the neck part [photo Dynatek]

The liner and the Boss material have different thermal properties, and this is the case at the composite shell too. The plastic known from accelerated aging caused by thermal cyclical stresses, what is an issue at the liner. The same evaluation was given for Type 4 and Type 3 vessels in term of pressure toleration. The metallic liners at Type 3 are designed to share the load with the reinforcement wrapping, while the Type 4 liners are do not carry of the load. The Type 4 is even lighter as the Type 3 vessels, but two attributions need to be expressed to compare; the static discharge and the low thermal conductivity.

The Type 4 tanks are banned at some markets, among others, China was also against to use it.

The composite tanks about 4-times the cost of the Type 1 cylinders for the same volume. For the hydrogen operation the 200 bar Nominal Working Pressure (NWP) considered as not sufficient to give acceptable autonomy for vehicles, since that would allow for an 80 litre volume vessel to fill up by only 1.15 kg of gas. Based on the experiments, two pressure system borne to be used for H_2, the 350 bar needs still quite a lot of space (about 2.5 kg at each 100 litre sized cylinder) and based on this, applied it for heavy segment, buses and trucks. Only composite tanks are used for this pressure and for H_2.

The service life for hydrogen storage shall have 15 years or less (upon the tank producer's product verification) according to the UN Regulation No. 134 [14]. For product verification, the minimum burst pressure has to be minimum 225 % of the NWP, means design pressure (or better to recognize as developed pressure) is 1.25xNWP and Safety Factor (SF) is 1.8. The containers for storage having glass-fibre composite, the minimum burst pressure has to be 300 % of NWP, equal to SF=2. The cyclical durability test is required to be demonstrate 11,000 cycles capability (representing 15 years).

At this point has to note, the Regulation No. 134 on hydrogen vehicles is insufficiently described. This is showing a bad sign how weakly the related industry consider on the topic of vehicle usage. The missing part of the Regulation is the provision of the periodic inspection, requalification. Comparing to, it is clearly described in the Regulation No. 110 on CNG vehicle regulation that periodic requalification (for the entirely gas system) is requested at each not more than 48 month, or earlier upon the local regulations. Such kind of statement must be part of the hydrogen gas system, vehicle regulation as well!

In the R.134 only found prescription, how to requalify a post-crash vehicle.

3.2. Compressed 700 bar

According to the burst tests of the composite cylinders reaching and exceeding the 100 MPa mark level, it became an industrial consensus to build tanks into the light hydrogen vehicles capable to fill by 70 MPa MAWP. As for the 350 bar system, only Type 3 and Type 4 tanks are suitable for this service. An overall tank capacity of 100 litre is ready to hold a close to 4 kg of H_2 (the newest Toyota Mirai is reportedly equipped by 142,2 litres combined capacity, what is around 5.6 kg stored gas quantity).

The problem is with the conclusion for the possible life expectation enlargement of the study [16], which quoted at the end of the chapter 2., the increase of the thickness is drastically increase the cost of the on-board fuel-systems.

The current carbon fibre material cost is about 77-78 % of the total fuel system (not includes the fuel-cell) even so, the production would grow up to half a million tank per year, assessed by the U.S. DoE [18]. To compare their figures, the automotive industry can produce around 7 piece of a simple 4 cylinder vehicle internal combustion engine for the same price of one H_2 tank system. Moreover, their cost assumption for 700 bar tank with 149 l water volume is not suitable for a light vehicle. To place the same capacity of storage into a structure of a light vehicle, need to count with 2 but more likely with 3 cylinders. That is even towards pushing the costs. The high production cost is indisputably target of the reduction at all the parties in the entire automotive industry.

A conference paper [19] found from an author of composite vessel manufacturer, related to their Type 4 performance approval. It declares the following:

> *"One of the key aspects of the analysis is to confirm that the design does not place the fibers above limits that could result in stress rupture of the fibers. The maximum fiber stress is limited to 28.5% for glass fiber and 44.4% for carbon fiber of the tensile strength of the fiber at design conditions. This corresponds to stress ratios, or safety factors, of 3.5 for glass fiber and 2.25 for carbon fiber, and is intended to provide reliability with respect to stress rupture in excess of 0.999999 over the life of the vessel."*

The applied minimum safety factors as it mentioned, according to standards and other sources is only 2, and 1.8 at the vehicle tanks. The question remains, how the over sizing factor will melt away by the time and by the nature of cost reduction. Refer back to the statistic based stress study [16], the carbon fibre probes had an 85% tensile strength stress, which seems significantly higher as the 44.4 %, but no other major influence had been applied for degrading the materials of the probe pieces. However, that should also be considered.

The HyCOMP project papers [29] were listing the different regulations and standards as it is follows, declare that there are different safety factors are to be followed.

Standard	Primary overall Stress Ratio related to NWP for CFRP	MAWP-Filling l Ratio	Minimum Stress Ratio in case of using CFRP
EN 12245	3.0	1.5	2.0 (PH)
ISO 11119-2	3.0	1.5	2.0 (PH)
ISO 11119-3	3.0	1.5	2.0
ISO 11439	2.35	1.3	1.8
ASME	2.25	1.25	1.8
EU 406/2010	2.25	1.25	1.8
JARI S001	2.25	1.25	1.8
GTR	2.25	1.25	1.8

Fig.14.: For the composite hydrogen storage tanks, the applicable different standards and regulations and their safety limit variations. [29]

As the HyCOMP project [29] were study the properties of the composite tanks, gave several recommendations for the industry and for future regulations. The SF is one of the most visible one. For the vehicle built-in tanks, they mentioned a reductions for the hydrogen operation and having differentiation in SF between the carbon fibre and fibreglass technics. As first, to reduce the design pressure as 1.25x the pressure of the NWP (given to the gas temperature 15°C). This 25% higher pressure means the same quantity of gas reached at 85°C gas temperature. Second, using the SF as 1.8x for carbon fibre and 2.0x for fibreglass. The project declared as well, that according to the sterile labour tests of the fibre tensile tests resulted, the 1.4 safety factor is providing the probability of 1 tank rapture per 1 million piece over the lifetime. Based on this statistical calculation 1.4 could be the "Theoretical absolute minimum" SF value.

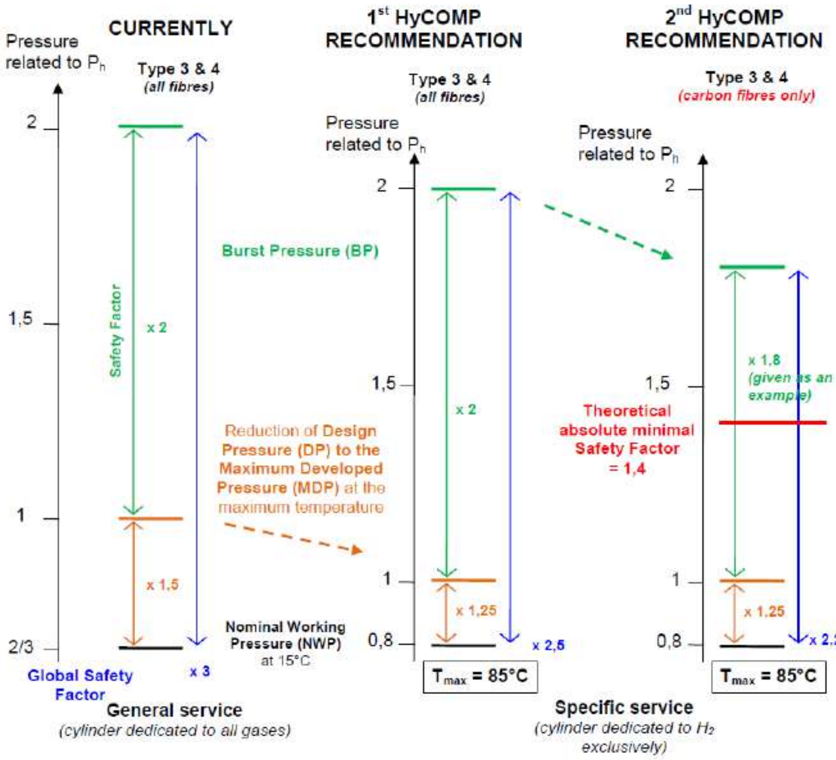

Fig.15.: The potential reduction scheme recommendation by the HyCOMP project [29]

3.3. Liquefied Hydrogen Storage System

The gas in fluid state can be the densest, this known and used for transport and stored at the various industrial gases, like Carbon-dioxide, Oxygen, Nitrogen and at the energy carrier gas, the methane as well. This last one is called LNG. The LNG is increasingly popular as a fuel at almost each of the transport sectors, and applications. Principally the liquefied hydrogen (LH_2) should work like the liquefied natural gas (LNG), storing in 1 cubic meter tank inner volume 72 kg of the LH_2 fuel. Nevertheless, the LH_2 works far different, as described it in the section 1.3.

For keep the cryogenic in fluid state, need to have a very good insulated tank. This problem technically solved for the heavy-duty (natural) gas vehicles, where super insulated double walled tanks are mounted and the frequent or almost constant consumption is secured. These vehicles are – if stopped them for any reason – prepared to hold the gas without having release and problem, between 5 days to 2 weeks, depends on the initial temperature of the filled gas, the level of the fluid in the tank, the actual weather, as the most important parameters.

Even at the almost perfect insulation, the surface of the fluid has a constant evaporation (saturation), as the second law of thermodynamics describes it. This saturated gas gathers above the fluid surface and as the quantity is growing, so increase the pressure in the tank. At the LNG fuel tanks, the settled maximum allowable working pressure (MAWP) is 16 bar. The most obvious difficulties to apply LH_2 as a fuel in the other applications than space ships or rockets at NASA, is the tiny pressure and temperature window in the Hydrogen liquid phase. The critical point for hydrogen is at 13.1 bar, in not even 13 K distance from the boiling point. This is mostly not an operable window without extensive loss from the containment.

To overcome this saturation problem, seems the only option left is to build-in an on-board mini re-liquefier. A patented solution came from Sierra Lobo Technology Development and Engineering Center [13], which is specialized itself in space technology. They research level solution is an active cooling of the inner tank shell by a circulating active-cooling loop connected to the 2-stage cold heat-exchanger, using helium as the medium. The system needs about 500 W electrical input, not mentioned for which tank size it is calculated. Regardless the energy is used by the 9.3 % Carnot efficient solution, the long-term reliability of the complete system can be questioned again.

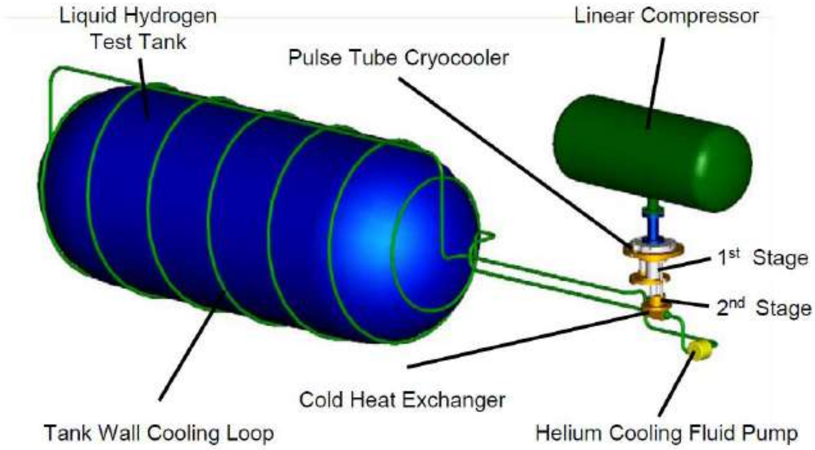

Fig.16.: An actively and continuously pulsing compressor system support the heat-exchanger at the Sierra Lobo patented solution [13]

3.4. Pressure Relief Device

As PRD have two, partly different device built in for securing on board safety. The compressed systems are using thermally-activated (TPRD) *"means a one-time use device triggered by excessive temperature and/or pressure which vents gas to protect the cylinder from rupture"*- declared by the definition. The regulation of hydrogen vehicles are definitely describe the TPRD as a *"non-reclosing PRD"*. Means, if it opens, the full containment of the vessel is releasing.

If the vehicle get into a fire, or any other reason leads to an over pressure, the TPRD let the gas release through a reliably sized vent pipe. Makes it possible that even in a fire, in the tank will not increase the pressure to rapture it. If something, the released gas can get fire and act as a burner, with smooth flame, without detonation. This is how CNG works, but there is a challenge to make the same at hydrogen, because of the behaviours declared in the first chapter.

About the function failure Donatella Maria Chiara Cirrone in her PhD thesis [8]:

> *"the TPRD failure to activate and an inadequate thermal protection of the tank to withstand the fire. In this case the tank can catastrophically rupture with a devastating blast wave and fireball, leading to life safety and property protection issues."*

3.5. Pressure relief valve

According to the definition it is *"a device that prevents a pre-determined upstream pressure being exceeded"*. For the service of LNG two of the PRVs are built in to the cryogenic tank system, one opens and at 16 bar at +/- 0.5 bar accuracy and for safety reason, if that would not work because of any reason, the secondary shall open at around 20 bar settled pressure. If the pressure drops under 16 bar, the system close again and stop venting in a timeframe of a few seconds. Note the different: the LNG even at the 20 bar is quite far from the critical point of 45 bar.

Also at case of LH_2, the PRV must open at the MAWP. The MAWP is not exactly described by the prior draft text of the UN Regulation (since the final Reg. 134 has no provision on the LHSS, the only citation here can be made reflects to the earlier draft, where it was containing). Technically MAWP should be not more than 10 bar. The secondary PRV not operates below 110 % of the settled pressure of the primary PRV according to the draft Regulation. For the secondary PRV only 2 bar left to avoid the rapid phase change of the liquid, which already becomes at 13 bar. This means, if the gas pressure comes in to the region of 10 bar, a frequent release starts and the risk of gas flame comes serious.

3.6. The relevance of the temperature variation

There are some further experiences from the CNG operation to address for better understand the difficulties to provide safety. These will be expressed with other topics at the section 4., discussion of filling infrastructure.

The materials used for the gas system of the vehicle – not only the CNG tanks – are considered to be used within a certain ambient temperature range, starts at -20°C (for some cold climate at some type of vehicles can order acceptance of -40°C as well, but not generally each model). From the low end the temperature window goes up to the vehicle industry used standard maximum temperature. The Regulation 110 [12] stated, the stabilized temperature of the gas in the vessels can be between -40°C and +65°C and the temperature window of the material can vary between -40°C and +85°C. The word of "stabilized" has an importance, since the temperature temporary can exceed the +65°C.

As ordered by the Reg. 110 the ductility values for the plastic liner needs to be delivered under -50°C, while the strain softening temperature should be minimum 90°C and the melting point at minimum 100°C.

The 200 bar NWP settled pressure – according to the CNG standard – relate to the temperature of the filled gas, since the gas density heavily rely on the temperature. Precisely described it by the standard: *"cylinder working pressure of 20 MPa will be filled to a maximum settled pressure not exceeding 20 MPa when the gas temperature inside the cylinder is 15°C"*. The allowed maximum gas density in the cylinder is the value to regulate. Determines; *"the final fuelling pressure shall not exceed 26 MPa under any circumstances and regardless of density"*. This means, in the system a temperature compensator can be implemented to stop the filling operation at a certain pressure, which depends on the actual gas temperature. This helps to fill up the vehicle tank closer to it's capacity, because during the fast filling (called the filling process as fast filling, if the filling rate is high, and the to fill up time takes only minutes) the temperature of the gas goes up significantly. Without the temperature compensator, the vehicles often would not filled up by more than 75 – 80 % of the initial capacity.

During the fast filling, the gas temperature increases rapidly, as it is visible on the graphic. A temperature measure analysis [20] compared two different composite tank design (both are 350 mm diameter, 200 bar NWP). The polymer tank liner has low heat absorption (thermal conductivity=0.36 W/m^2K), resulting 68°C gas temperature increase, 16°C more as the Type 3 version equipped by aluminium liner (thermal conductivity=204 W/m^2K). The different is resulting 11 % longer filling time. Moreover, as the gas cools down in the cylinder and reach the stabilized temperature (in this case the initial 25°C), the pressure different remain remarkable: 213 bar compare to 203 bar, so the range of the vehicle, which is almost 5 %.

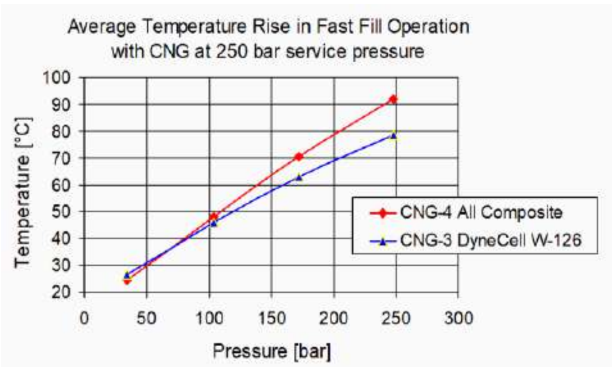

Fig.17.: Temperature comparison of Type 3 and Type 4 CNG cylinders during fast fill to 250 bar storage service pressure [20]

This is the same, how the compressed hydrogen filling works too, but might the temperature swing can be higher, as the pressure rates are bigger. There are available examinations on the temperature cycles during hydrogen fillings. The Joint Research Centre of the EC (JRC) introduced [21] their experimental results on filling-emptying cycles, and a computational fluid dynamics validation work [22]. The filling sequences from empty to full, pressure holding and pressure dropping cycles, are temperature measured at the different points of the tanks. They detected differences.

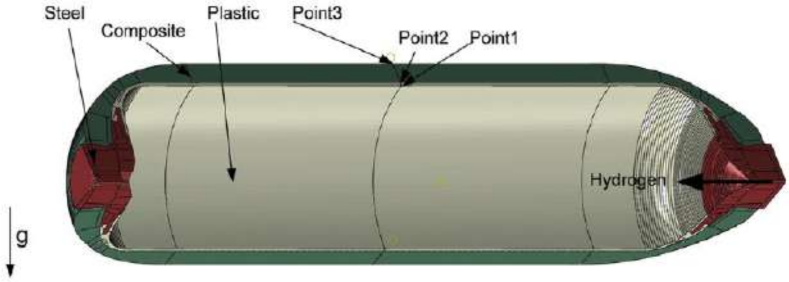

Fig.18.: Simulated temperature measuring point allocations on the 3D Type 4, 700 bar hydrogen cylinder, at the filling-emptying cycle tests [22]

The analysis experienced temperature data from two different sized Type 4 and one Type 3 vessels. Altogether 165 different measuring cycles have been performed, includes different average filling speeds, the so-called Average Pressure Ramp Rates (APRR). Some statistically averaged data from one of the Type 4 tank measurements, without APRR modification, as an illustration:

There took 253 seconds to reach the final pressure from the initial (up from 1.99 to 76.89 MPa), the bottle inner surface temperature increased from 11.2°C to 86.9°C. Remarkably:

> *"after emptying, however, stratification in gas temperature is significant and a difference of 27°C from bottom to top of the tank is observed"* [21].

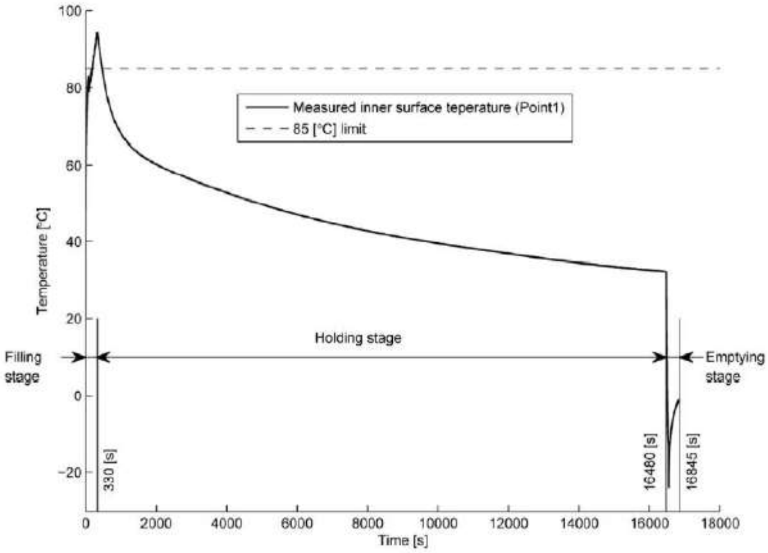

Fig.19.: The measured temperature on the liner's surface was rapidly increased during the filling, up to 93.95°C, while the rapid emptying – took 365 s – lead to a rapid surface cool down [22]

Taking the information from the CFD work, known that the Type 4 cylinders has a high temperature difference to survive. At the end of the filling up, in the 330th second time-point shown 94°C on the surface of the inner liner (up by 76.15°C). In the same time-point as the filling ended, the composite shell outer surface heat up was not even 10°C. It took another 20 minutes to heat up by about 36°C, getting the temperature close to the inner liner's, which one became 31.5°C colder during the heat exchange.

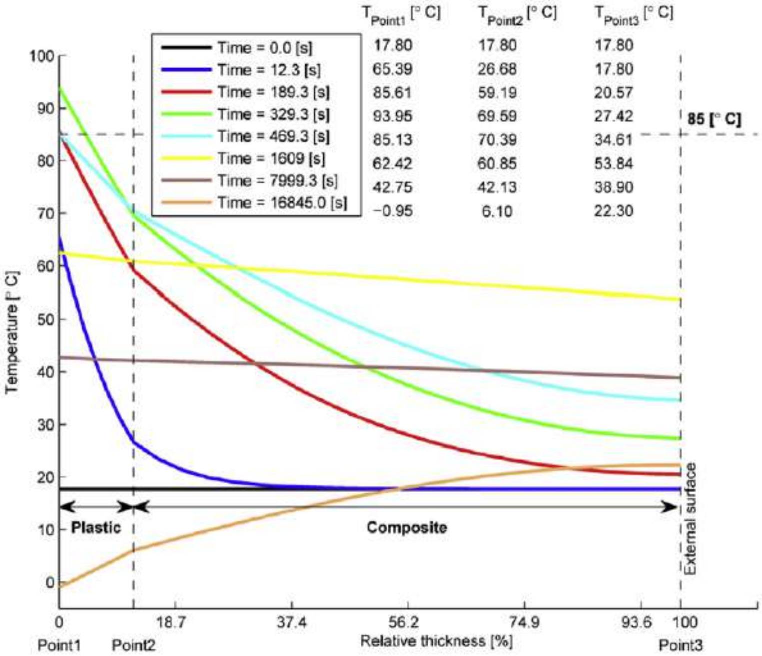

Fig.20.: The temperature development at cross section of the Type 4 vessel's wall vs. time [22]

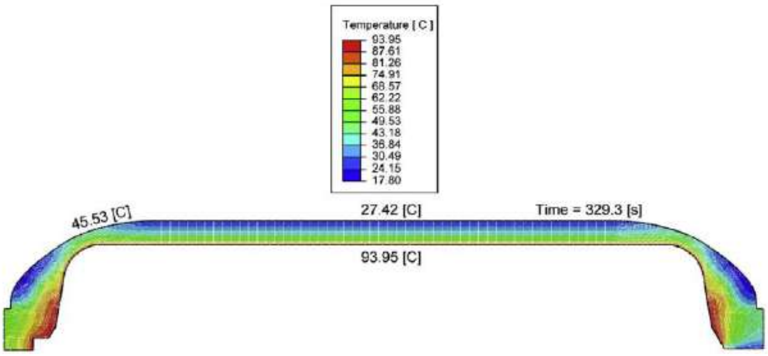

Fig.21.: Temperature distribution in the Type 4 vessel's wall at the end of the filling stage [22]

The gas filling properties measured for a few cycles with hydrogen pre-cooling solution as well, using -42°C to -30°C initial hydrogen temperature and different APRR. The solution resulted the tank initial temperature decrease down to -13.5°C. This might increase the rapidity of the temperature increase to allow the fuelling even faster and even closer to 100 % of State of Charge.

Imagine if the ambient temperature is not as preferential as the lab's 17.8°C is, but as warm as +40°C, or staying under the direct sunlight, even above. The rapid heat flux during the fast fill brings the material close to the T_g temperature (described it in the end of chapter 2.). If the installation is similar to the common CNG bus design, where the tanks are on the top of the bus mounted, the initial temperature of the surface under the direct sunlight heated up easily to around 60°C. In this circumstance, the operation gets out of the thermal window.

The measurement show us another nature of the composite cylinders: the heat propagation is slow, especially at a point-like heat exposure, happens in a fire. The gas can heat up too slowly and unequally, and not able to activate the TPRD early enough. This happened at some of the serious CNG accidents (see chapter 3.8.).

3.7. Pressure swing during lifetime, temperature, humidity and other harsh environmental exposure

As it is shown at the previous chapter, the temperature of the bottle is changing cyclically during and after the filling of the vessels. This phenomenon is reflecting also to the filling technology. Beside of the temperature, it is also obvious that the buffers are dilating, like breathing. At this point, the all composite has an extremely bad cooperation behaviour between the liner and the outer enforcement wrapping structure. Unlike to the reinforced concrete structures – where the long-life of the structures are based on the equal expansion coefficient of the iron and concrete – here the liner is not only warming up far more, but the expansion coefficient is widely different to the wrapping. This gives for the liner an independent live and if the inner pressure gets low, the liner can reshape.

Fig.22.: The blistered liner can see on the left cut up cylinder, at low pressure the strung-out liner come off the epoxy-fibre layer, and the hydrogen accumulating between. On the right the one already cracked liner is visible. The increase of the hydrogen passage through the wrapping resulted. [Source of the photo is uncertain]

The conditions of the various environment is also can be a notable treat on the material's lifetime. The vehicles are under long-term treat of UV ageing, various acid exposures (like battery). Typically the most critical treat is the road itself, which extremely exposes the gas connections. Finally, need to address the possible severity of the collisions.

Fig.23.: Bus tank after impacted with an over-bridge [28]

Cannot miss from this list, the cylinder's improper treatments, like an event as falling. That can occur an external abrasion, or damaging on the surface of the wrapping by sharp, abrasive tools and through effecting the fibre-epoxy structure.

3.8. Incidents and Accidents related to the fuel systems

Need to declare, the CNG operation had relatively few accidents, those became to the media headlines. All of them are connected to the fuel tank systems. There had been reported several fire incidents (the fire caused by other source), where the CNG cylinders emptied through TPRD actuation – as it should be. Nevertheless, the still often cited Robert Zalosh summarized in 2008 [23]:

"at least two CNG cylinder rupture reported due to fire exposures that did not cause PRD actuation".

Fig.24.: The case of a CNG propelled Civic in 2007 in Seattle, where the PRD was not opening and actuating releasing the gas. The ruptured tank was landed beside of the excavator [Photo 23, 27]

Fig.25.: The bursted and burned cylinder residuum from the Civic [27]

Additionally to the number above, as the TPRD was failed, Mr. Perrette and Mr. Wiedemann reported in 2007 [24], three CNG bus fire cases from Germany and France. In the event at the depo in Saarbrücken (2003), 15 articulated busses were staying besides, each equipped ten roof mounted, doubled TPRD protected Type 3 CNG vessels. One of the busses got fire from the engine compartment and in the fire, one after the other tanks released their gas content as it is design to do so. The released gas burnt in the depot and the fire propagated from the back of the bus to another one, which were parked at 1.5 meter behind. *"19 of the 20 CNG tanks exposed to the fire did behave as expected."* Unfortunately, one TPRD was not releasing and about 15 minutes after the fire started, that tank burst. *"A large fragment was propelled in the tank axial direction. It broke through a nearby wall (hole at 3 meters from ground level) flew through the air and damaged another wall located 25 meters further and ended up it's journey on the roof of a bus parked in a nearby depot."* [24]

Fig.26.: The above arrow shows where the wall was leaked through by the exploded tank [24]

There were some well reported conclusions on the German case. First, the tanks were mounted with two TPRDs on both of the ends of the tank, while just front of the tank a top roof was open, let the fire come out from the passenger compartment and directly heated the tank's middle section. The flames were not heat the TPRDs fast enough, while the middle section was experience a heat stress. *"This remark underlines that tank fire protection and bus fire safety can not rely only on the performance of isolated protected tank systems."* [24]

At the Montbéliard accident (2005) the Authors could declare: the TPRD connected to Type 4 tank had not sufficient gas through put, to fulfil the French regulation and the pressure reduction couldn't be fast enough. The fire initially was a battery fire which propagated throughout the complete bus. Just 3 months later in the same year, a same type of bus in Bordeaux have been burned out, because of vandals threw a Molotov cocktail inside the bus and the first cylinder exploded again.

Fig.27.: The burned out bus in Montbéliard, and the residue of the cylinder, which splitted in two parts. The initial problem came from the electrical circle of the bus [24]

Mr. Zalosh and Mr. Weyandt with the Motor Vehicle Fire Research Institute made a fire test [25] with hydrogen filling on a Type 4 tank and a Type 3 tank, built into an SUV, to see, if that works similarly to the CNG cases. With propane burner under the tank reached the tank ruptures at both of the cases. Instead of releasing the gas, the Type 4 tank within 6 min 28 sec, the Type 3 tank within 12 min 18 sec. At both of the cases, the composite wrapping layers were preventing the hydrogen to warm up and rise the pressure significantly above their settled release value. The occurred blast wave pressures were calculated to be as high as 13 MJ and 15 MJ. Vehicle parts found over 100 m away. Resulted hydrogen fireballs detected with a maximum diameter of 7.7 m immediately after the rupture. *"The results of these tests suggest that the danger zone associated with hydrogen cylinder rupture extends to a radius of roughly 100 m from the hydrogen vehicle."* [23]

Fig.28.: Fireball captured by IR camera, from left to right, 10 msec, 45 msec, 107 msec after the rupture [25]

3.9. Over-usage related accident

A self-confident Hungarian vehicle owner in 2015 additionally built into his, from factory CNG powered LCV three piece of type 3 tanks. His action is even stranger to understand, since the clear sign on the tank: DO NOT USE AFTER 08/2012. This intention could not be bigger and better displayed.

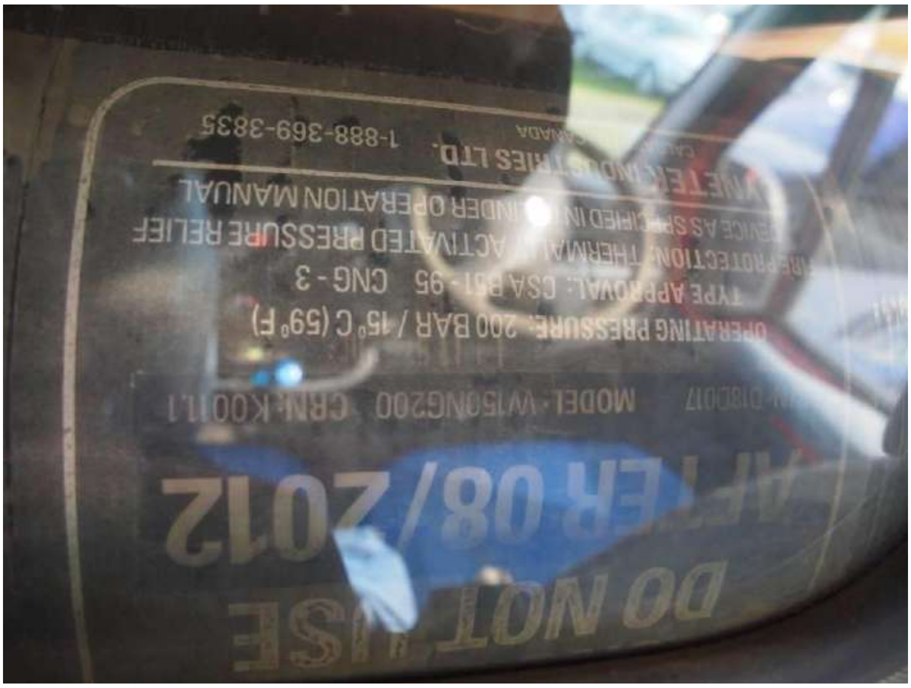

Fig.29.: The additionally built-in tanks in the luggage compartment appear through the window on the LCV cabin back wall. The driver had this view as turned behind. Could not face to even bigger notice that the tanks are expired more than 3 years earlier [Author]

He bought the tanks under a miserable circumstance, without knowing the origin, the seller, and it was relatively cheap. The vehicle owner built a self-made supporting system, connected the pipes to the vehicle original system, and fitted some old valves into the added tanks, which last feat alone would be enough to describe his action as highly dangerous and punishable act.

As finished the “tuning”, opened the valves and found that everything works properly. Drove to the CNG station and without any notice about the modification to the employee, let the vehicle fill. However, the station employee at a certain point recognized that the normally filling quantity exceeded and let the filling continue. Somewhere around 100 bar one tank was ruptured into two parts. The blast wave was speed up the part of the tank to tore off the vehicle’s sliding door, flying into a parking urban bus’s window, about 6 meters away. Attacked the handrail, from where changed the direction and flew out through the front window. Another part of the tank simply trampled to the ground a fuel dispenser. The employee seriously injured. The gas was not ignited, and no flame occurred, because of natural gas. In the presence of Hydrogen that for sure would happen.

Fig.30.: The carbon fibre wrapping was capitulating way under the design pressure. In the middle, the metal liner material flown. [Author]

4.0. Hydrogen filling infrastructure

The hydrogen fuelling infrastructure is currently in embryonic phase, based on the missing business case, since the vehicles are not yet existing in the quantity as it would needed. Need to note, a hydrogen fuelling equipment cost far too much, 2-4 times the price of a CNG equipment. However, even at the CNG case the CAPEX is the biggest barrier for a wider scaled penetration.

While the chemical industry, which is producing and consuming annually about 70 million tonnes of hydrogen, from the safety point of view exist in the hand of well prepared and serious professionals. There, the potential of risk is deeply understood and the operation is fully managed accordingly. Despite, operation not without some hydrogen related serious accidents. Compare to that, the fuel retail sector acting like boutiques, with only a few hundred hydrogen sales points globally. In term of hazard recognition, it is way behind the chemical industry, far not as competent and heavily cost sensitive.

The filling station's gas equipment are even more stressed as those in the vehicles. Just having the example: for the vehicle fuelling to 70 MPa, the station's buffer storage system is working with 85 MPa nominal working pressure. Those systems are expressed by two order of magnitude more cycles as in a vehicle. The life expectancy is also thought to be longer.

In the case of vehicles arriving to the station for refuel in large number, the buffer cylinders refilled in high frequencies, the heat fluxes repeating each other before it could cool down. The danger of this kind of stress declared in the last part of chapter 2.2.

4.1. Accidents in hydrogen infrastructure and take away messages

As it is presented in the chapter 1., any incident related to the hydrogen is serious. Knowing this, the industry is recording systematically all the incidents or accidents. The purpose is mainly educative, the collected information needs to be used for develop the industrial practice. *"The sharing of lessons learned from safety events can serve to help prevent similar events from happening in the future…"* emphasized the importance of the database the presenter of PNNL, US in 2012. [30]

The European FP6 and FP7 supported hydrogen project serial, to enforce the competence within the HySafe project (2004-2009), main objective:

> *"was to strengthen, integrate and focus fragmented research efforts to provide a basis that will allow removal of safety-related barriers to the implementation of hydrogen as an energy carrier. Synthesis, integration and harmonization of these efforts aimed at breaking new ground in the field of hydrogen safety and at contributing to the increase of public acceptability of hydrogen technology within Europe by providing a basis for communicating the risks associated with hydrogen. One of the means to achieve those objectives was the development and establishment of the Hydrogen Incident and Accident Database, HIAD…HIAD is intended to become the up-to-date repository of any accidental event related to hydrogen technology."* [31]

The fact is ridiculous and unacceptable that the Hydrogen Incident and Accident Database (HIAD), online since 2010 is disappeared from the net (at least in the time being of the preparation of this paper).

The ODIN Portal is presently offline for maintenance.

Apologies for the inconvenience.

In case of questions, please contact the ODIN web administrator.

Fig.31.: This information is the only response on a white screen of the https://odin.jrc.ec.europa.eu/ as the official HIAD site

The HIAD was collecting hydrogen events in Europe since 1985, listing until 2006 together 38 events and 279 person in explosion, or fire were affected [31]. At later communication in 2012, the figure was given about 250 accidental events recorded in the data source, as well 835 people involved until the end of 2008.

Based on a publication dated in 2009, the French Ministry has an accessible collection on hydrogen events, called ARIA, which one is listing from 1992 to mid-2007 altogether 215 accidents, out of which 92 came from abroad [32]. No any other qualified data registry found from the European Union side. Compared to, the US keeps tracking the H2Incidents.org or the h2tools.org sites, (thanks to the DoE and to the contributor PNNL) hundreds of reports categorized and give summarized information to each findings, and not least give us the lessons learned notes. Nevertheless, the places, the involved companies are hidden information, the only to get as fact, the date of the accident.

Despite of a small number of the existing hydrogen fuel stations, quite a numerous incidents can be reviewed in the US library. Just examples from the issues:

- Leaking from a screw fitting on the cylinder
- PRD valve failed on the storage, at the release of approx. 300 kg gas through the vent pipe the gas ignited itself at the exit
- Hydrogen production plant high pressure hydrogen pipe ruptured, the gas ignited and explosion occurred
- Assembly error (the bolts on the ring between the coupling flange and one of the cylinders had not been adequately torqued) of a pipe-joint at a hydrogen buffer cylinder, the led to a hydrogen leak, creating flammable mixture and that ignited, detonation wave was serious.

Researchers of Japan analysed the accidents of hydrogen fuel stations in Japan and USA [33]. They paper from 2016 used databases from Japan collecting 21 hydrogen fuel-station cases between 2005 and 2014, and from the USA collecting 22 cases between 2004 and 2012. They noticed that 14 of the 21 incidents in Japan were caused by inadequate torque, sealing, and manufacturing error. Besides, *"common cause is mainly design error, that is poorly planned fatigue. More precisely, the vibration fatigue of piping joints and the fatigue of filling hoses caused the incidents in Japan."*

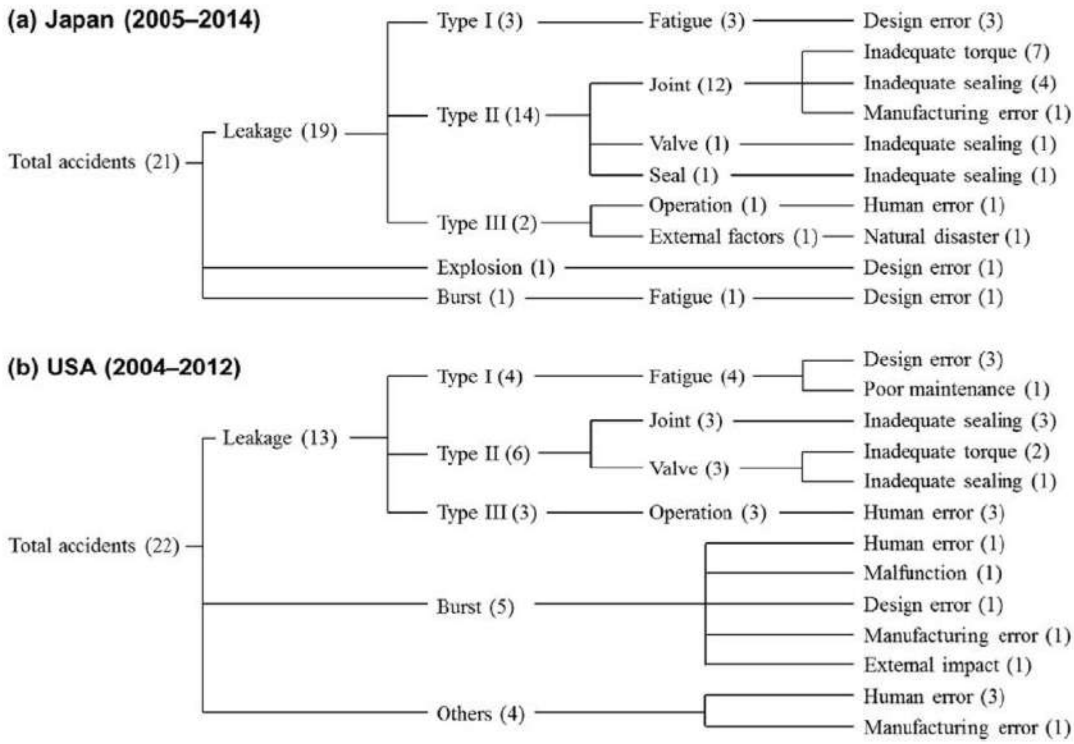

Fig.32.: The categorization of the Hydrogen refuel-station incidents and accidents from Japan and USA [33]

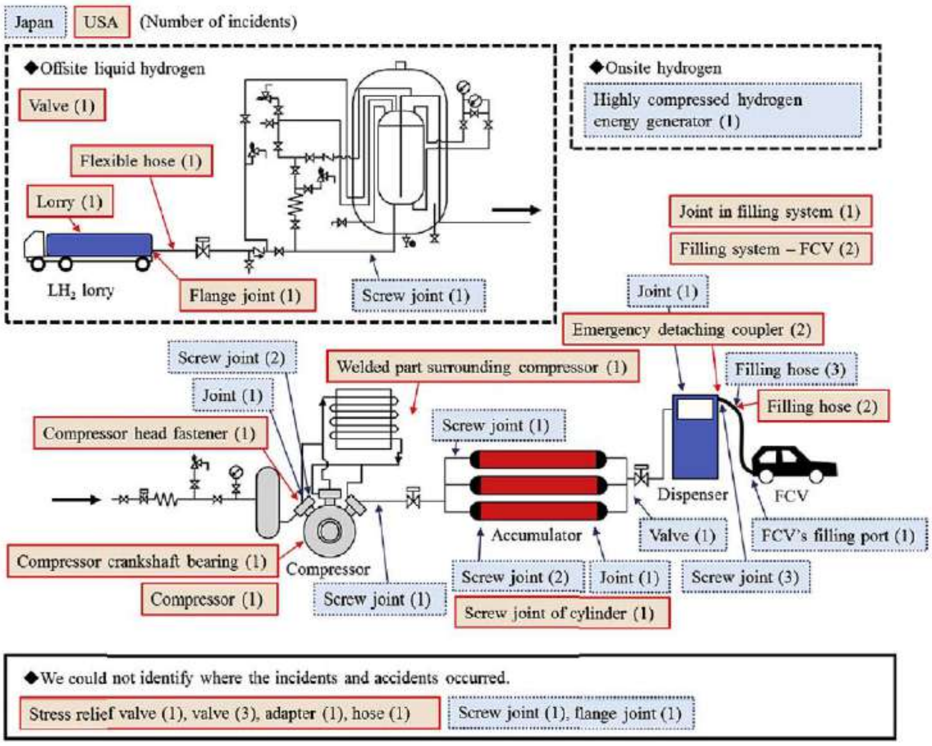

Fig.33.: The Japan researchers localized the diversified faults of the different incidents and accidents, which disseminated well on the graphic [33]

4.2. Not tight enough and the station flew away

Before the Honourable Reader would conclude, that these events happened long ago and the industry becomes out of the childhood, need to show a recent event from 2019. That was not so much presented in the media. For sure, this was not a greenhorn company's undertrained incident, first comes some facts:

- The relatively new, in 2016 opened station is delivered by a highly experienced company, which one has about 50 stations worldwide, it is the largest electrolyser manufacturer, produced over 3500 pieces since 1927;
- The hydrogen technology company's all solutions are comply with all relevant international standards and regulations;
- A JV company between the mentioned hydrogen technology company and one of the worldwide largest industrial gas company owns the station.

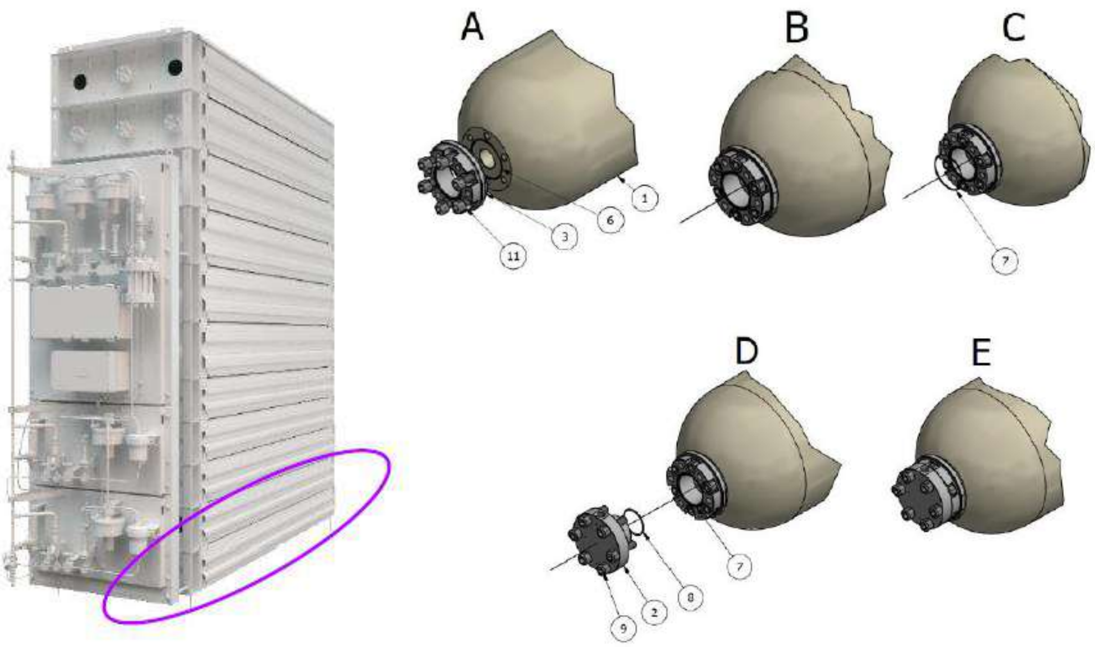

Fig.34.: The high-pressure hydrogen storage unit and the tube's assembling illustrated [34]

The unquestionably experienced hydrogen technology company explained [34], how the improper screwing resulted the accident on the only 2.5 year old station. Using the coloured drawing, the failure sequence can be explained as follow:

"- Blue bolts not torqued properly
Red sealing fails
- Started with small leak on the red sealing area
- Small leak wears red sealing out and escalates
- Large leak exceeding capacity of leak bore, causing pressure increase inside blue sealing area
Bushing with Plug lifts and the blue seal fails
- Insufficient pre-tension of bolts leads to lift of the plug and blue sealing fail immediately
- Spread of Hydrogen leaks out in uncontrolled way"

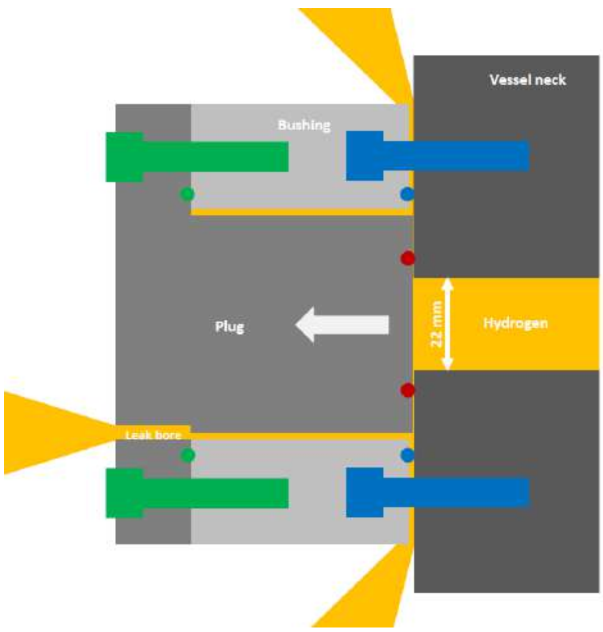

Fig.35.: The drawing for the explanation, how the not properly torqued blue bolts were resulting the start of the small leak and the sequenced progress of the accident [34]

Fig.36.: The incriminated station proper design includes fire and pressure protecting wall around the equipment room [photo: Eirik Helland Urke]


Fig.37.: The pressure wave lifted up the roof of the compartment and through away in several hundred meters [photo: Heiko Junge / NTB scanpix]

The escaping hydrogen habitually self-ignited, resulted a blast wave and damaged the building. The outside wave was so strong that on the driveway in over 30 m distance passing by vehicle, the airbags suddenly opened. Thankfully that was the only slight injury occurred by the accident. The Fire department secured 500 m safety zones, closed down main roads, and took more than 2.5 hours to get control on fire, using a robot to cool down the site.

This Norwegian accident was followed by a deep investigation, implemented short and long-term actions, safety routines, as well modification in the explosive area design. [34] Based on the actual, ongoing standardisation process, it can be sadly declared: nothing from this lately mentioned design sanctions the related industry concluded, or even considered.

4.3. Analysis by the French Ministry

Recently a small leaflet published by ARIA in 2020 [35] notice it:

> *"An analysis of 372 events involving hydrogen (produced or generated accidentally) in the ARIA database is a reminder that hydrogen remains a hazard even for proven industrial processes. For example, 73% of hydrogen incidents involved fires and/or explosions, 27% involved non-burning hydrogen leaks or hydrogen-induced stresses on materials without human consequences, 15% of fires and/or explosions involving hydrogen resulted in the death of at least one person and 43% resulted in injuries."*

While an earlier publication [32] of the French Ministry's ARIA, summarized a strong view on the hazards of using hydrogen in the industry:

> *"With regard to the origin of accidents involving hydrogen, the analysis shows that in over 70 % of the cases "organisational and human factors" contribute to the deep-rooted causes of the accidents. Constant vigilance must be called for at all hierarchical levels in the facility - management, supervisory staff, technicians, subcontractors – while bearing in mind that there is a permanent risk of ignition in the presence of hydrogen."*

Bear in mind of these words, and will find quite suggestive the following sentences:

> *"The lack of operating experience with hydrogen energy systems in consumer environments continues as a significant barrier to the widespread adoption of these systems and the development of the required infrastructure…..Although an understanding of hydrogen's physical properties is well established, and there have been many experimental efforts attempted to fully characterize risks and hazards related to hydrogen, the actual risks and hazards are best be determined within the context of real systems and real operating experience. Likewise, previous experience with hydrogen has not been with systems that will interface with consumers, but in controlled environments using trained personnel."* [36]

These words came in 2014 from the introduction of the Final Technical Report made by the working tasks group under the International Energy Agency's Hydrogen Implementing Agreement.

Despite of the known risks, the IEA not only continuously supporting, but getting louder to emphasize the hydrogen as an energy vector and fuel, only in 2020 published 5 different reports to boost the Hydrogen. Need to raise the question, what have been changed in the understanding of the associated risks in such a short time? Beside of course the fact that IEA removed the safety knowledge library from the www.ieah2safety.com, what includes the "Knowledge Gaps White Paper, 54 pages", with other might relevant knowledge contents collected by their collaborated "Task 19" working group experts. Similarly, to the European Commission Joint Research Centre related HIAD database.

5.0. Vehicle stock in Europe

After the overview of the Hydrogen related technical and safety aspects, and understanding the difficulties if all these *"will interface with customers"*, let us place these information into the context of the vehicle industry and stock. The figures from the statistical overview [37], published by the European Automobile Manufacturers Association (ACEA) can show us the complexity of the situation.

5.1. GDP and purchase power relativity across the European Union

It is not a surprise, that after 3 decades of the ruined Iron Curtain, we still need to live within the EU with a large discrepancy in the GDP per capita values, as it is well published by the Eurostat [38]. At the 2019's data analyse can find that Actual Individual Consumption (AIC) between Luxemburg and Bulgaria was 2.33x. Bulgaria was producing per capita only 53 % GDP of the EU-27 average and Luxemburg 2.6-times of the average. Here might worth to compare the extreme size of this different to that one finds in the USA. In the USA, the most advanced state is Massachusetts reaching +29,5 % GDP over the USA average, while Mississippi is struggling at 37 % lower than average value, while the next worse Idaho has 29,9 % less than US average GDP per capita value.

Volume indices per capita, 2017-2019, (EU-27=100)

	Gross domestic product			Actual individual consumption		
	2017	2018	2019	2017	2018	2019
Luxembourg	263	261	260	136	136	135
Ireland	185	191	193	95	95	95
Denmark	130	129	130	117	117	116
Netherlands	129	130	128	114	115	114
Austria	127	128	126	120	119	118
Germany	124	123	120	124	124	122
Sweden	122	120	119	113	111	109
Belgium	118	118	118	115	115	114
Finland	111	112	111	114	114	113
France	104	104	106	110	109	109
EA19	107	107	106	107	106	106
Malta	100	99	100	82	84	85
Italy	98	97	96	100	100	99
Czechia	91	92	93	84	84	85
Spain	93	91	91	93	92	91
Cyprus	89	91	90	95	96	95
Slovenia	86	87	89	80	81	83
Estonia	80	82	84	74	75	76
Lithuania	79	82	84	89	91	92
Portugal	78	78	79	83	85	86
Hungary	69	71	73	65	66	67
Poland	70	71	73	77	78	79
Slovakia	71	71	70	68	69	69
Romania	64	66	70	70	74	79
Latvia	67	69	69	70	70	71
Greece	67	67	67	78	78	78
Croatia	63	64	65	64	65	66
Bulgaria	50	51	53	55	57	58
United Kingdom	107	106	104	116	115	113
Switzerland	162	161	158	128	126	124
Norway	150	155	147	133	132	131
Iceland	129	128	126	117	118	116
Turkey	66	63	59	69	66	67
Montenegro	46	48	50	57	59	60
Serbia	39	40	41	48	48	49
North Macedonia	37	38	38	42	42	42
Albania	30	30	31	38	38	39
Bosnia and Herzegovina	31	32	32	41	41	41

Note: countries are sorted according to their 2019 volume index per capita for GDP.
Source: Eurostat (online data code: prc_ppp_ind)

eurostat

Fig.38.: The GDP per capita and the consumption per capita relative to the EU-27 average (100%) varying in the EU in a wide range [38]

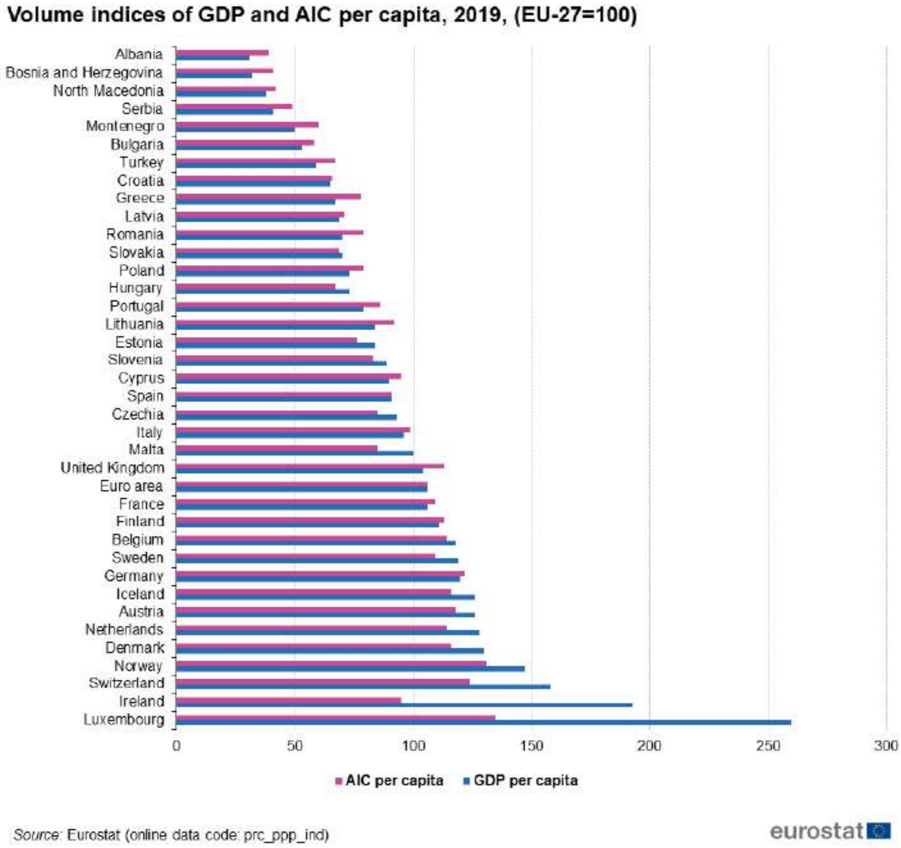

Fig.39.: Eurostat gave visibility of the EU-27 GDP and AIC values [38]

5.2. The new vehicle registration in the Member States in the shade of GDP

If we make a comparison to the economic figures with the registration data of the new vehicles per citizens, the data trend lines are similar, but the discrepancy is even stranger, as showing 5 piece to 90 piece of new vehicles registered per 1000 capita.

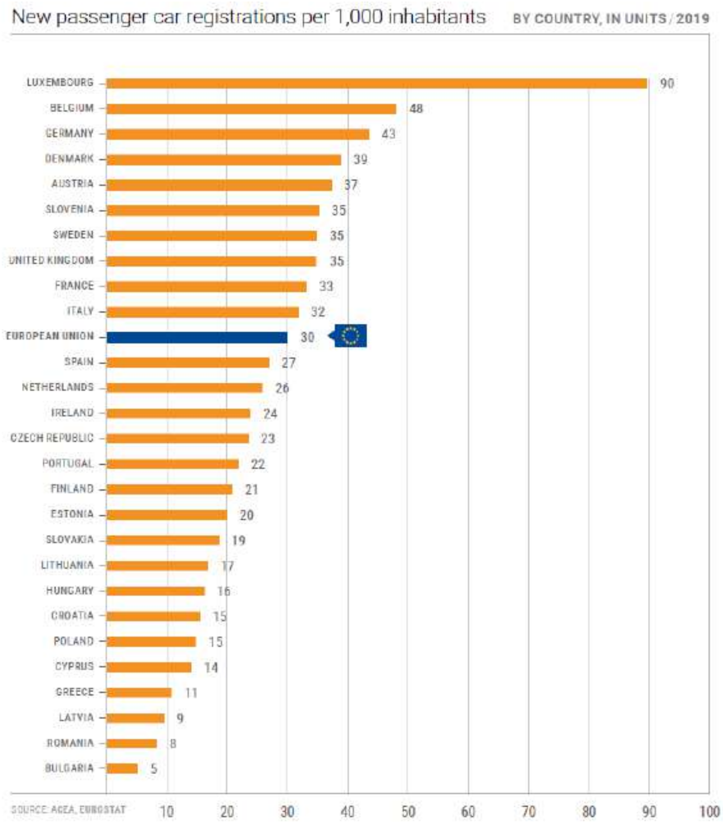

Fig.40.: The new vehicles registered in the EU countries shared to the citizen's population data [37]

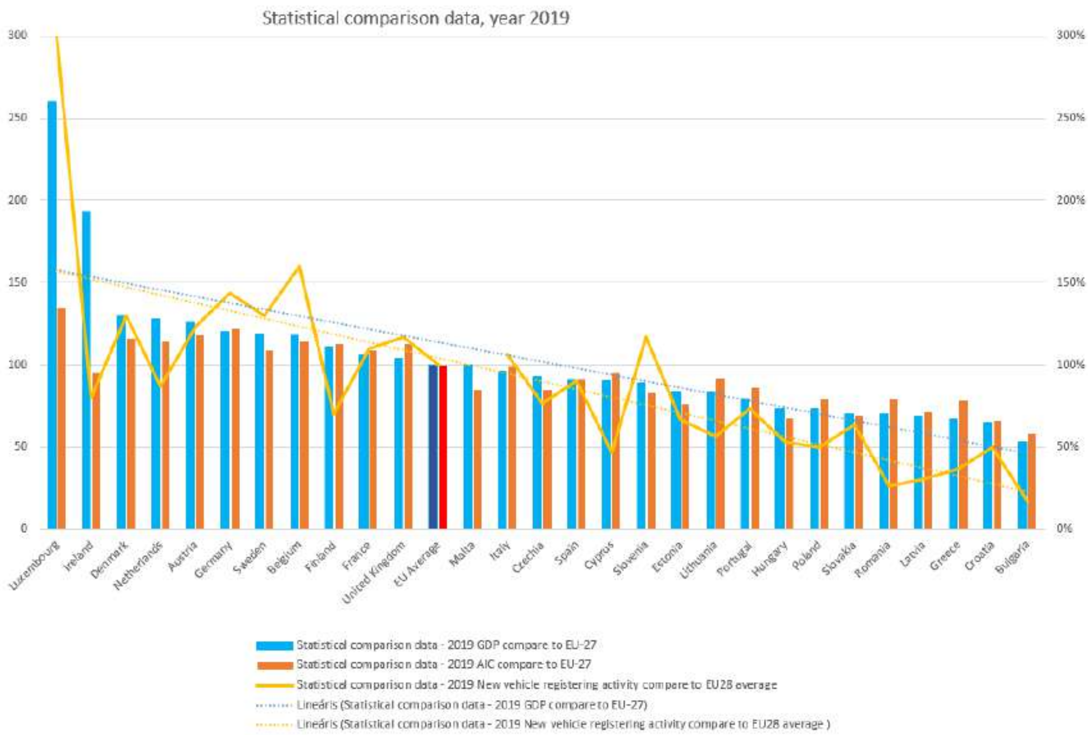

Fig.41.: The relation between new vehicle registration activities in the different EU markets and AIC is obvious, but it is not parallel. Below the „EU Average" the new vehicle registration activity trendline decreasing by a factor-2 [Author]

5.3. Motorization rate in the EU countries

The past three decades we have been accomplished since the communist regiems fired out of the countries, which now belongs to the EU, was at least enough to partly equalize the motorisation rates. At least in the number of the circulating vehicles. The different in the number of the vehicles is not more than twofold between the member countries [37].

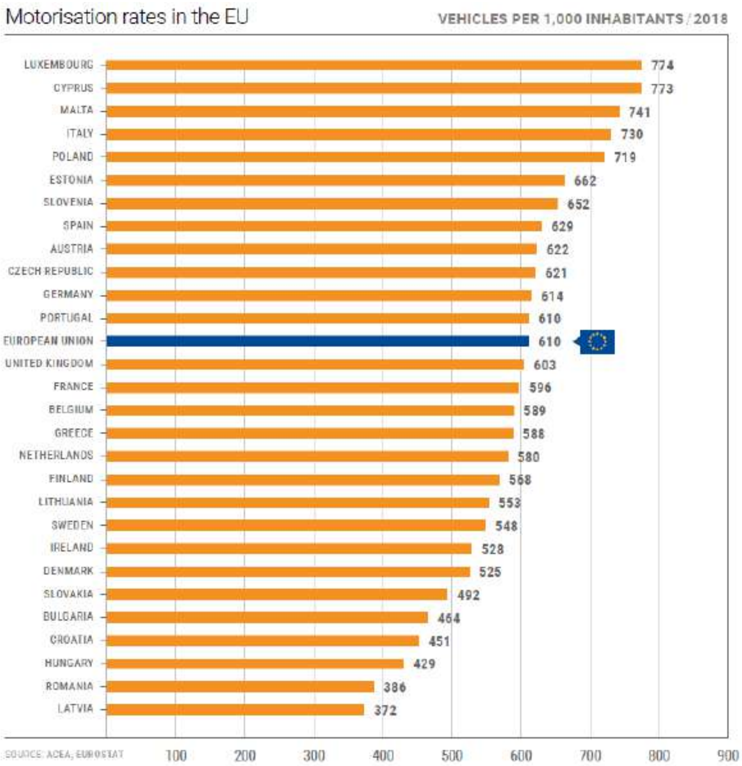

Fig.42.: The average vehicle stock is 6.1 per 10 citizens in the EU (2010), the figure is contiuesly growing, as the motorization in the post communist countries are increasing by a faster rate [37]

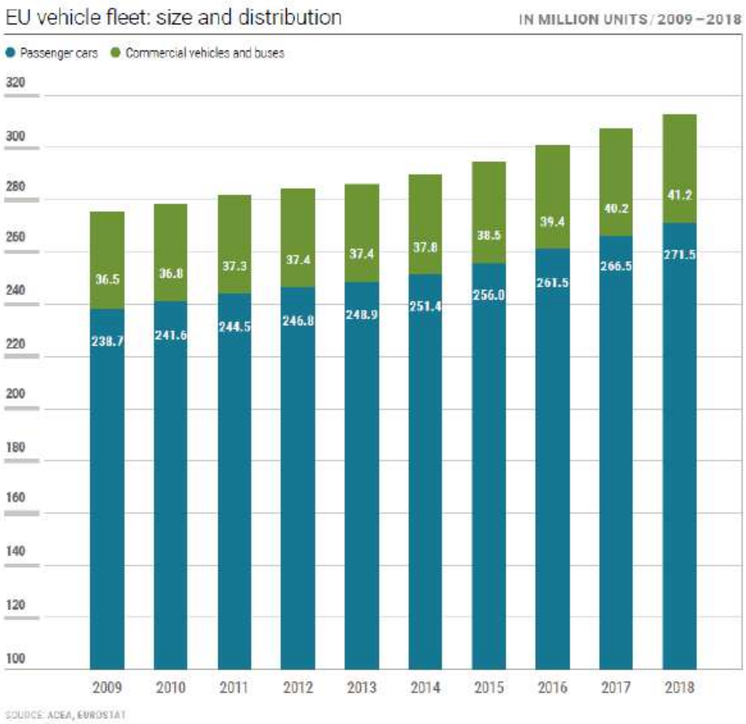

Fig.43.: Between the beginning of the decade to end of 2018, the number of the circulating motorvehicles grown 13.6 % in the EU [37]

Starting 2019 with 312.7 million motor vehicles in circulation (EU-28), and counting with the data of 10.8 years as average for the personal cars, would need as rounded 29 million new registration yearly (and take away from road the same quantity) to keep the average age of the rolling stock. Not considering the fact that the commercial vehicles have a higher average age and represents 13 % of the total number of vehicles, as it seems from the graphic. This is a very much simplified calculation also because not taking account, how the secondhand vehicles are relocated between the countries, and how much the annual growth of the park looks like. Well, keep this value as only for rough estimated needs.

5.4. How the European new vehicle sales collapsed in 2020

Fig.44.: The average age of the vehiclestock in the EU without Bulgaria, Cyprus and Malta is 10.8 years, reported in 2019 [37]. Can not be missed the significantly different figures along the two sides of the former ironcurtain

Despite of the needs of 29 million vehicles to be replaced in the EU-28 with new ones, the factual figure was for 2019 only 17.9 million, means a deficit of 11.1 million. The European market was not more than 19 % of the global. [37] Shockingly can find the newer market result for 2020, which one shows a -24.6 % collapse in the passenger car sales for the EU28, which representing a free fall by 3.77 million vehicles [39]. The commercial vehicles sales made a drop by -18.9 %. Since it is recorded, never happened such a bad result.

These new vehicle sales figures are telling us: in 2020 not even as many as 4.4 % of the total EU-28 vehicle stock have been registered. To spotlight the figures otherwise; around 53 % less vehicle arrived to the European roads as it should be, to keep the rolling stock’s average age at 10.8 years.

Fig.45.: Passenger car registration in the EU without the UK, fall by 23.7 %, in 2020 [39]

5.5. Clearing out the COVID-19 effect and found the lost entry category

It is easy to tell us, the sales figures in 2020 reflecting to the COVID-19. Having serious lockdowns, production stops, and millions lost their jobs worldwide and EU-wide either. However, the situation is far worse than a "simple" pandemic caused economic crisis. The monthly sales figures already on the January-February period clearly reflects the -7.5 percent drop. This value alone would mean a deep depression for the European Automotive Industry. Similarly lower figures is clearly visible for July to October period, where the figures are primarily not related to the pandemic, but contrary, the effect should take account, that the previous delays in the procurements had to enforce the sales in these months (as actually happened for July). To note, the basis data in September was far lower as normal, since in 2019 mass of the deliveries were affected by the delays of homologation processes.

The -7.5 % alone a minus of 1.34 million vehicles per year. In the over a decade history the only year when similar drastically drop happened in the sales, was the 2012. Well, there is a serious fundamental reason for this -7.5 % or might even stronger drop in sales. This fundamental to be found in the strengthened European regulation.

As the latest emission level, the Euro 6d regulation came into effort; it made disproportionately more expensive the small and compact vehicles. These two segments, which together continuously losing their shares, in 2019 still represented 44 % of the European market (27 % and 17 % respectively) [37]. The small and compact vehicles are the entry level. Generally can declare, these are the low budget vehicles among the new ones. Because of this nature, a significant number of the customers are simply not able, not ready to accept that unprecedented price increase. The newest level of pollution regulation and the CO_2 regulation as combined, responsible for it.

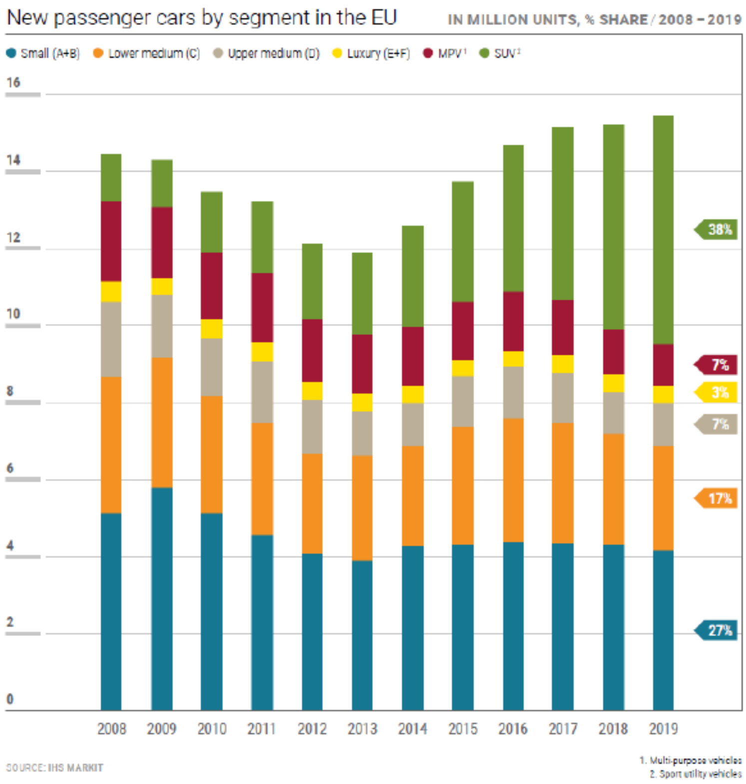

Fig.46.: The customer preference have been drastically changed in the last 12 years, the small and mid-sized car segment as well the MPV moved into the SUV category, what is just the opposite direction what the carbon-chasing political will would like to see [37]

5.6. The preference of The Customer vs. the EU politics

The small and compact vehicles a decade ago was accounting for about 2/3 of all the new sales. That market was heavily transformed to the differently sized SUVs. Let's find some explanations, why it happened:

- The SUV is an umbrella name for the higher than normal body styled vehicles, can be based on the small vehicle, most of the examples are on compact and mid-sized vehicles and goes to the large luxury SUV segment. Actually there are just rarely sold pure off-road types. Because of this, for some extra cost the Customer can purchase an upgraded category which is different to a lower constructed basic vehicle on the same platform, but not as costly as the next coming category in the regular term.
- The Customers are favouring the more spacious vehicles in the similar length and price category, what is given by the SUV.
- The Customers are also favouring the higher positioned sitting, which gives safer feelings for them.
- For the Customers the more comfort and given space are more valuable as much they sensitive for the higher consumption value, which naturally comes out from the bigger front surface and more vehicle weight.

The changing taste of the Customers resulted: since 2016, the CO_2 figures moved in the opposite direction as it was ordered by the regulations of the European Commission and the Parliament. The share of the less than 95 g/km vehicles went down. The share of the 96-130 g/km vehicles went down. The share of the larger than 130 g/km vehicles went up. All of this happened besides of the continuity of the technical improvements. It is a clear sign from the new vehicle customer preferences. The Voter's answer for such a question, which never been politically raised for the Citizens to answer it, but continuously governed without their democratic delegation.

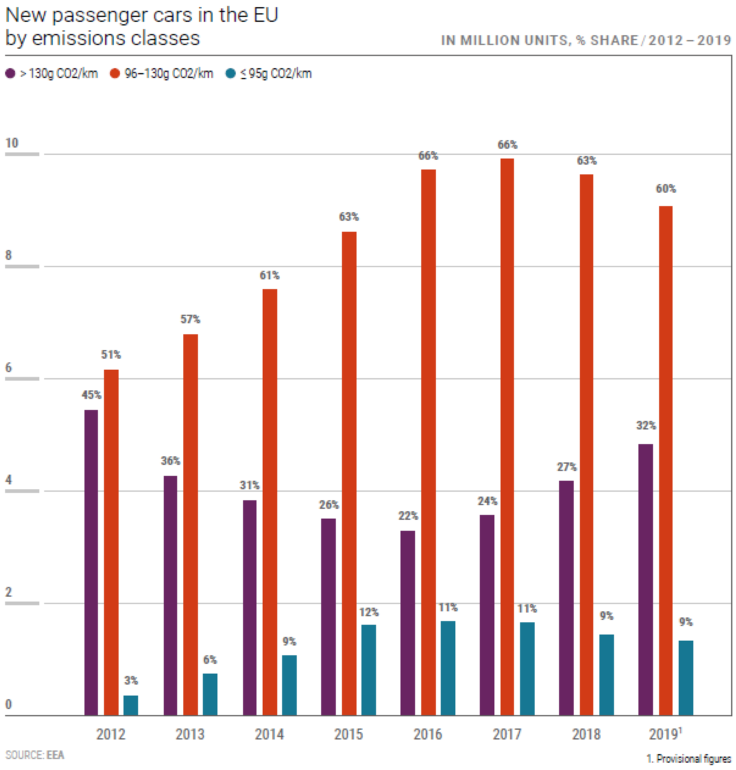

Fig.47.: It should be a clear answer how the new vehicle buyers are seeing the CO_2 reduction. Between 2016 and 2019 the share of >130 gCO_2/km passenger cars grown from 22 % to 32 %, while the overall sales went up by 4.9% in this period [37]

The real conspicuous figure will just come out later. The market share of the >130 g/km vehicles in 2020 increased towards, because the small vehicles are widely missing from the sales. Especially, if we clean out from the picture the subvention based battery and plug-in vehicle sales figures, as ridiculously called them zero and near zero emission vehicles.

5.7. The regulation accelerated vehicle stock ageing

The other painfully unfavourable result of the regulations occurred new vehicle price increase is the ageing of the vehicle stock. This progress is unfortunately accelerated. Especially this happens at the lower income member states. It is clearly detectable on the following trend-lines that the new registration numbers Europe-wide gone far from the needs to keep the vehicle park in condition. If comparing the available size of the rolling stock with the new registration figures – and not considering the large scale used car imports from the western to the eastern countries – the GDP dependent correlations exist in the numbers.

There is a wide different between refreshing the existing vehicle park by 11.6 % new vehicles in one Member State comparing to another State, where it is less than 1.1 %. Furthermore, 67 % more vehicles per capita existing in the first as in the last here mentioned country. There is no need for further argumentation: not possible to keep forcing the same regulatory measures.

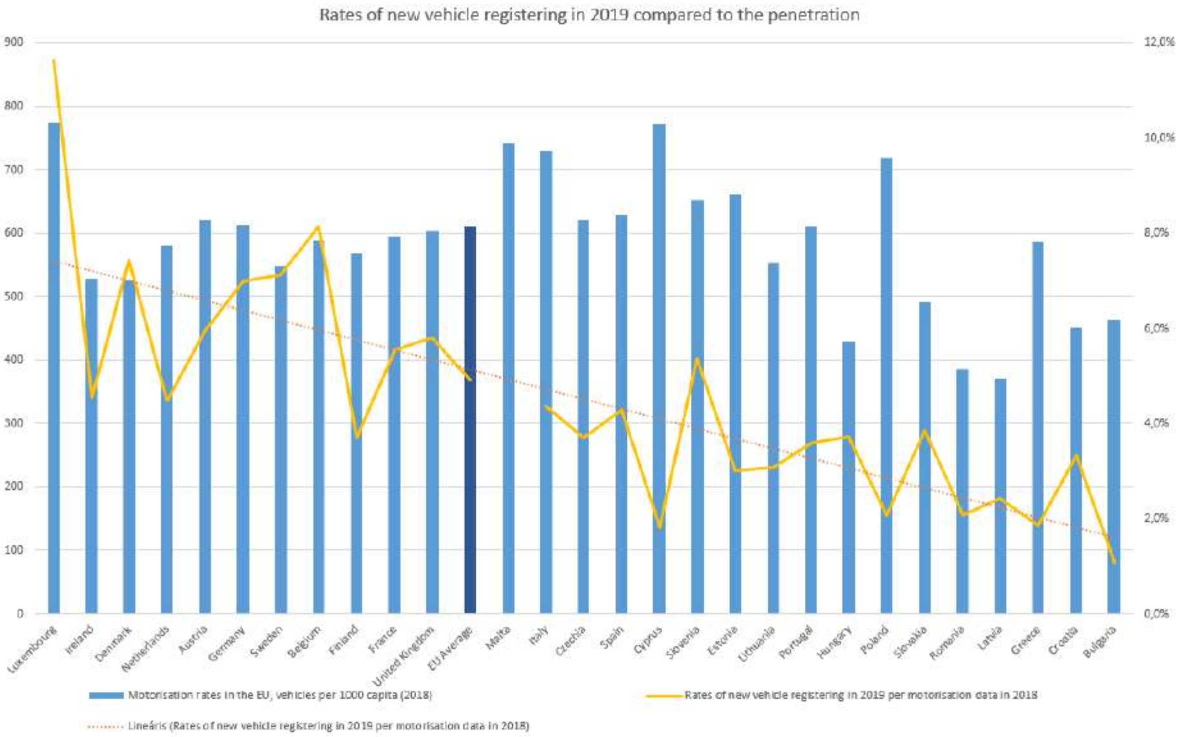

Fig.48.: There is a 10-fold different between Luxemburg and Bulgaria in the new vehicle registering per circulating vehicle numbers. The relation between GDP and the speed of fleet refreshing is not even close to show a parallel trend line [Author]

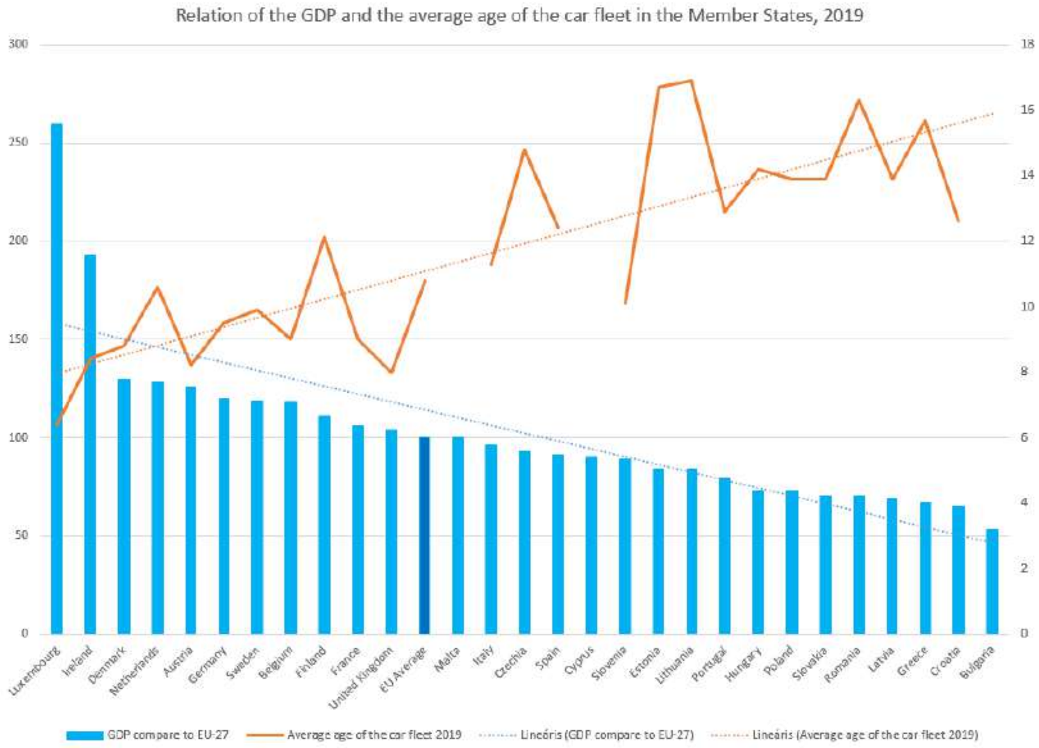

Fig.49.: Obvious inverse relationship can be found between the GDP and the average age of the vehicle fleet across the Member States. Data for Malta, Cyprus and Bulgaria not released by ACEA [Author]

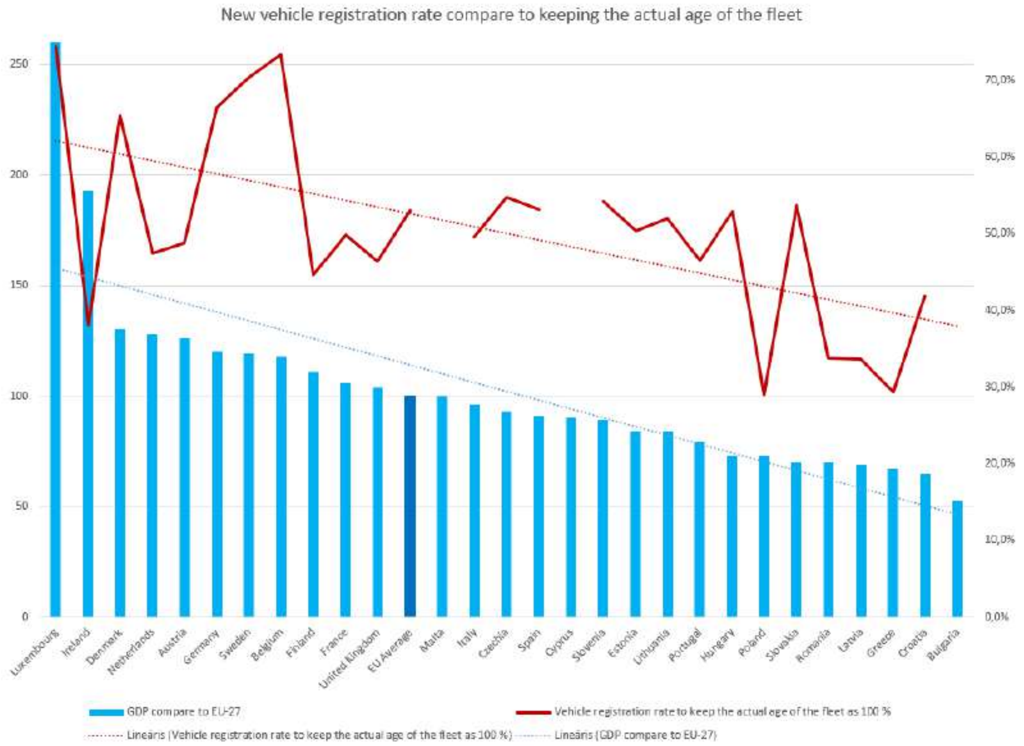

Fig.50.: The new vehicle registration numbers in 2019 in none of the Member States are supporting to keep the average age of the rolling stock. Even in Luxemburg registered only 75 % of that vehicle quantity, which could keep the age-level. At the low end, the figure is under 40 % of that new registration, which would keep the age of the very old vehicle park [Author]

5.8. The parallel truth of the vehicle fleet's age and safety

Not to miss the safety aspects of the vehicle stock's widely different condition, across the European Member States. It is more than loquacious to see the number of road fatalities per capita. The road fatalities in 2019 was 48 per million as the European average, around 30 in the well being countries and tended to be from 60 up to 90 where the rolling stock is old [37].

At this point, an important measure comes to be not only the age of the vehicles – which determinate the level of the built-in assistant systems – but also the quality level of maintenance, and so the State of Original Vehicle (SoOV).

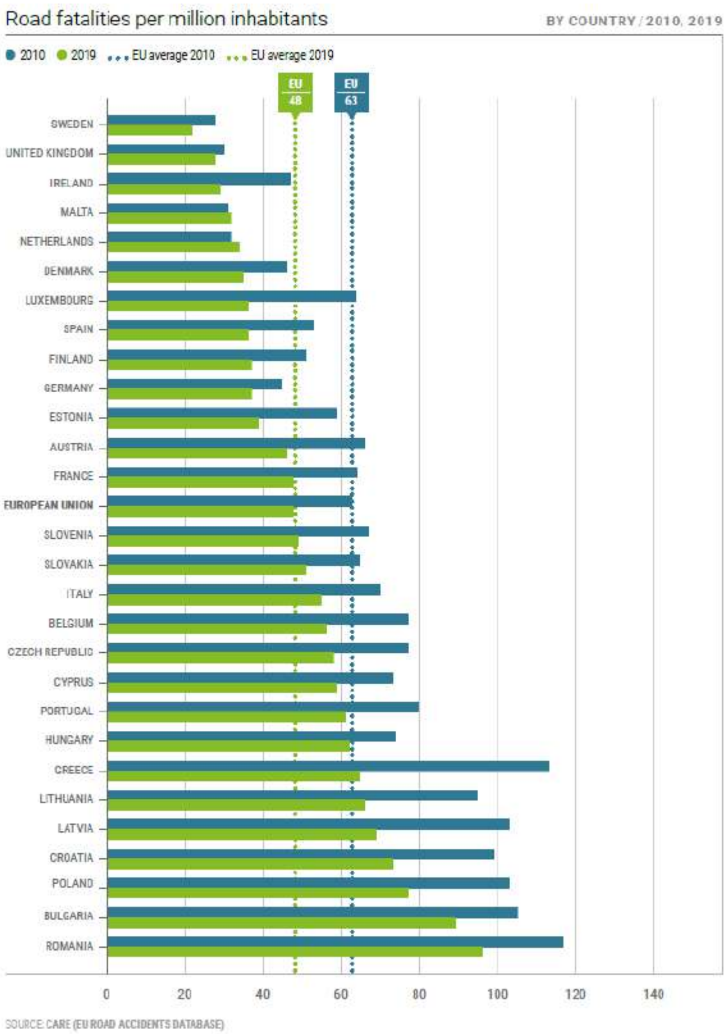

Fig.51.: Road fatalities, again it is closely correlated to the age of the vehicle park and that is to the GDP [37]

Do not need a high scientific prove to claim for; in the lower incoming member states the vehicle owners are ready to spend drastically less amount for maintain the technical condition of the vehicles. In the real life the vehicles are falling out from the branded service network. This generally cancel the vehicle-type specific treatment, maintenance, repair, which should provide by the trained personal on the knowledge basis of the vehicle producer. Generally, other than oil change, only the not avoidable repair are spent for the older vehicles. On this reason, parts are built in from the aftermarket production, without the approval of the OEM. On this nature degrading even faster the technical performance of the vehicle, the SoOV.

Europe could not yet organized an equal treatment of the vehicle owners. An example: the recalls are not treated equally, especially if a vehicle ownership moved from one member state to the other. In such relocation, it is almost sure that the new owner never get a notice from the producer about a recall, even within the EU. The OEMs (or they importer companies) are often cancelling their warranty liabilities also, if the vehicle is elsewhere re-registered.

Nevertheless, these questions are not even popping up at the ages of any vehicle above 10-12 years. In 2019, half of the member states (13, to be precise) had the average age above 12 years of the passenger vehicle stock, four of those are close, or far above the 16 years. Still talking about the average.

For Hydrogen tanks, the limitation is 15 years.

5.9. The vehicles and the incomes of the state budgets

ACEA concluded 14 major economic countries from the EU, where the governmental incomes only related to the vehicle and parts sales, and registration like taxes, were approximately 140 billion Euro. An amount, what is close to 10.000 euro per each sold new motor vehicle. The ownership and fuel related taxes without highway tolls are tending to be 290 billion Euro. This amount is in order of magnitude 1200 euros per each circulating motor vehicle, in every year [37].

In order to secure these revenues, it is also necessary to maintain the safety conditions and manage the modification needs, even priory the hazard occur.

6.0. Disputable safety aspects of the hydrogen-powered transport route

As it was seen in the previous chapters, there are a long list of dubious solutions and systems exist. As most of the cases, the biggest obscure is the human user. Compare to any chemical industrial solutions, the wide-scale deployment of the hydrogen can not be supported by a closed, and well monitored, precisely regulated, skilled, and highly trained business environment. As it is cited earlier: in consumer environment, it will interface with customers.

In the previous sections quoted many, deeply knowledgeable industrial experts were equally claiming for the associated risks of the hydrogen application. This risk is nothing-same level to petrol, diesel, compressed gas, or petroleum gas applications.

A robust risk analysis should be done before wondering any wide-scale rollout, and not only the applicable technology (which is even not delivered a calming result), but also should put to the table the machine – system – human – timeline coherence analysis.

For start, the next coming sub-points offered to integrate, weight them, and prepare hazard reduction solutions before any market entry would take place.

6.1. Hydrogen leakage

Almost any quantity which releasing to the environment is forming highly flammable mixture with an extreme low ignition energy requirement.

The human body cannot realize the hydrogen leakage, not like at methane, which one is odorized for provide safe usage. The fuel-cells are not tolerating the odour content like in the natural gas.

As it have seen, the leakage in almost any intensity means serious, invisible hazard.

The first issue should have been solved: the human recognition ability of the presence the leakage and H_2 gas in a closed area.

6.2. Low energy requirement for igniting

As it is described in the section 1.4, the igniting energy for hydrogen-air mixture is extremely low and the electrostatic discharges are able for cause flame. This happens at most of the releases.

The next issue to solve: If H_2 release need to happen at any civil environment – accidentally or in order – it should have been avoid the possibility of self-ignition.

No any plan, technical solution have seen to solve this problem.

6.3. Serious detonation behaviour

Beside of the unique flammability behaviour, the risk of serious detonation is also grounded the need to consider a prohibited access to those areas like tunnels, ferries, closed parking houses, etc. for the hydrogen on board vehicles.

It should be considered the worst-case scenario before the first vehicle hit the roads, and the preventing measures need to prepare.

Here we are facing to a similar situation to the airports, where even tiny nail scissors is strictly forbidden to take with on-board.

6.4. Material degradation

Since the smallest leakage is a highly safety issue, the producer should declare first at each type approval: each built-in parts of those connected in any way to hydrogen, a specified and proved lifetime, with a safe margin demonstrated plan for replace those parts to new ones before the lifetime would expire.

This plan needs to ensure it's functionality, and without limit the vehicle owner's freedom in service choice.

6.5. Fibre based composite structures

The pressure vessels, according to the requirements of the standards and regulations are tested in many different ways. The testing experiences largely based on the knowledge, received from handling other gases. Nevertheless, the carry on studies reported wide range of unknown behaviours, when the exposures are complex. It can not be calming for any industrial player to have test results only on a few different exposure-pairs, while in the reality far more type of stresses works actively.

The current situation is similar to a newly developed medicine, which immediately after the early few lab tests just take out to the stores, to continue testing it on the people.

It is obvious, the testing procedures needs to be improved further for the Hydrogen service. Examples to improve the test criteria towards:

- exposed material to hydrogen,
- continues heat exertion, especially at storage cylinders,
- the continues, high frequency filling occurred heat exposure, which can bring the bottles way above the currently known T_g temperature, combination with overpressures above the design pressure,
- the imposing of acids,
- the scratches, combined with other exposes,

This list can be far longer.

The Safety Factor, which was calculated primarily to be good enough for fail less than $1/10^6$ piece of the tanks, theoretically means: each half a million produced hydrogen-powered vehicle will impose as a bomb. The industry is producing close to 100 million motor vehicles around the globe each year…

Not found any test method until now, which could analyse the actual condition of the composite structure, and determinate the accumulated ruptures.

It have seen, the composite structure work like the batteries: they are losing their capacity by the time.

6.6. Design of the TPRD valves

The performance of the currently used TPRD valves are not reassuringly always

- opens early enough in case of fire, or overpressure;
- at opening, release the hydrogen gas at such a flow, which would avoid safely the self-ignition.

The current TPRD solution can not be tested at the inspection, nor at the daily use. There is no sign, if it works or if does not. This situation is similar to that: if the airbag system would not have a self-checking circle. We only see that it is built-in, but no information about, if it can, or can not be activated when accident happens.

Without ensuring these basic features, the current TPRD system is far from fulfilling even the first Safety Integrity Level requirements.

6.7. Overall performance of the periodic inspection

Weaknesses:

- There is no method yet available to test the vessels.
- There is no evidence on the functionality of the TPRD.
- Hydrogen leakage is only detectable at an inspection, if a sensitive detector is available, and the inspector can check every parts, connections, etc., but the result is haphazard and only applies to that moment of the inspection.
- In these circumstances, how much the inspector can undertake from it's duties?
- If that is not given to make the inspection with 100 percent result, how the liability of the inspector is reduced?
- How can the equality of the inspection assured worldwide?

6.8. Operator liability

It is widely handled on that way, the vehicle owner/operator is principally responsible to

- assure the proper technical level of the vehicle;
- ensure the safety and environmental performance of it.

How can fulfil it in the relation of the hydrogen system, as no any possibility given for detecting failure?

Before handing over any hydrogen vehicle to any customer, should have been newly declared the limitations of the liabilities. Adaptation of the liabilities to the hydrogen-powered vehicles environment needed. The legal clarification have to uniformly rule in the whole world.

The legal protection for the operator unquestionably need to take place. Not limiting it at resales, at relocation. Not giving chance to reduce this protection by any prior accident, by missed visit of vehicle workshop, or at any in the future coming reason/explanation.

This is the same problem area, as given at an accident occurred by a self-driving car. The owner cannot control the situation.

6.9. Pressure vessel and vehicle tracking

The accumulated ruptures should safely work with all of the above exposes together, not for 15 years, but even in the life spread of a veteran vehicle. Until this could be demonstrated, other methods need to serve, like a Storage Vessel Change Program (SVCP), determinate it safely ahead of the end of the life.

This SVCP has to ensure from the beginning that a vehicle will receive the continues monitoring and ensuring the needed parts and vessel replacement, even if the vehicle is sold to another member state, to a third country, or to the third World. The SVCP should not place any responsibility to the new owner's shoulder after a resale.

The only way, what could ensure the reliable functionality of a SVCP, if the authorities in the countries all over the world would use a reliable vehicle register and tracking system, includes their required replacement program and information about each of the vessels built-in.

6.10. Avoidance of aftermarket products and used parts

Many of the parts of the hydrogen are simple, but the materials and precise quality need highest priority. However, the automotive industry is known from different quality and price levelled parts production, of which the vehicle producers are carefully selecting their suppliers. They are not only selecting based on the continuously high quality and purchase price criteria, but the supplier provided warranty-package counts too.

The rest of the parts are being sold as aftermarket product, with a low level of risk-sharing willingness and responsibility from the parts producer side.

As talking about the parts of the most dangerous system what the automotive industry ever handled, the only acceptable quality and responsibility level is that one, which the vehicle producer can accept. This means, have to avoid the usage of any parts other than the vehicle producer selected, no matter how minor and insignificant is it. Nevertheless, the UNECE regulations are declaring; the gas system components are an integral part of the vehicle type approval, listing some of those key components, but the list does not contain everything.

6.11. Popping up questions around mechanic occupation and avoidance

The responsibility to control the quality of the repair and maintenance work at the independent workshops heavily on the side of the governing authorities, and the vehicle producers have almost zero impact. Are there any authority prepared for this task? At least, is it on the horizon?

Since it was declared by the publication, which belongs to the French Ministry *"hydrogen remains a hazard even for proven industrial processes"* [35] how could be handled safely by a single, privately owned workshop?

What going to be the scheme to avoid the prone to tinkering nimble-fingered owners, to touch the gas system?

As the accidental vehicles are tended to be repaired in the body workshops (which services are not branded by the vehicle producer, especially this is the case at a certain age of the vehicles), how is going to secure the knowledge basis, for ensure the safe working environment? How will provide skilled and well-trained mechanics and fault-free technology background, clearly documented procedures? All-in-all, how the whole warranty-chain will build up to keep the hydrogen system related responsibility away from the owner?

Because even a single point will be missing from this warranty-chain, after an accident the hydrogen powered vehicle should be considered as non-reparable, what have to effect the insurance costs, making these type of vehicles even more not affordable.

At this type of questions need to know, the gas vehicle (especially, but not uniquely the hydrogen powered one), cannot even enter to any workshop, without having there a proper gas detection equipment and emergency system, protocol, etc.

The vehicle that need to be repaired, require a safe de-fuelling at almost any bodywork. As declared it earlier, the self-igniting phenomenon prohibit the simple release of the gas. Moreover, at the hydrogen it is not enough to decrease the pressure until the ambient pressure, needs to assure a total purging. Furthermore, after the repair it is necessary to ensure that the fuel-cells does not get any impurities, since 99.99% clear hydrogen is the only acceptable medium for the stacks.

Questioning further, how to avoid any repair – belongs to the gas system – build-in used parts from another dismantled vehicle?

How is going to avoid any repair using aftermarket parts? Since even a single O-ring which made by not suitable compound can make a serious accidents.

How is going to prevent the modification of the gas system on the hydrogen-powered vehicles by tuners or what is even worse, by the self-confident owners?

How all of these above is going to be managed with one hundred percent success, to be safe at all of the workshops? Moreover, this question is present for all the markets, where a single hydrogen vehicle later on can pop-up even just for driving through.

6.12. Safety throughout in the refilling-network

As it became clear, the filling infrastructure is not tending to be a professional industrial environment. Simply, there is no way to grow-up to that level of organization on the possible business model, to avoid the *"organisational and human factors contribute to the deep-rooted causes of the accidents."* As it stated by the French Ministry. *"Constant vigilance must be called for at all hierarchical levels in the facility - management, supervisory staff, technicians, subcontractors"*. Contrary, the fuel-station operators are mainly small enterprises, under or without an umbrella of a multinational (oil-) company. However, even an "umbrella" take place, the hierarchical control can be detected only at the investment decision and construction level, and weakly on the operational period.

How to overcome on this and apply such a high level graded safety, which can be present in the large-scale chemical industry? Again, equally so, even in the desert.

6.13. Told us, zero-emission, but large amount of vapour

With a large number of FCEV vehicles a significant water steam emission would create. This fact is undeniably rising two uncomfortable problems.

Firstly, the roads with steam on their surface even at above the water frizzing temperature cause slippery surface and so drastically ruins the safety of the road. Around and under the zero degree it is actively providing ice surface for the roads.

> *"As a climatologist who has studied the Earth's climate for nearly forty years, I have learned that carbon dioxide is not a climate control knob; it is merely a minor player in climate change. Water vapor is the most important greenhouse gas and it accounts for nearly 90% of the net warming of the planet due to the radiative impact of the Earth's atmosphere."* [David R. Legates (2019)]

Secondly, the water vapour has a greenhouse effect, with significant quantity of the hydrogen-powered vehicles can provide warming. According to the American Chemical Society (ACS) *"water vapour is the largest contributor to the Earth's greenhouse effect. On average, it probably accounts for about 60 % of the warming effect.*"

If believed, an FCEV goes 100 km with consuming 1 kg of H_2, means 90 g/km water vapour is emitted. That is 0.9 dl/km. 1 million vehicle with 20.000 km yearly mileage means: yearly 1.8 billion litre water is vaporized into the air. Currently more than 1 billion vehicles circulating on the globe, results a total water quantity of the Lake Balaton could be vaporized each year.

7.0. Conclusion

I believe, even only one of these above sub-points 6.1. – 6.13. could not be successfully defended by the industrial players, it must mean: the overall risk associated to the hydrogen-mobility is higher than anything what can be accepted.

In that case, the hydrogen need to keep further in the industrial environment and not let leaking-out into the civil ambience.

As a final word, let me provide a special quotation here, where the personality of J. Robert Oppenheimer should give us a hidden meaning:

> *"We do not believe any group of men adequate enough or wise enough to operate without scrutiny or without criticism. We know that the only way to avoid error is to detect it, that the only way to detect it is to be free to inquire. We know that in secrecy error undetected will flourish and subvert"*.

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