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HAZARDS AND CHALLENGES OF USING HYDROGEN AS MOTOR VEHICLE FUEL

Abstract

Global interest in the use of hydrogen as an alternative fuel to classical petroleum-based fuels has already assumed the form of concepts and plans based on which, by 2030, cars powered by this most popular element in the universe are to appear on roads of almost the entire world. This is not the first attempt in the history of mankind to use hydrogen in transportation. The first approach was at the beginning of the 20th century and the "golden era" of airships. The beginning of its end was the disaster of the British airship R101. It was the largest British airship, constructed to handle connections with the colonies. It crashed in France on its way to India due to a hydrogen leak on the night of 1 to 2 October 1930. After this disaster, work on large-scale, long-range airships was halted. Almost 100 years later, hydrogen is again appearing in transport in the broad sense, but this time as a fuel. Taking into account the physicochemical characteristics of hydrogen (the widest explosive limits after acetylene and the lowest minimum ignition energy of all gases) and the high ease of its penetration through all kinds of joints, seals and valves, it is necessary at this stage to develop and implement safety procedures related to transport, storage and refuelling of hydrogen vehicles. Procedures and operating principles of hydrogen stations used for fuelling both trucks and cars developed and implemented on the territory of the United States should be a starting point before construction may be started of dozens of similar facilities in our country as declared by Polish decision makers.

Keywords: hydrogen fuel, Polish Hydrogen Strategy, hydrogen mobility, fire and explosion hazards

ZAGROŻENIA I WYZWANIA WYNIKAJĄCE Z ZASTOSOWANIA WODORU JAKO PALIWA DO POJAZDÓW MECHANICZNYCH

Abstrakt

Globalne zainteresowanie wykorzystaniem wodoru jako paliwa alternatywnego wobec klasycznych paliw ropopochodnych przyjęło już formy koncepcji oraz planów, na podstawie których do roku 2030 na drogach całego niemalże świata pojawić się mają samochody napędzane tym najbardziej popularnym we wszechświecie pierwiastkiem. Nie jest to pierwsza w historii ludzkości próba wykorzystania wodoru w transporcie. Pierwsze podejście to początek XX w. i „złota era" sterowców. Początkiem jej końca była katastrofa brytyjskiego sterowca R101. Był to największy brytyjski sterowiec, skonstruowany do obsługi połączeń z koloniami. Rozbił się on we Francji w drodze do Indii z powodu wycieku wodoru w nocy z 1 na 2 października 1930 r. Po tej katastrofie wstrzymano prace nad wielkogabarytowymi sterowcami dalekiego zasięgu. Prawie 100 lat później wodór ponownie pojawia się w szeroko rozumianym transporcie, ale tym razem jako paliwo. Mając na względzie cechy fizykochemiczne wodoru (najszersze po acetylenie granice wybuchowości i najniższą minimalną energię zapłonu spośród wszystkich gazów) oraz dużą łatwość przedostawania się przez wszelkiego rodzaju łączenia, uszczelki i zawory, należy już na obecnym etapie opracować i wdrożyć procedury bezpieczeństwa związane z transportem, składowaniem oraz tankowaniem pojazdów wodorem. Opracowane i wdrożone na terytorium Stanów Zjednoczonych procedury oraz zasady obsługi stacji wodorowych służących zasilaniu w paliwo samochodów zarówno ciężarowych, jak i osobowych powinno być punktem wyjścia przed wybudowaniem deklarowanych przez polskich decydentów kilkudziesięciu analogicznych obiektów na terenie naszego kraju.

Słowa kluczowe: paliwo wodorowe, Polska Strategia Wodorowa, mobilność wodorowa, zagrożenia pożarowo-wybuchowe

1. Introduction

Poland belongs to a group of countries in which interest in implementing hydrogen fuel in a very broad range of areas - from the use of hydrogen technology in power and heating, through transport and the decarbonisation of industry, to new technologies for obtaining hydrogen - is gradually growing. The Polish Hydrogen Strategy also covers areas related to the safety of hydrogen transmission, distribution and storage, as well as the development of relevant regulations [1]. Publicly available hydrogen stations are already being built in Poland where this fuel can be refuelled in vehicles such as: Honda Clarity, Hyundai Nexo, Toyota Mirai, Mercedes-Benz GLC F-CELL, BMW Hydrogen (7 and X5), and the first company using hydrogen-powered cars is Telewizja Polsat [2]. According to available data, fifty-three such vehicles were registered in Warsaw in 2021 [3].

According to plans stemming from the implementation of the first phase of the EU project "Clean Cities - Hydrogen mobility in Poland", an intensive development of hydrogen filling stations for both cars and city buses will take place. By 2030 there are to be 50 such stations in Poland. For comparison, in the whole of the United States as of May 2022 there are 48, of which 47 are in California and 1 in Hawaii [4].

The main sites for hydrogen production in Poland are to be, depending on the region of the country, one of the five planned “Hydrogen Valleys” - Mazowiecka, Dolnośląska, Podkarpacka, Śląska and Wielkopolska. Hydrogen valleys are geographical areas (cities, regions, islands or industrial areas) where hydrogen has a variety of uses, often including production, storage, transport and distribution with final conversion to electricity or in the chemical industry. Given the nature of hydrogen, which is extremely problematic in transport and storage, the consolidation of low-carbon transport projects, as well as high-tech industries, is the most rational approach to the development of the hydrogen economy in the medium and long term horizon.

According to declarations made by PKN Orlen, round-the-clock hydrogen refuelling stations capable of serving trucks, buses and cars (with a pressure standard of 700 bar for cars and 350 bar for heavy transport) will be built in Katowice and Poznań. The first modular station will be in Włocławek [5].

There are no widely available guidelines or materials concerning safe handling of hydrogen to be used at hydrogen filling stations in Poland. This is not the case in the United States where the hydrogen filling station giant, the State of California, publishes information intended to promote the use of hydrogen as a fuel and also to try to inform about the potential dangers that arise from its use in road transport.

2. Properties of hydrocarbon

Hydrogen is an odourless, colourless and tasteless gas. In comparison, natural gas is also odourless, colourless and tasteless, but in this case a sulphur-containing odorant called mercaptan is usually added to make natural gas detectable by smell. Hydrogen fuel would not work well with odorants because they have a negative effect on most fuel cell systems.

Hydrogen has a wide explosive range in air (4.1-75%) and can ignite more readily than other fuels, e.g.: natural gas (5-15%) or petrol vapour (1.4-7.6%). The risk of ignition of a hydrogen/air mixture is limited by its low density and hence it tends to disperse quickly so that its flammable concentration remains within dangerous limits in the open air for a short period of time, but it must be borne in mind that a small amount of ignition energy, from e.g. static electricity discharge, is sufficient to initiate an explosion of an air-hydrogen mixture.

Hydrogen fires are characterised by low radiant heat. When pure hydrogen is ignited, it burns with an invisible or nearly invisible flame, producing thermal energy, UV light energy and water vapour. A hydrogen fire gives off significantly less energy as radiation than a typical hydrocarbon fire [6].

3. Extraction, storage, transport and distribution of hydrogen

3.1. Technologies of hydrogen production

Depending on the sources, 11 types of hydrogen production processes are available, as listed in Table 1. They are based on three elementary methods:

- thermal method - steam reforming, thermal decomposition of water and gasification;
- electrochemical method - electrolysis using electricity or from hydrocarbon combustion, photoelectrolysis;
- biological method - phytobiological, anaerobic digestion, fermentation with microorganisms [7].

According to [8], also use is made of the method of radiolysis - the radiation decomposition of hydrogen peroxide.

Table 1. Basic production methods of hydrogen

Type of process	Energy	Raw materials	Technology	Efficiency
		Hydrocarbons (H)		(%)
		Non-hydrocarbons (N)		
Electrolysis	Electricity	Water (N)	Anion exchange	62–82
		Brine (N)	Proton exchange membrane	67–84
			Solid oxide cell	75–90
			Chloro-alkaline	no data
Electrophotolysis	Electro-photonic energy	Water (N)	Photoelectrochemical	0.5–12
Photolysis	Photonic energy	Water (N) / algae (H)	Photosynthesis	1.6–5
Biophotolysis	Bioenergy	Microalgae	Photofermentation	< 1
	Photonic energy	Cyanobacteria	Hydrogen from algae	1–3
		Photosynthesis-bacteria		2–7
		Fat (H)		12–14
		Nutrients (H)		
		Waste (H) / biomass (H)		

Type of process	Energy	Raw materials	Technology	Efficiency
Bioelectrolysis	Bioenergy	Biomass (H)	Microbial electrolysis	70–80
	Electricity	Hydrogenases	Nitrogen bonding	10
Biolysis	Bioenergy	Microorganisms	Dark fermentation	60–80
		Fermentation bacteria	Hydrolysis	no data
		Biomass (H) + water (N)	Reforming of the aqueous phase	35–55
		CO (N) + water (N)	Biol. shift reaction	no data
Biothermolysis	Thermal bioenergy	Biomass (H) (microwaves) + acid	Hydrothermal co-digestion	no data
				35–45
Thermolysis	Thermal energy	Water (N)	Water thermolysis	20–55
		Biomass (H) (anaerobic)	Pyrolysis	35–50
		Biomass (H)	Gasification	35–50
		Carbon (H)	Coal gasification	74–85
		Fuels (H)	Steam reforming (SR)	60–85
		Fuels (H)	Membrane reactors	64–90
		Biomass (H)	Partial oxidation	60–75
		Methane (H) + CO_2	Autothermal	60–75
			Dry reforming CO_2	no data
Thermoelectrolysis	Heat and power	Fuels (H)	Reforming with plasma	9–85
Chemical	Chemical reaction	Water (N)	Redox	3–5 wt
		Metals (N)		no data
		Metal hydrides (N)		no data
		Gaseous hydrides (N)		no data
		Metal hydroxides (N)		no data
Radiolysis	Radiation	Hydrogen peroxide (H_2O_2) γ-radiolysis	Radiolysis	no data

Source: F. Dawood, M. Anda, G.M. Shafiullah, *Hydrogen production for energy: An overview*, “International Journal of Hydrogen Energy” 2020, 45, 7 [8].

3.2. Storage of hydrogen

Hydrogen may be stored in the following forms:

1. Liquefied hydrogen in cryogenic tanks - due to its boiling point of 20.4 K (at 1 bar pressure) it requires high performance cryogenic insulation. The energy density of liquefied hydrogen is 120 MJ/kg or 9 MJ/dm^3. Liquefied hydrogen tanks used in passenger cars provide an energy density of 5 MJ/dm^3.
2. Compressed hydrogen - the standard for compressed hydrogen tanks is to store the gas at a pressure of 700 bar, enabling an energy density of approximately 4.7 MJ/dm^3, which is still ca. twice as low as in liquid form. High-pressure hydrogen containers are made of carbon fibre.
3. Bound hydrogen:
    a) Metal hydrides - Hydrides are metals or metal alloys with adsorbed hydrogen molecules on the surface. In this way, hydrogen can be adsorbed on the developed metal surface in an amount of up to 7% of the metal mass. Hydrogen is released when the metal is heated. The term “metal hydrides” also used in Table 1 refers to the combination of hydrogen with the metal matrix PMMH (porous metal matrix hydride) not to hydrides in the chemical sense.
    b) Chemical compounds, e.g. ammonia, methanol, methane - this storage method does not require high pressures or low temperatures. Conversion to hydrogen is necessary in the case of power supplies, e.g. fuel cells. Before fuel cells can be supplied with converted hydrogen, they need to be purified from carbon monoxide, which can damage some types of cells [8].

Five types of containers are used to store hydrogen under pressure, depending on the needs and expectations regarding its compression level:

Type I. Aluminium tanks (maximum pressure 175 bar) or steel tanks (200 bar).

Type II. Composite tank - aluminium body with windings made of glass fibre (263 bar), aramid or carbon fibres (299 bar).

Type III. Composite vessel - glass, aramid or carbon fibre applied to a metal matrix made of steel or aluminium. For example, a combination of aluminium with: glass fibre (305 bar), aramid fibre (438 bar) or carbon fibre (700 bar).

Type IV. Composite tanks - made of carbon fibre with a thermoplastic polymer liner. Such tanks are used in Toyota Mirai (700 bar).

Type V. Layerless all-composite tank - a carbon fibre body bonded to a proprietary epoxy resin (1000 bar). Composites Technology Development built the first prototype tank for testing in January 2014. Target applications include the aviation and aerospace industries [9].

3.3. Transport of hydrogen

The distribution infrastructure comprises the following elements involved in the fuel supply process: pipelines, liquefaction facilities, tanker trucks, storage tanks, compressor stations and vehicle refuelling pumps. An efficient hydrogen infrastructure requires that hydrogen can be supplied from the point of production to the end user: production plant, power plant or filling station.

Companies supplying pure hydrogen are already operating in the United States. To transport large quantities of hydrogen, it must either be pressurised and delivered as compressed gas or liquefied. The increased demand for hydrogen will require regional expansion of infrastructure and the development of new technologies, such as high-density chemical carriers for pipeline hydrogen transfer and high-capacity refuelling technologies for fuel cells used in bulky transport vehicles.

The location of hydrogen production has a strong influence on the choice of the optimal delivery method forced by economic calculation. For example, a large centrally situated hydrogen production plant may produce hydrogen at a lower cost because production is higher, but the cost of delivering the hydrogen is higher because the destination point is further away. In comparison, distributed production facilities produce hydrogen locally, so delivery costs are relatively low, but the cost of producing hydrogen is likely to be higher because production volumes are smaller.

In countries with hydrogen economy relatively better developed as compared to Poland, hydrogen is transported from the place of production to the place of its use via pipelines and roads in cryogenic liquid tankers or gas trailers. The pipelines are built in regions with high demand (hundreds of tonnes per day), which is likely to remain constant for decades. Liquefaction plants, tankers and gas trailers are being used in regions where demand is lower or is still emerging. There have also been attempts at delivering hydrogen by sea or transoceanic transport using tankers or chemical tankers on a massive scale [10].

At destinations where hydrogen is used as fuel, additional infrastructure components are required and are commonly used. These include compressor stations, storage facilities, dispensers, metering, safety (e.g. leak detection) and pollution detection and removal systems. The stations used to distribute hydrogen for road vehicles equipped with fuel cells should compress the hydrogen to a pressure of 350-700 bar and a mass flow rate of up to 10 kg/min. High-performance technologies are currently being developed to meet these requirements.

In order to begin using hydrogen as a popular energy carrier at all, it will be necessary to establish an infrastructure adapted to the needs of a hydrogen economy from scratch. The key problem faced by representatives of both science and industry is to develop a technology that will help significantly reduce the energy intensity of hydrogen extraction processes. Currently available solutions for producing green hydrogen by electrolysis require an energy expenditure of 55 to 70 kWh/kg. Another energy expenditure is to achieve the required compression to pressures of 350 or 700 bar required by hydrogen vehicle fuel cell technology.

The main challenges for hydrogen supply include: reducing costs, increasing energy efficiency, maintaining hydrogen purity and minimising hydrogen leakage. Further research is needed to analyse the trade-offs between hydrogen production options and hydrogen supply options, considered jointly as a system and the construction of national and hydrogen supply structures (e.g. within the European Union). Their development will take time and is likely to involve combinations of different technologies. Transmission infrastructure needs and resources will vary by region and customer specificity. Infrastructure models will also evolve as hydrogen demand grows and delivery technologies develop and improve [11].

3.4. Distribution of hydrogen

The hydrogen dispenser systems used in the US market are designed as driver self-service installations (following a brief training by a certified person). According to an official document drafted by the 2020 California Governor's Office of Business and Economic Development [6] hydrogen refuelling is "fast, easy and safe". During the entire refuelling process, the system carries out leakage checks to ensure safety conditions in accordance with fire protection regulations [12-15]. The capacity of passenger car tanks ranges from 3 to 6 kg of hydrogen, and it takes about 3-5 minutes for a full tank to be refuelled. Buses provided with hydrogen cell have tanks from 40 kg upwards, and take 6-20 minutes to fill (which is comparable to the time it takes to fully refuel a diesel bus). The hydrogen station is equipped with several different integrated safety systems which are intended to ensure safety during refuelling. If flame detectors or gas sensors detect a fire or a leak, the safety systems automatically stop the hydrogen flow, seal the storage tanks and safely remove the hydrogen if necessary. Easily accessible emergency stop switches are intended to enable manual shutdown of hydrogen equipment and shut off the gas supply. The safety system includes fire separation walls and isolation valves to maximise safety. In addition to these physical barriers, hydrogen station safety systems also incorporate electronic monitoring systems that shut off the gas supply to the dispenser in the event of anomalous flows. Analogous to the systems planned in Poland, the operating pressure at stations in California is 350 and 700 bar (referred to as H35 or H70 in the US, respectively).

The hydrogen dispenser looks similar to a classic liquid fuel dispenser and has dedicated hoses and nozzles, similarly to petrol and diesel - for both operating pressures. Newer stations (from around 2019) are provided with two H70 hoses and nozzles, with or without an H35 hose. Future stations are expected to be even larger with at least four dedicated hoses and nozzles. Similarly as nozzles provided in petrol and diesel dispensers, it is not possible to attach a higher pressure hose to the fuel filler for a lower pressure vehicle tank, in the same way that a diesel refuelling nozzle does not fit into a petrol tank.

The difference from conventional dispensers is that the amount of fuel dispensed is displayed in kilograms. Once refuelling begins, hydrogen flows from the storage tanks to the dispenser and through the nozzle into the vehicle in a closed system. For 700 bar filling, the hydrogen passes through a booster compressor or is released from high pressure buffer tanks before passing through a gas cooler and entering the dispenser. The dispenser performs automatic pressure safety checks on the fuel line, fitting, nozzle and FCEV (Fuel Cell Electric Vehicles, hydrogen powered electric cars) tank before and during refuelling. For example, if the nozzle is found to be incorrectly connected to the tank socket and fails the initial pressure test, refuelling will not start. During filling, the dispenser performs one or two pressure validation checks, temporarily (for at least 5 seconds) stopping the flow of hydrogen. The 700 bar dispenser communicates with the vehicle being refuelled via infrared systems built into the dispenser nozzle and vehicle socket. Data on the pressure and temperature of the hydrogen storage in the vehicle tank are used by the dispenser's controller to optimise filling both in terms of refuelling time and the amount of fuel dispensed.

Refuelling times are dependent on ambient temperature and the system capability to pre-cool the hydrogen. Optimally, for a 700 bar station (shown in Figure 1), hydrogen can be pre-cooled to a temperature of not less than -40 °C, resulting in a refuelling time of approximately 3-5 minutes under typical atmospheric conditions.

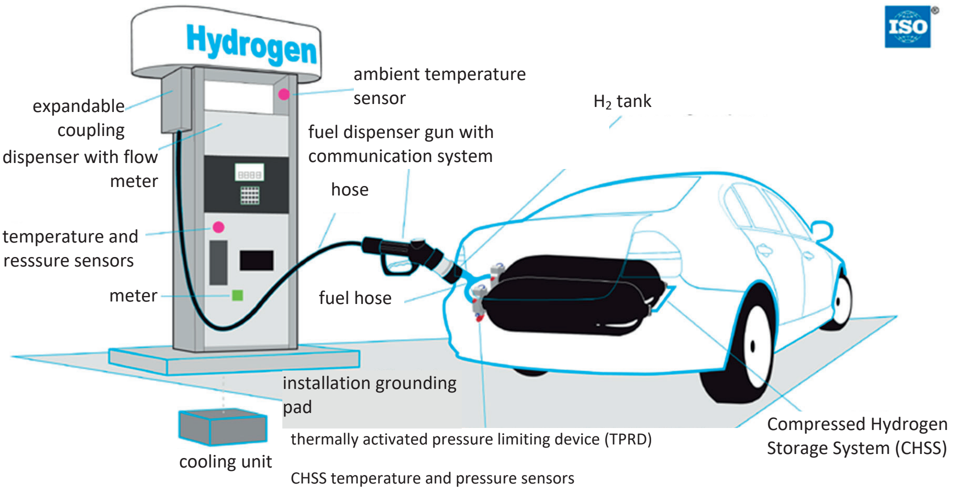

Fig. 1. Schematic diagram of the hydrogen distributor installation

Source: G.B. Vacin, T. Eckerle, Hydrogen Station Permitting (Guidebook). California Department of General Services, Office of State Publishing, Sacramento (CA) 2020.

The systems used to supply vehicles with hydrogen are controlled and monitored by electronic systems. Apart from the correct flow of hydrogen, the control system can monitor for leaks in the system - detecting hydrogen gas leaks or the presence of a flame from hydrogen combustion. Hydrogen detectors are typically placed above the likely leak site where hydrogen can accumulate and at the inlet of ventilation ducts. Infrared (IR) cameras can image heat over a wide field of view. Ultraviolet (UV) detection is used for dedicated hydrogen flame detection, but precise positioning of the sensor field of view is required due to the possibility of activating safety systems through it when exposed to sunlight, welding work or using a camera flash.

4. Fire and explosion hazards associated with the use of hydrogen in transport

The principal document containing general fire safety requirements for hydrogen stations is [12]. This NFPA standard has been developed to ensure the safety of hydrogen station users by reducing the likelihood of injury or death caused by fires, explosions or incidents involving vehicles delivering fuel to stations. An important element highlighted in this regulation is the provision of the maximum level of safety available in the event of fire and other local threats:

- to persons occupying the building or the facility,
- to members of the public in the vicinity of the building or facility, and
- to firefighters and emergency responders in emergencies

Buildings should be designed, situated and constructed so as to protect occupants in the most effective manner from injury or death by fire. This includes the safety of persons who are not in direct contact with the hazard during the initial phase of fire development. The design is intended to provide the time necessary to evacuate or defend such persons in place. Design and construction should also take into account the needs of the emergency services. This includes ensuring free access to the building during rescue operations and maximum safety for rescuers.

The risks to be considered at the hydrogen station include:

1. Uncontrolled release of hydrogen.
2. Fire affecting hydrogen containers, pipelines or distributors.
3. Fires of hydrogen.
4. Mechanical failure of the system, including containers, pipeline or dispensers.

The construction of the building, as well as its immediate surroundings, needs to assure limiting the damage caused by a fire, explosion or a hydrogen vehicle-tanker transfer incident. The facility must be designed, constructed and maintained and the activities associated with the facility conducted in a way that prevents fires and explosions and its location shall protect the surrounding area as far as possible from the effects of such incidents.

Guidelines contained in NFPA 2 (Hydrogen Technologies Code) do not differ specifically from the NFPA 52 guidelines (Vehicular Natural Gas Fuel Systems Code) applicable to flammable and explosive gas tanks or CNG and LNG distribution stations. The obligation to implement an emergency plan, training of personnel, installation of non-sparking technologies, prohibition of open flames, etc. are identical.

5. Safety considerations for the use of gaseous and liquid hydrogen

The unique properties of hydrogen, which make it a valuable energy carrier or fuel, require that appropriate design and procedures be developed to avoid the inadvertent creation of hazards. The combination of hydrogen behaviour and the individual components of hydrogen fuel distribution systems determines the nature of potential risks. The main hazards and problems associated with hydrogen systems can be categorised and prioritised in the following way: fire and explosion hazards associated with very high operating pressures and low temperatures (the transition of hydrogen to the liquid phase occurs at -240°C), hydrogen embrittlement (degradation of the metal due to the penetration and accumulation of hydrogen atoms within it) and exposure to hazardous and damaging agents (exposure to cryogenic temperatures, flame temperatures, thermal radiation from a hydrogen flame and formation of oxygen deficient atmospheres caused by increased hydrogen content or inert gases such as nitrogen or helium).

Hydrogen in the gaseous phase penetrates materials and even the tiniest leaks very easily, diffuses faster and has greater buoyancy than other gases. Released hydrogen rises rapidly and spreads out, but if it is in a confined space, it can accumulate under ceilings, footings or roofs in concentrations which can create an explosive hazard.

Ensuring the integrity of hydrogen storage tanks and pipelines is one of the greatest challenges in building and operating such systems. Hydrogen leaks are virtually undetectable without the use of detection systems, and for large leaks the only indication of its existence will be acoustic effects. The rate at which hydrogen passes through containment barriers depends on the material of the barrier. The permeation rate at ambient temperature is exceptionally low for metals, such as steel. In contrast, polymeric materials are characterised by a bigger permeability and there is a risk of hydrogen accumulating to concentrations between the lower and upper explosive limits, especially if a leak occurs in a room with a small volume. Due to its low density at ambient conditions, hydrogen is normally transported and stored in gaseous form at elevated pressures.

The consequence of contact between liquid hydrogen and the environment (due to its low temperature) is that all other gases except helium will pass into the solid phase. This can lead to blockages in pipes, orifices or shut-off valves. Reducing the volume of condensing gases can create a vacuum that could draw in even more gases in a process called cryopumping. Should the leak continue over a longer time, large amounts of solidified gases can build up, displacing the liquid hydrogen. When the temperature in the system rises, if the system is shut down, e.g. for maintenance, the pressure may rise rapidly or flammable or explosive mixtures may form as a consequence of the regasification of the accumulated gas mixtures [16].

5.1. Fire hazards

The main risk posed by hydrogen systems is the uncontrolled combustion of accidentally released hydrogen. This is due to the high probability of hydrogen escaping through the smallest leaks to form flammable mixtures, the ease with which they ignite, and the possibility of high-energy processes such as fire or explosion.

Low-energy sparks (not perceptible to humans) from electrostatic discharges may also serve as an initiator of ignition or explosion in hydrogen-oxidant mixtures. Due to easy ignition of hydrogen-oxidant mixtures, the majority of methods aimed at reducing the risk of a hydrogen fire involve the separation of these substances, which is virtually impossible in above-ground installations other than by creating hydrogen systems that are as tight as possible.

There are several types of hydrogen combustion: combustion at the leak point, deflagration and detonation.

In the case of a spot fire, the fire is completely smokeless and, depending on the rate of hydrogen oxidation, it can look much like a working Bunsen burner, up to effects similar to those produced by high-energy jet engines and which are virtually invisible in white light. Hydrogen flames, on the other hand, emit much less heat and radiation in the ultraviolet band, which can lead to burns similar to those from solar radiation.

In confined spaces, hydrogen fires (for a stoichiometric mixture with air) can lead to a pressure increase of up to eight times the initial value [16].

5.2. Explosion hazards

Besides acetylene, hydrogen is one of the most easily detonated gases. When a mixture of hydrogen and oxidiser is in the explosive range, once the activation energy has been supplied, the resulting flame will spread rapidly throughout the mixture.

Combustion may proceed in two ways: either as deflagration or detonation. The difference between those two phenomena is the speed at which the shock wave travels. If the velocity is above 400 m/s, then it is detonation, and below that, deflagration. The maximum velocity of the detonation wave for hydrogen (stoichiometric mixture with oxygen) is 2450 m/s.

The shock wave may ignite further gases in its path. As regards deflagration combustion, the flame propagates as a result of heating adjacent to the flame front to the ignition temperature of the layers of the combustible mixture by radiation, convection and conduction.

In contrast, in the case of detonation, the compression in the shock wave raises the temperature of the gas mixture until it spontaneously ignites. This process is much faster than the corresponding deflagration process - a stable detonation wave travels at supersonic speed.

The pressure build-up during a detonation explosion $(dp/dt)_{max}$ is ca. 106 bar/s – by comparison the same parameter in deflagration combustion is ca. 2000 bar/s. This means that detonation of hydrogen-air mixtures can produce pressures up to 16-fold higher than the initial pressure, and up to 50-fold higher when deflated. One important point is that relief systems, designed to protect hydrogen systems from overpressure, rely on sensing pressure build-up. Detonation waves travel faster than the speed of sound, and relief systems are unable to react to an approaching shock wave to protect the system from a pressure surge.

Such high dynamics of detonation combustion arise from a different flame propagation mechanism as compared to deflagration combustion. As a consequence of these differences in pressure build-up over time, no technical safeguards exist that could limit the effects of detonation combustion in confined spaces. The use of pressure relieving surfaces is inefficient due to the speed of the process [17].

Detonation in the liquid or condensed phase may occur when the solid phase oxidant is mixed with liquid hydrogen. The effect can be comparable to that achieved if explosives are used.

Awareness of potential risks is essential for the safe operation of hydrogen systems. The answers to the following questions allow an analysis of the safety level of the designed system:

- Can any foreseeable system failure lead to the formation of hydrogen mixtures with any oxidant?
- What is the effect of the safety barriers used on the effects of an explosion, including fire separators, valves, orifices, etc., both inside and outside the system?
- What can be the consequences for the environment of high pressures, high temperatures and the rapid spread of flame fronts?

The principal cause of accidents that involve hydrogen systems is human error. As part of the work of the ISO (International Organisation for Standardisation), in-depth analyses of 96 hydrogen accidents were carried out and, based on these, the causes were then identified and categorised. A summary of the results is given below with an assessment of the percentage. In some cases more than one factor leading to a hazardous event may have been relevant, consequently the percentage shown for these categories is more than 100%.

The categories of human error were divided into several factors. Operational and work area errors were considered to be responsible for 26% of the causes of accidents, and were due to failure to ensure proper working safety conditions during installation, maintenance, operation or service. It was also caused by lack of training, lack of work procedures, or a combination of both.

Gross procedural violations (or faulty procedures) were found to be the cause of 25% of incidents. The main factor recorded in 22% of incidents were design errors, which included inadequate design of entire systems or their components, including failure to specify a safety margin for a device or omission of other relevant information, failure to consider fatigue parameters for components, incorrect choice of materials, incorrect values in design documentation and specifications due to typing errors. The use of technical solutions insufficiently verified at the level of previous studies and analyses was found to be responsible for 14% of accidents.

Other identified categories included failures, non-conformities and material defects. System component failures, defined as anomalies that occur due to system faults rather than intentional human action, accounted for up to 8% of events. Material failures accounted for 3% of events and included damage to materials and components as a result of stresses that were predicted by design standards.

Material incompatibility, such as components made of incompatible materials that were erroneously included in the design or appeared during installation, was a cause of 3% of incidents. Quality defects in the materials used were attributed to 1% of incidents.

The first four categories (human errors at every stage from design to operation and service, and failures, non-conformities and material defects) account for 87% of incidents, of which 51% involve errors in operating procedures. The third and fourth categories account for 36% of incident causes involving design and planning. The four categories therefore represent the main cause of adverse incidents and are a consequence of human error. The summary presented earlier did not include the location of such incidents: up to 20% of the events occurred in valves for various reasons, and further 21% were due to air contamination of the systems.

The above statistics indicate two basic objectives for the design and operation of the hydrogen system:

a) minimising the possibility of human error,
b) implementing a system or systems that are capable of remaining safe in case of such an error in the hydrogen system.

The causes of accidents and the extent of their consequences may not only directly affect system operators, but may also arise from a lack of understanding of the physico-chemistry of hydrogen, the technical parameters of individual installations at particular locations and the effects of the accident on the environment by the rest of the personnel in the organisation.

The safe handling of hydrogen systems is a team effort that requires effective communication, well-designed and delivered training, and an effective and efficient control system within the organisation. Individuals at all levels should receive training consistent with their involvement and responsibilities. When handling large quantities of hydrogen, it may be necessary to coordinate activities with the surrounding community, including firefighters and local emergency management structures [16].

6. Technical security measures

6.1. Fire detection

As mentioned earlier, uncontaminated hydrogen burns with a flame that is practically invisible in the white light band. Many methods and types of detectors are available for hydrogen flame detection. Some important factors to consider when selecting a hydrogen flame detector are:

- detection distance and size of the protected area;
- resistance to false alarms from light sources such as sunlight, lightning, welding and others that may interfere with the proper functioning of the detection system;
- response time of the detection system;
- sensitivity to the relevant radiation spectrum.

Hydrogen system operators should be equipped with a portable hydrogen flame detector for use in and around the hydrogen system. The simplest and inexpensive way to detect hydrogen flames is the use of ordinary straw brooms scattered in the areas of the most likely hydrogen leak and its ignition. Mobile flame detectors do not provide the full range of protection around large hydrogen plants. Flames can go undetected at massive hydrogen leaks during gusty winds, which can endanger personnel and prevent safe evacuation [16].

6.2. Active firefighting systems

When dealing with a hydrogen system or installation, the provision of a fire protection subsystem should be considered. Fire protection equipment may consist of:

- system (automatic or manual) to shut off the hydrogen supply from the tank,
- sprinkler or water spray system,
- powder or halon replacement extinguishing system.

Small fires can be extinguished with powder extinguishers, carbon dioxide extinguishers, nitrogen or steam.

Strategies for extinguishing hydrogen fires are based on the assumption that the fire is not extinguished until the hydrogen source has been isolated, as there is danger of spatial explosion of a large flammable cloud that could be formed from unburned gas. Water can be safely used for defensive action in the vicinity of a hydrogen fire [16].

7. Safety procedures

Safety procedures must be developed at the earliest possible stages of design and planning. Fire or explosion scenarios need to be described in appropriate documents (these will be, in the Polish legal system, the explosion protection document and the fire development scenarios contained in the fire safety manual).

Procedures, training materials and the training process itself should be adapted to the main hazards in the operation of hydrogen systems. This should include incidents such as:

- hydrogen leakage (controlled and uncontrolled),
- hydrogen fire,
- hydrogen explosion,
- overpressure in the system,
- hydrogen contamination (oxidiser or inert gas),
- pipeline damage,
- leakage of liquid hydrogen,
- migration into flammable clouds,
- failure of the electrical and lightning protection system,
- static electricity,
- failure of safety critical equipment, and
- inability to vent highly cooled gas or liquid hydrogen.

Particular sections of the emergency procedures must include the following content:

- evacuation procedures and emergency escape routes,
- procedures to be followed by personnel remaining to handle critical systems prior to evacuation,
- procedures for counting all personnel once an evacuation has been completed,
- emergency and medical response duties for those personnel who are to perform them;
- principles for notifying of fires and other emergency situations,
- names (or job titles) of the persons responsible for giving further information or explanations on the obligations under the emergency plan,
- actions to be taken by the personnel constituting the rescue teams,

- rules for extinguishing operations before the arrival of the rescue services,
- networking and communications,
- premedical rescue procedures,
- procedures for summoning external emergency services,
- designation of safe areas,
- procedures for external communication and contact with the media,
- rescue and recovery operations,
- establishment of a command post with predefined terms of reference for designated persons,
- inventory of hazardous materials and compilation of their safety data sheets in the designated areas.

An alarm system should be established to alert personnel in an event of an emergency situation. Emergency procedures should be reviewed periodically to ensure that they are adequate and up to date. Safety and fire service personnel should be involved in developing emergency procedures and carrying out emergency drills in accordance with the emergency scenarios developed [16].

8. Simulation of a hazard during an uncontrolled emergency hydrogen release

In order to estimate the extent of the adverse impact on the surroundings in the event of an uncontrolled release of hydrogen and its subsequent ignition and explosion of the gas cloud, the ALOHA ver. 5.4.7 program was used. It allows entering details of an actual or potential chemical release and then generates an estimate of the extent of the hazard zones for different types of accidents. ALOHA allows modelling the dispersion of toxic flammable gas clouds, the phenomenon of BLEVE (Boiling Liquid Expanding Vapour Explosions), jet fires, surface fires and explosions of gas and liquid vapour clouds.

The scenario analysed assumes the leakage of hydrogen compressed at 40 bar pressure in the gaseous phase with a temperature of 3°C equalling to ambient temperature. Note: even in the latest version of ALOHA it is not possible to enter pressures above 68 atm, which makes it impossible to perform a full simulation for high pressure vessels.

Cylindrical tank: diameter 1.4 m; height 10 m; volume 15 m^3

Mass of hydrogen in the tank: 60 kg

Damage: mechanical, leakage from a hole of diameter: 10 cm

Ignition initiation: spark, e.g. due to tank shell damage or flame

Hydrogen release time 1 min

Simulation results (range of thermal radiation and overpressure wave) are presented in Fig. 2.

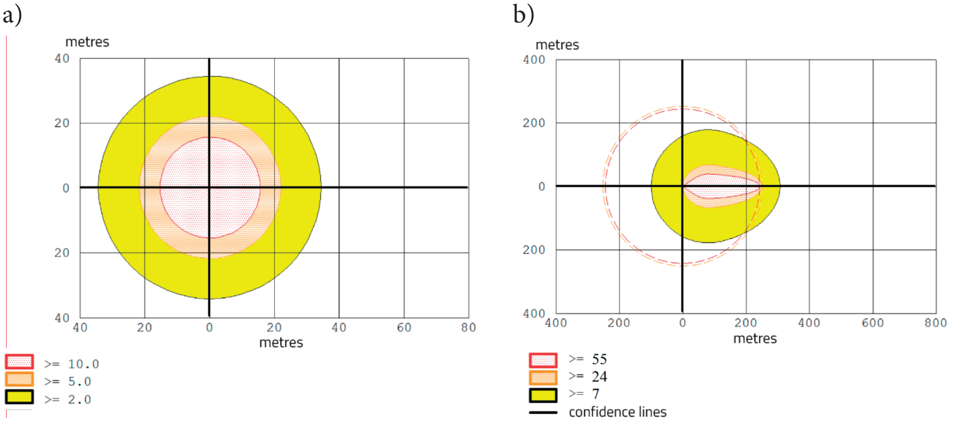

Fig. 2. Range of the danger zone: a) burns: 10 kW/m^2 - heat radiation dose potentially lethal in 60 s, 5 kW/m^2 - 2nd degree burns in 60 s, 2 kW/m^2 - pain in 60 s; b) overpressure wave: 55 kPa - destruction of a building, 24 kPa - serious injuries, 7 kPa - broken glass

Source: own study

The simulation results have shown that in the case of passenger vehicle refuelling even a slight amount of hydrogen at a pressure as low as 6% of the operating pressure could lead to: destruction of buildings within a radius of 244 m, serious injury to people within a radius of 252 m, and lead to window panes falling out within a radius of 308 m. The thermal effects of the explosion could lead to: fatal burns within 16 m and second degree burns within 22 m.

9. Summary

Looking at US solutions, it is possible to identify areas where due diligence is absolutely necessary when planning the development of a hydrogen refuelling station network. As analyses of accidents and incidents that have occurred in California in recent years have shown, the main area that requires accuracy and reliability is the design of such stations, which needs to be done by a team of experts in both building and chemical, fire and process safety engineering, taking into account the specific nature of hydrogen when designing the facilities and installations. Critical to safe operation and maintenance will be very well developed and carefully prepared training materials for operators at all levels of management as well as precise procedures for dealing with breakdowns. An equally important element will be the reliability of inspections of individual plant components, with particular emphasis on components exposed to extremely low temperatures and rapidly heated to ambient temperature, which will also be subjected to high pressures. This applies primarily to hoses and metal distributor tips, but also to other fittings, such as for supplying storage tanks. It will also be important to choose the location of tanks or installations so that the range of potential impact of a fire or explosion does not include human settlements or strategic facilities. The most crucial in risk reduction seems to be such location of tanks that even under extremely unfavourable conditions of a catastrophe no domino effect could occur. Site planning should take into account the possibility of developing hydrogen-using companies so that the negative impact of installations or hydrogen storage facilities in the event of a disaster does not exceed the safety zones originally defined. This also applies to activities from outside the industrial area that makes use of hydrogen in large quantities, i.e. the need to prohibit the construction of human habitats or installations or production facilities in the danger zone. It is also worth considering the location of hydrogen extraction sites and the development of routes such that it is not necessary to use road infrastructure such as tunnels.

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