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REVIEW OF HYDROGEN PROPERTIES, PRODUCTION, STORAGE, LOGISTICS, AND SAFETY CRITERIA

A HIDROGÉN TULAJDONSÁGAINAK, ELŐÁLLÍTÁSÁNAK, TÁROLÁSÁNAK, LOGISZTIKÁJÁNAK ÉS BIZTONSÁGI KRITÉRIUMAINAK ÁTTEKINTÉSE

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Abstract

While the physical and chemical properties of hydrogen make it an excellent energy carrier and an alternative solution to carbon-based energy sources, its colourless, odourless nature, low ignition energy, reversible Joule-Thompson effect, susceptibility to Boiling Liquid Expanding Vapor Explosion (BLEVE) and rapid phase transition (RPT) physical explosions, hydrogen damage, and hydrogen embrittlement reveal characteristics that complicate its production, storage, logistics, and pose challenges to safety in end-user applications. This study explores both the advantages and disadvantages presented by hydrogen's physical and chemical properties, discussing its production, storage, logistics, and overall economic aspects. Furthermore, it emphasises the essential safety standards that must be considered in handling hydrogen throughout these processes.

Absztrakt

Míg a hidrogént fizikai és kémiai tulajdonságai kiváló energiahordozóvá és a szénalapú energiahordozók alternatívájává teszik, színtelen, szagtalan természete, alacsony gyulladási energiája, reverzibilis Joule-Thompson-effektusa, forrásban lévő folyadékot kitágító gőzrobbanásra és a gyors fázisátalakulás okozta fizikai robbanásokra való érzékenysége, a hidrogén betegséget és hidrogén ridegedést okozó hatásai, megnehezítik a hidrogén előállítását, tárolását, logisztikáját, és kihívást jelentenek a végfelhasználói alkalmazások biztonsága szempontjából. Ez a tanulmány a hidrogén fizikai és kémiai tulajdonságaiból adódó előnyöket és hátrányokat vizsgálja, kitérve a hidrogén előállítására, tárolására, ennek logisztikájára és általános gazdasági szempontjaira. A tanulmány továbbá a hidrogén kezelésénél figyelembe veendő alapvető biztonsági előírások hangsúlyozásával zárul, amelyeket e folyamatok során végig figyelembe kell venni.

Keywords

hydrogen, green hydrogen, metal hydrides, hydrogen damages, embrittlement

Kulcsszavak

hidrogén, zöld hidrogén, fémhidridek, hidrogén betegség, ridegedés

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INTRODUCTION

The increasing population and the rising increase in energy demand are unquestionable. As humanity continues to elevate its luxuries daily, the energy need is escalating day by day like never before (Figure 1.) [1].

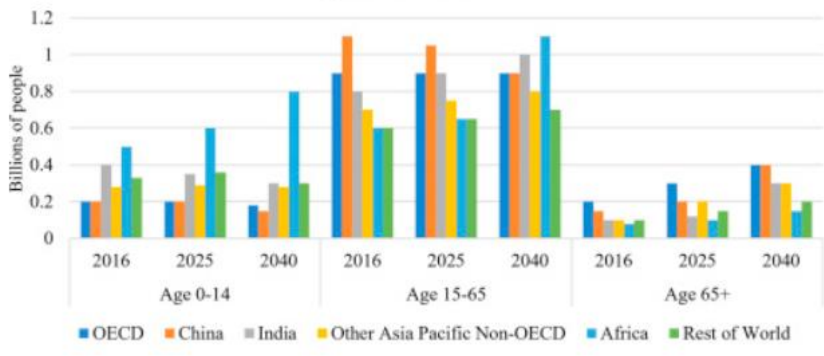

Figure 1: Population Increase of the World in different age groups [1]

The increasing demand for energy raises the carbon footprint from energy consumption (Figure 2.). This extraordinary energy need also leads to a global increase in CO_2 concentration. Efforts worldwide to promote and use alternative energies aim to reduce emissions of non-renewable gases and help decrease our footprint on this planet. However, new energy fields occasionally emerge due to technological advances and growing human luxuries, with ongoing studies in areas such as hydrogen.

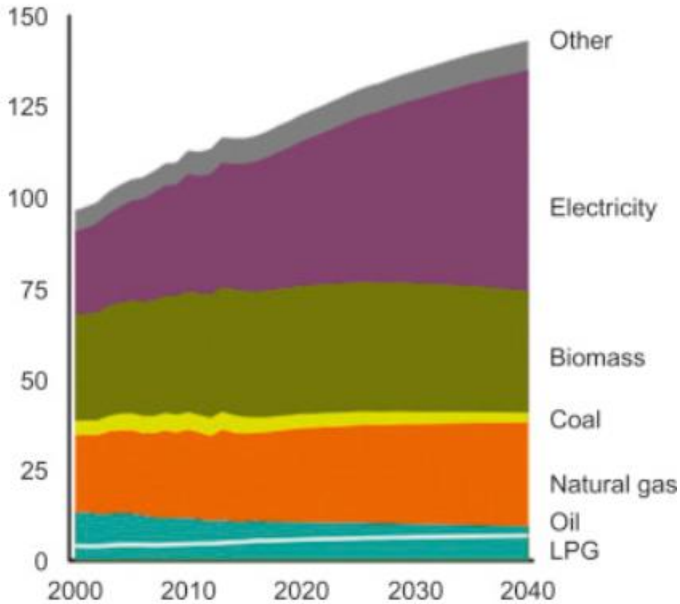

Figure 2. Increase in the consumption of the various energy fuels in the world by 2040 [1]

HYDROGEN

Hydrogen has become one of the most widely used chemicals globally because of its high energy density, lightweight, and clean burning characteristics of it. Some of the sectors that hydrogen is used the most are the chemical, refinery, metallurgy, food, glass, and electronic industries. Moreover, the high energy density, meaning high energy per unit mass, and the emission of only water vapour have fastened increased academic studies in recent years [2]. The aim of these studies is to reduce carbon emissions and enhance the calorific value of other energy sources, such as natural gas. Hydrogen is in molecular form in its natural form. It is a colourless, tasteless, and odourless gas. It can be changed from a gas to a liquid state at -252°C. It can dissolve in water and alcohol. It is the least dense gas with a density of 0.08999 g/L. The energy required for converting molecular hydrogen to atomic hydrogen is approximately 435 kJ/mol. Atomic hydrogen is highly reactive, and it can create covalent or ionic bonds with other atoms. During this formation, it follows the duet rule rather than the octet rule. In its molecular state, hydrogen exists as either para or ortho hydrogen. At -273°C, the ratio of para-hydrogen is higher. The bonding of hydrogen atoms in a hydrogen molecule changes its physical properties [3]. Hydrogen is the lightest, simplest element, quickly forming combinations with other elements, and it is the most abundant element on Earth. However, it's essential to note that hydrogen is not a primary energy source; it exists in compound states with other elements, such as oxygen in water, carbon, nitrogen, and fossil fuels. This circumstance allows hydrogen to function as an energy carrier [4]. The need for hydrogen in various sectors over the years is projected to increase, and it is estimated that the demand will go up to 519 million metric cubic meters by the year 2070. Figure 3 projects this growth in different sectors [5].

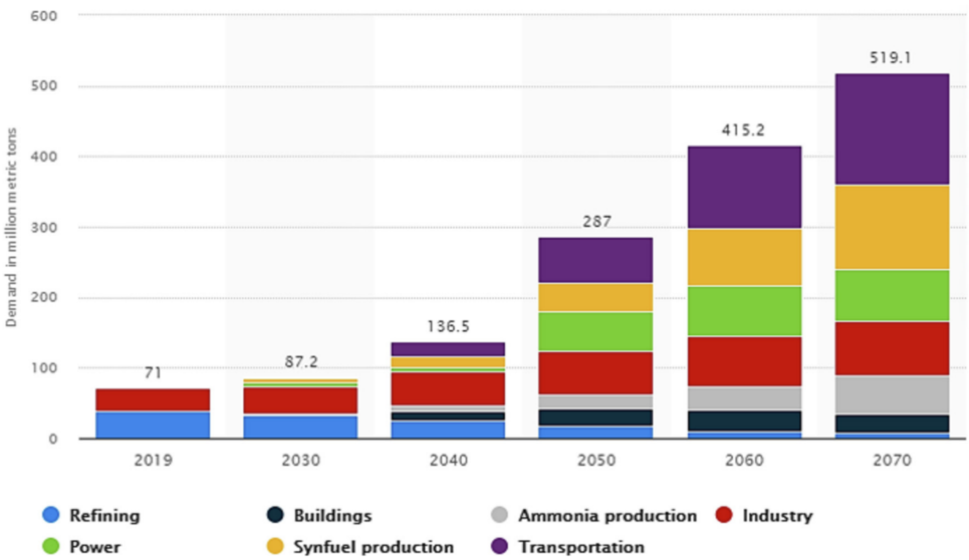

Figure 3: From 2019 to 2070, H_2 demand forecast [5]

In addition to the advantages of hydrogen, there are disadvantages that lead to the research and efforts worldwide to get focused. One of the points that makes hydrogen an ideal fuel is its high combustion energy release, but this feature, combined with its ability to be stored at high pressures, also brings up safety concerns due to the low ignition energy of hydrogen. The hydrogen density in different storage methods can be seen in Table 1 [6].

Storage form	Energy density		Density (kg/m³)
	kJ/kg	MJ/m³	
Hydrogen gas (0.1 MPa)	120,000	10	0.090
Hydrogen gas (20 MPa)	120,000	1900	15.9
Hydrogen gas (30 MPa)	120,000	2700	22.5
Hydrogen liquid	120,000	8700	71.9
Hydrogen in metal hydrides	2000–9000	5000–15,000	–
Hydrogen in metal hydrides typical	2100	11,450	5480
Methane (natural gas) at 0.1 MPa	56,000	37.4	0.668
Methanol	21,000	17,000	0.79
Ethanol	28,000	22,000	0.79

Table 1. Energy density by weight, volume, and mass density for various hydrogen forms.

HYDROGEN PRODUCTION

Hydrogen can be produced with many methods, such as steam reforming, partial oxidation, methane pyrolysis, coal gasification, and electrolysis. A significant portion of hydrogen production these days comes from steam reforming and coal gasification; these two techniques cover almost the entire production of Hydrogen in the world. The production of hydrogen from natural gas or coal is referred to as grey hydrogen. The distinction between grey hydrogen and blue hydrogen lies in the absence of carbon capture and storage in grey hydrogen production. In blue hydrogen, the process includes decarbonisation technology for the emitted CO_2. Green hydrogen is produced through water electrolysis. To mitigate carbon emissions, increasing the production of green hydrogen is essential. Figure 4 provides a schematic overview of hydrogen production techniques.

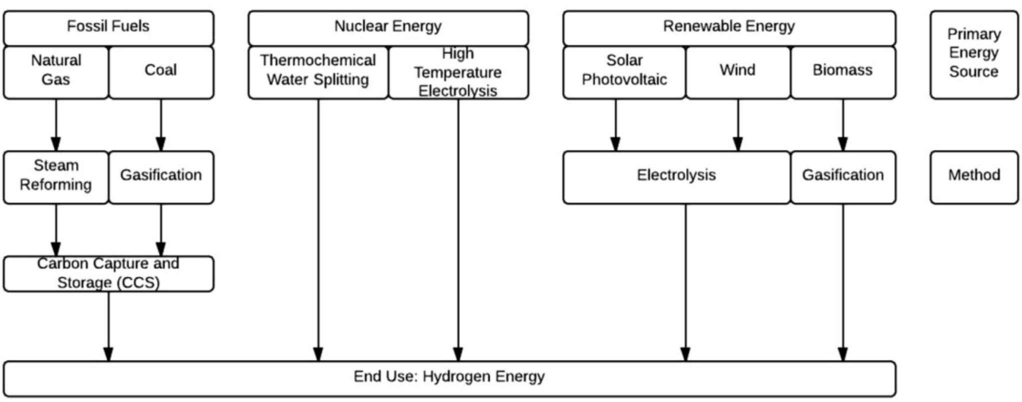

Figure 4: Hydrogen Production Methods [4]

As can be seen, alternative energy sources such as solar energy and wind turbines can be used to produce green hydrogen. The important fact here is the ability to integrate alternative energy with hydrogen production.

Steam Reforming of Natural Gas is still the most widely used technique among these techniques today. Petroleum Recovery and Refining is the most common application of hydrogen use today. Table 2 illustrates the technology of different hydrogen methods, the energy source used in this technique, the resulting product, the production cost, and the carbon emission value [5, 7].

Hydrogen Color	Technology	Source	Products	Cost ($ kg/H_2)	CO_2 emissions
Brown Hydrogen	Gasification	Brown coal (Lignite)	$H_2 + CO_2$	1.2–2.1	High
Black Hydrogen	Gasification	Black coal (Bituminous)	$H_2 + CO_2$	1.2–2.1	High
Grey Hydrogen	Reforming	Natural gas	$H_2 + CO_2$ (Released)	1–2.1	Medium
Blue Hydrogen	Reforming + carbon capture	Natural gas	$H_2 + CO_2$ (Captured 85-95%)	1.5–2.9	Low
Green Hydrogen	Electrolysis	Water	$H_2 + O_2$	3.6–5.8	Minimal

Table 2. Energy density by weight, volume, and mass density for various hydrogen forms [5]

Steam Reforming

Steam reforming is still the most widely used method for hydrogen production. The process basically involves the conversion of fossil fuel (methane) into CO and H_2 at temperatures of 700-900 °C of water steam, and 3-35 bars of pressure, using a nickel catalyst (Figure 5).

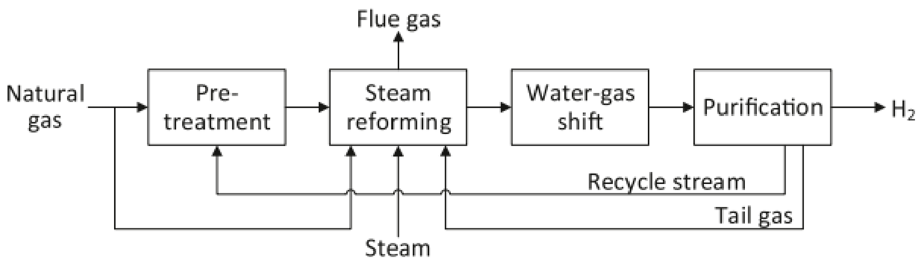

Figure 5: Primary Process Steps of Hydrogen production by steam methane reforming *[8]*

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \quad (1)$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (2)$$

Coal Gasification

As Natural gas, coal is also easily accessible, and it is known as being cheap. The production of hydrogen by gasification of coal can be a bit more expensive compared to natural gas steam. Even though it is cheap as a raw material, the technology itself can be more expensive [9].

The process of coal gasification basically involves the partial oxidation of coal with steam at high temperature and pressure. CO and H_2 are produced at the end of the reaction as a result. CO is later again reacted with steam, which leads the production of H_2 and, additional CO_2. One significant problem of this technique is the high level of CO_2 emissions. Therefore, day by day, Carbon Capturing technologies are advancing to address this concern.

$$3C + O_2 + H_2O \rightarrow H_2 + 3CO \tag{3}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4}$$

Electrolysis

Electrolysis is an electrochemical separation method of hydrogen and oxygen using electrical energy applied to water. This method has become one of the most researched hydrogen separation techniques in recent years, primarily used to obtain green hydrogen since it is entirely carbon-free.

$$1\ H_2O + Electricity\ (237.2\ kJmol^{-1}) + Heat\ (kJmol^{-1}) \rightarrow H_2 + \frac{1}{2}O_2 \tag{5}$$

Cathode:
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{6}$$

Anode:
$$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \tag{7}$$

Equation 3-5. needs cell voltage of 1.23 V to achieve the separation of water into oxygen and hydrogen, 0.4 V is needed for oxidation and 0.83 V is for reduction. However, an effective cell voltage of 1.48 V is needed for efficient water electrolysis. Even though water electrolysis is well-known technology for a long time currently only 4% of hydrogen can be obtained from water. The four well know technology of electrolysis are Alkaline Water Electrolysis, Anion Exchange Membrane Electrolysis, Proton Exchange Membrane Electrolysis, and Solid Oxide Water Electrolysis. These electrolysis methods are distinguished based on their working principles, the electrolyte used, and the ionic agents (OH^-, H^+, O^{-2}) employed. Each technology has its own advantages and disadvantages [7].

HYDROGEN STORAGE

Hydrogen storage technology can be categorized based on factors such as pressure, temperature, safety criteria, energy density, and volume. Depends on the types of hydrogen storage, the physical or chemical properties of hydrogen can change. Hydrogen can be stored as molecular form as a liquid or gas, or it can be adsorbed to the materials through very light van der Waals bonds. Atomic hydrogen also can be absorbed chemically into metal hydrides. Figure 6 illustrates different storage types both physically and chemically.

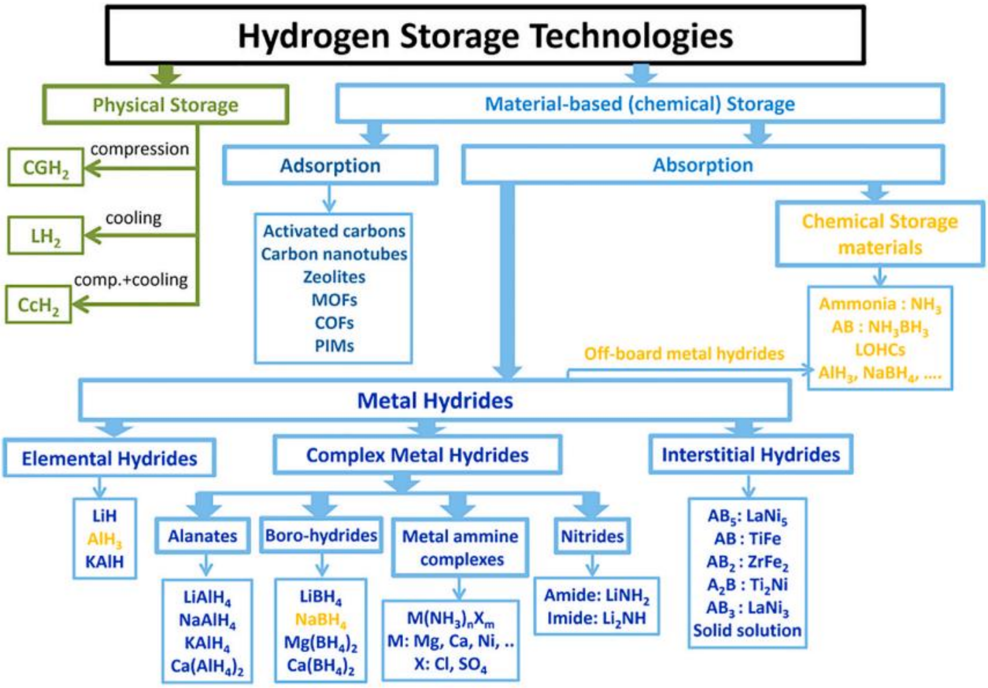

Figure 6: Hydrogen Storage Technologies [10]

Taking LPG as an example, the liquefaction of propane occurs at around -42°C or at pressures of approximately 2-3 bar. LPG tanks in cars are typically made of steel with a thickness of 3-4 mm, and the material of the tank, which operates at around 7 bars inside the car, is not critically essential. Similarly, natural gas can be compressed as a gas at pressures of 200-250 bar at 20°C, or it can be liquefied by cooling down to -162°C at atmospheric pressure. When stored in liquid form, natural gas occupies twice the volume compared to its gaseous state.

The literature explores various storage methods for hydrogen, as hydrogen gas storage requires reaching pressures up to 800 bars. Studies are conducted to reduce this pressure or to develop materials capable of withstanding such pressure.

Compressed Hydrogen

Compressed Hydrogen is a method of storing hydrogen in gas form at high pressure. This technique is still the most used in the world and can increase the density of hydrogen from 0.1 g/L to up to 40 g/L by pressurizing hydrogen to 700 bars from 1 bar [10].

To go up to these pressures and withstand these intense pressures, materials need to be designed accordingly. The material design options are metallic (1), metal with fiber resin (2), carbon fiber composite (3), composite (4), space-filling skeletons (5). And the pressures they can handle are approximately 30, 100, 450, 700, and 800 bars, respectively [11]. As is evident, a tank going up to these pressures to store hydrogen in a car will always cause safety concerns, and these safety considerations should always be kept in mind.

Liquid Hydrogen

Storing a substance in liquid form is more advantageous in terms of volume. When hydrogen is liquefied at -253 °C, it becomes highly advantageous in volume. However, issues such as temperature insulation arise in this type of storage, and current research is focused on minimising hydrogen efficiency losses and developing lightweight and stronger composite tanks capable of isolating temperature [12].

Material-Based Hydrogen Storage

Metal-based hydrogen storage is based on the principles of either adsorption or absorption of hydrogen. The varying parameters in these two techniques depend on the energy required for hydrogen to be adsorbed or absorbed by the metal and the energy and temperature needed during desorption. The advantages and disadvantages of metal-based storage generally revolve around these principles. Adsorption is on the van der Waals bonds formed between molecular hydrogen and the material, leveraging selected materials' large, based surface area. On the other hand, absorption technology utilizes ionic, covalent, and complex hybrids for hydrogen storage and relies on the principles of both storing and desorbing hydrogen during separation [10].

One of the examples of these techniques is ammonia. While ammonia is the second-most-produced chemical in the world, it can be found in liquid form, not too far from atmospheric temperature and pressure. It can be changed to hydrogen under the same parameters. While this technology is advantageous for not causing CO_2 emissions, it faces some economic uncertainties considering the conversion expenditures [12].

Metal hydrides, on the other hand, are advantageous because they can absorb and release hydrogen at room temperature. However, the economic viability of metal hydride technology varies depending on the materials' structure.

The required amount of hydrogen for a regular car to cover 400-500 km is 5-8 kg [13]. The Metal Hydride tank needed to store this amount of hydrogen weighs around 500-600 kg, creating a weight disadvantage for cars.

Figure 7 indicates that an economic comparison has been made among different storage types in terms of storage, transportation, and conversion [14]. Even though NH3 is very advantageous and can store much hydrogen compared to other storage techniques, the conversion rate is very expensive. We can decide which storage method is needed depending on the usage area of hydrogen and logistical values (such as how long it will be transported, etc.). For example, ammonia can be advantageous for long distances as it has low transportation costs.

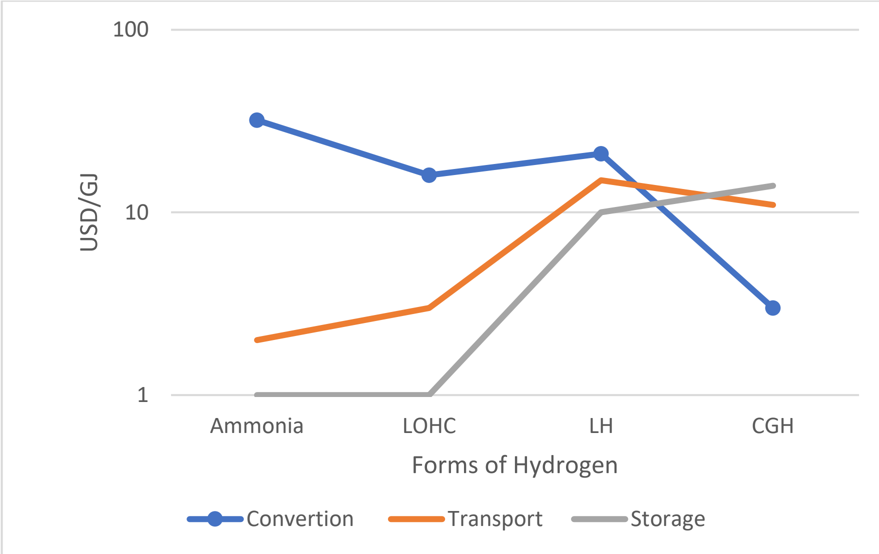

Figure 7: Cost of hydrogen value chains

As you can see from the storage methods, even though new materials are being studied or improved to keep the pressure low or the temperature near room temperature, most of the hydrogen is still being stored using conventional methods, which are physical storage.

HYDROGEN TRANSPORTATION

Hydrogen transportation can be done by road, railway, and ship. These transportation methods include compressed or liquefied hydrogen by roads, compressed hydrogen by pipeline, and compressed, liquid, ammonia or liquid organic hydrogen carriers from hydrogen by ships. Each has advantages and disadvantages depending on the distance, weight, or volume. Figure 8. shows the transportation techniques briefly [15].

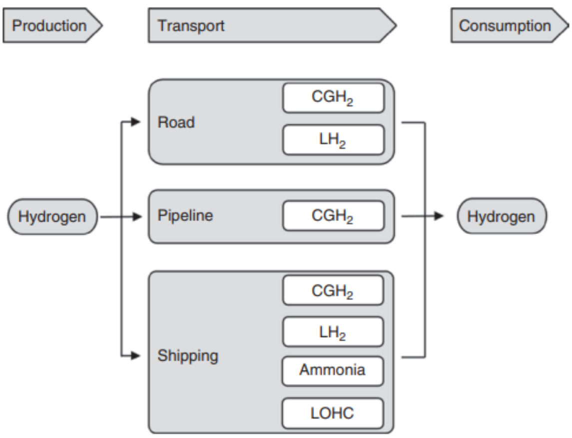

Figure 8: Hydrogen Transportation Methods [15]

Pipeline Transportation

Hydrogen transportation by pipes might be very advantageous in terms of economics and by volume if the high amount of hydrogen transportation is the topic, but embrittlement of hydrogen, permeation and leaks and the cost that can protect from these problems are the point of question. It is well known that hydrogen is very small, and the diffusion efficiency of hydrogen is 4 times higher than natural gas; therefore, the components of pipelines must be designed for this purpose [15]. The transportation distance can go up to hundreds of km and there are examples of these all around the world, especially from source to end users, but meanwhile pressure goes up to 100 bar, meaning all the mentioned safety problems are being raised as a question [16].

Road Transportation

Road transportation allows gaseous and liquid hydrogen to be carried. The gaseous hydrogen can be carried in vessels, can be filled in a production plant and carried to the end user, and empty bottles can be changed there. 200 to 1000 kgs of Hydrogen can be carried with 200 to 500 bar pressure, but this has limitations, for example, in the USA, the maximum is 250 bars. It can also be carried in Liquid form; it has advantages when it comes to volumetric storage density, around 4000 kg of hydrogen can be carried at -253°C with cryogenic tanks [15].

This high pressure for compressed hydrogen brings limitations all around the world, safety issues are big concern, therefore the distance, speed, volume and even acceleration or brakes of the truck should be considered. And we should not forget that these applications are advantageous only for short and middle range of transportation.

Ship Transport

Hydrogen can be transported by ships in compressed, liquid or ammonia form. For compressed form, again, high pressure for the cylinders will be needed. For liquid form cryogenic technologies, a low temperature will be needed. One advantageous carry method by ships is in the compound form as ammonia. -33°C and 8 to 10 bar pressure are the parameters of ammonia transportation, which is promising in terms of safety and brings this method up considering the safety criteria (Figure 9, 10) [17].

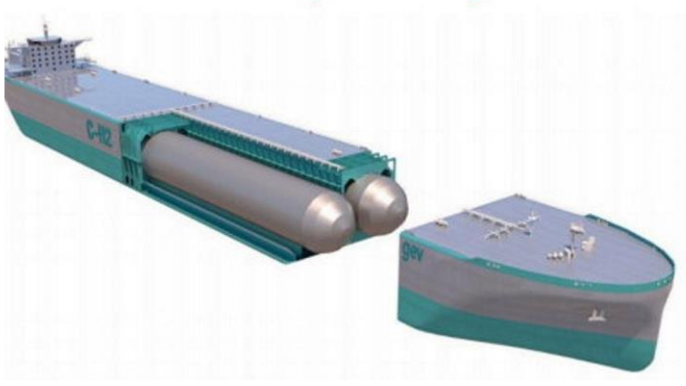

Figure 9: Compressed Hydrogen Transportation

Figure 10: Liquid Hydrogen Transportation By Ships

SAFETY OF HYDROGEN

As previously noted, hydrogen production and storage typically require either high pressure or extremely low temperatures. These demanding conditions naturally lead to concerns about safety. With the growth in hydrogen production, there is an increasing focus on safety protocols, prompting some countries to revise their legislation accordingly. Research efforts are expanding in areas such as operational safety, appropriate equipment selection, and personnel training. If hydrogen use in vehicles continues to rise, the safety standards for refuelling stations should be incorporated into this framework, and corresponding regulations and safety norms ought to be formally established.

It was mentioned that hydrogen is the lightest element in the world, meaning it is lighter than air, which means it goes up in case of release. Even though it is said that hydrogen is neither toxic nor harmless, the fact that it is colourless and odourless makes it hard to detect. Also, it should not be forgotten that hydrogen has a reverse Joule-Thompson effect, meaning that pressure drop increases the temperature. International Electrotechnical Commission and ATEX directives in Europe consider that the ignition energy of hydrogen is 0.017 MJ. Considering that a person cannot feel below MJ, the hydrogen with 0.017 MJ can be ignited, and even touching the t-shirt can cause it to be ignited.

There is also one more phenomenon, which is called Hydrogen Embrittlement. Hydrogen is compatible with organic materials but can cause embrittlement when metal or alloys are used for storage or transportation. The interaction of atomic hydrogen with the crystal lattice of the metal is quite possible because hydrogen atoms weaken the lattice [18-20].

When a gas mixture, or dust, self-propagates its flame and creates high-pressure waves, it is called an explosion reaction. The size of the pressure wave determines the degree of the explosion. If it is small, it is called deflagration; if it is big, it is called detonation.

Physical Explosion

There can also be physical explosions in the form of BLEVE (Boiling Liquid Expanding Vapour Explosion) or RPT (Rapid Phase Transition). A BLEVE is a physical explosion due to an immediate vessel rupture, including superheated liquids inside [21]. RPT is a physical explosion as well, and this should be considered when LH2 is close to the water source because this explosion happens when heat transfer happens between the cryogenic fluid and water, and it creates a vast explosion [16]. That's why installation systems of H_2 should consider these phenomena.

Hydrogen Damages

Besides the models of the explosion, it is worth talking about Hydrogen Damage; hydrogen is well known for its corrosion, and this corrosion can be classified by environment, appearance, and mechanism. All these forms of damage result from the diffusion of atomic hydrogen into the metal. This diffusion can cause a High-Temperature Hydrogen Attack, Hybrid/Hydrogen Embrittlement, Hydrogen Blistering, and Cracking [22]. Equation (8) shows that when steel or carbon is exposed to hydrogen for a long time under high pressure or temperature, it undergoes hydrogen attack over time, and hydrogen, reacting with carbon, forms methane.

$$8H + C + Fe_3C \rightarrow 2CH_4 + 3Fe \tag{8}$$

Hydrogen Safety: Considering the Standards

There are various standards to guide the training of people, installation, maintenance, design, repair, and inspection of the equipment used in hazardous areas and classification of environments with flammable gases, liquids, and dust, which poses a risk of fire or explosion. The most well-known standards are IECEx standards, NFPA codes and ATEX directives. IECEx is an international standard for explosive areas. The 60079 series covers the design, installation, repair, maintenance, inspection, marking, and classification of the equipment used in explosive atmospheres. NFPA is the American code, and ATEX is not a standard but a European directive covering essential health and safety requirements. Therefore, hydrogen also falls into these standards depending on the location. Also, there are ISO standards such as ISO/TR 15916 for essential consideration for the safety of hydrogen systems, ISO 16111:2018 for metal hydride storage devices and systems, ISO TC 197 for hydrogen fueling stations, and NFPA 2 for hydrogen technologies code.

An explosion occurs when the concentration of flammable gas in the air is between the lower flammable limit (LFL) and the upper flammable limit (UFL). For hydrogen, this is between 4% and 77%. This means that when the hydrogen concentration is more than 77% or less than 4% against air, it is not going to explode [23].

In any industry where explosive gas is present in the atmosphere (it can be dust too), the area is classified as Zone 0, Zone 1 and Zone 2 after calculations are made. Zone 0 indicates a continuous presence of explosive gas; Zone 1 indicates an occasional presence and Zone 2 is not likely to occur. Once this Zone area is classified, all the equipment selection, safety measures, maintenance and repair activities must be done according to this.

After the Zone is selected, the selection equipment for that Zone should have appropriate specifications. Each piece of equipment has a label that includes its explosive atmosphere, gas group, and temperature range. International standards define these values, and the ignition temperature for hydrogen is determined to be 560°C, which is why hydrogen has a T1 temperature classification as per the IECEx standards. It is important to remember that these values may have a slight difference from one standard to another; for the best value, a test might be needed. However, IECEx 60079 standards accept hydrogen as temperature class T1.

The temperature classification ranges from T1 to T6, and T6 is the most conservative one. Hydrogen's ignition temperature of 560°C is classified as T1, but it is essential not to forget that it is 0.017 MJ, which is very low.

Moreover, universal standards ensure each piece of equipment has a specific gas/dust group for explosive gases/dust. For gases, the groups are IIA, IIB, and IIC. IIC is the most conservative gas group, and hydrogen, along with acetylene, falls into this group.

Considering these standards, careful consideration is crucial when Hydrogen is present in the area.

CONCLUSION

Focus on logistics rather than hydrogen production. Therefore, proper storage, whether in batteries, underground, or integrated with natural gas, is essential. The key is to produce hydrogen from alternative sources with zero carbon emissions and integrate it into the system. Hydrogen filling stations utilizing excess electricity from solar or wind energy are a smart option.

While there is an increasing focus on storage advancements, traditional methods are still widely used. This raises safety concerns due to the increased pressure associated with hydrogen compression, necessitating extra safety measures. Although standards in this field are growing, there is a need for clearer guidelines and academic research regarding distance evaluations, zoning, hazardous area classification, equipment selection, and employee training in filling stations.

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