EH2TA

Education in Hydrogen Technologies Area

PRODUCTION OF HYDROGEN AND SAFETY

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CONTENT

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INTRODUCTION

The potential for hydrogen uses in industry and energetics is significant. Even though, for a long time, it was overlooked. However, one of its disadvantages is that it can mostly be found only in chemical compounds in nature as it is a highly reactive gas, and it must be derived from water or methane.

The advantages outweigh the disadvantages significantly, which is why its use is becoming more common. Hydrogen can store energy effectively for an extended period without considerable energetic losses. It is one of the important differences from batteries which can store electric energy only for days. For that reason, hydrogen is considered the right direction for storing energy gained from renewable resources, which offer unstable electricity production.

There are many benefits of hydrogen. It is the most common element in the universe, the third most common element on Earth, and it can be found in many substances. An unlimited amount of hydrogen is in water, it is also the basic element of organic matter, and most importantly, it is a part of all used hydrocarbon fuels. Hydrogen has a high energy density (for one unit of mass) and can be transported and stored. When used as a fuel, the advantage is zero-emission combustion. Suppose it is used to produce energy in engines with inner combustion or fuel cells. In that case, it emits heat, electric power, or mechanical power and an unharmful byproduct – water, leaving out CO2 and other waste substances, which are a common part of burning any hydrocarbon fuels in any form. Carbon is the main part of greenhouse gases, and Hydrogen energy should reduce its production. The prevailing problem is nitrogen oxide emitted inside of the hydrogen engine. Its amount depends on the oxygen surplus, temperature, pressure, and the time when the flue gases are kept in the combustion engine at high temperatures.[1]

Colours of Hydrogen

Hydrogen is resourced in different ways; therefore, it is divided into groups labelled by different colours.

Brown and Grey Hydrogen

One means of hydrogen production is resourcing them from fossil fuels (brown) and natural gas (grey).

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[1] Získávání vodíku z obnovitelných zdrojů [online]. Available at: https://eu.fme.vutbr.cz/file/Sbornik-EnBio/2006/08%20-%20Brandejska.pdf

Hydrogen is generated as a byproduct of different industrial processes. The most common hydrogen generation is by "steam-reforming", meaning the source is heated with water at a high temperature. Grey hydrogen is the most produced one nowadays. However, steam-reforming is dependent on fossil fuels, and a large amount of CO_2 is generated during this process; therefore, it is not considered for future hydrogen production.

Blue Hydrogen

Grey and Brown hydrogen can be improved by capturing produced CO_2 using Carbon Capture and Storage (CCS) technology and Carbon Capture and Use (CCU) technology. This way, so-called blue hydrogen is produced. Total CO_2 production in this process is lower even though the source is natural gas or methane, as significant part of the emissions is captured.

Pink Hydrogen

Pink hydrogen is produced by nuclear energy and is low emission. Sometimes, it is labelled ad purple or yellow. The labelling is still undecided.

Green Hydrogen

The primary purpose of hydrogen technology is to cut the dependency on fossil fuels and produce "Green hydrogen". This type of hydrogen is produced during an electrolysis process when water molecule is split into two atoms of hydrogen and one atom of oxygen using electricity. When the source of energy for this process comes from renewable resources, it is considered "green" and therefore "green hydrogen".

Hydrogen has the significant potential to decarbonize the use of energy. To fulfil its potential, there are a few barriers we have to overcome, mostly associated with storage, transportation and distribution. [2]

[2] Plyn budoucnosti. Jak daleko je Česko na cestě k jeho využití? - Ekolist.cz. Ekolist.cz: životní prostředí, příroda, ekologie, klima, biodiverzita, energetika, krajina, doprava i cestování [online]. Available at: https://ekolist.cz/cz/zpravodajstvi/zpravy/vodik-v-cesku.jak-daleko-jsme-na-ceste-k-vyuziti-plynu-budoucnosti

1 HYDROGEN

OBJECTIVES:

- To name primary characteristics of hydrogen and its isotopes;
- To recognize hydrogen colours and to compare its means of acquisition;
- To define the temperature at which hydrogen becomes liquid.

KEYWORDS:

Hydrogen, hydrogen colours, hydrogen isotopes, critical temperature

Hydrogen is the simplest and the lightest known element. It is 14.38 times lighter than air and conducts heat 7 times better than air. It is one of the main biogenic elements. Together with carbon, nitrogen, oxygen, sulphur, and phosphorus, hydrogen creates the building blocks for life on Earth, hence there is high content of hydrogen in the oil and natural gas. The proton number of hydrogen is 1 and the symbol H.

Pure hydrogen is rare on Earth, while it easily diffused into the universe or bounds with other elements creating so called hydrides.

The most common hydride is water H_2O which consists of two atoms of hydrogen and one atom of oxygen.[3]

1.1 CHARACTERISTIC OF HYDROGEN

Hydrogen is colourless, tasteless, and odourless gas. Due to its high reactivity and boiling point the use of odorants is limited. Hydrogen flame is almost invisible in daylight. It diffuses quickly even through seemingly high-density materials (some metals and plastic). It is lighter than air and, in the atmosphere, rises at the speed of 20 m per second. If expanding rapidly it can self-ignite.

It has very low ignition energy and can be initiated with energy of only 0.02 J. The critical temperature of hydrogen is -239.96 °C. It cannot occur in a liquid state above this temperature. That is why storing hydrogen in a liquid state is energetically and economically demanding. Hydrogen also causes so-

[3] KOTEK, Luboš. Specifika analýzy rizik vodíku. Automa: časopis pro automatizační techniku [online]. Available at: http://www.odbornecasopisy.cz/index.php?id_document=31466

called hydrogen embrittlement and hydrogen corrosion. These processes occur mainly where the materiel is under mechanical stress and their initial phases is not visible to an eye as they happen inside the material. In case of temperature rises faster than 20 K per hour, hydrogen is trapped in the cracks, accumulates in the cavities (so called "hydrogen traps") and causes the expansion of the cracks.[4]

Isotopes of Hydrogen

A hydrogen atom consists of one proton. It is the simplest isotope in the universe. The isotopes are differentiated by the number of neutrons they contain. Hydrogen has three known isotopes that occur naturally on Earth. The most abundant isotope is protium ($_1H$), consisting of one proton and no neutron. The next isotope is deuterium ($_2H$), consisting of one proton and one neutron. In chemical formulas, it can be found under the symbol D. The third isotope is tritium ($_3H$), consisting of one proton and two neutrons. Deuterium Oxide D_2O (Heavy Water) is present in water. Its concentration grows during water electrolysis. Its melting point (3.79 °C) and boiling point (101.4 °C) are higher than for H_2O. Tritium is a radioactive gas with weak β radiation, and unlike deuterium, it is unstable and has a half-life of 12,3 years. In chemical formulas, it can be found under the symbol T. It is produced in nuclear reactors during the production of plutonium from natural uranium. It is used in hydrogen bombs, fluorescent colours, or luminous clock hands.[5]

1.2 HISTORY

The British Scientist Henry Cavendish is considered to discover hydrogen when experimenting with acids and their reaction with base metals. During these experiments, he discovered colourless, flammable gas, which was given the name Hydrogen. The discovery was made in 1766. Cavendish also ruled out the hypothesis that water is a chemical element. The name Hydrogen comes from Greek hydro and genes – water forming and was first used by the French chemist A. L. Lavoisier who coined the French word hydrogène. Sir W. R. Grove, a British scientist, was the first to experiment with water electrolysis. He used electricity to divide water into hydrogen and oxygen. He has also discovered that electricity is produced when combining oxygen and hydrogen, during a process opposite to electrolysis. He conducted an experiment with two platinum plates inserted into two separate

[4] DLOUHÝ, Petr a Luděk JANÍK. Bezpečnost. Česká vodíková technologická platforma [online]. Available at: http://www.hytep.cz/cz/vodik/informace-o-vodiku/bezpecnost/496-bezpecnost

[5] Hydrogen: The Isotopes and Forms. In: Infoplease [online]. Available at: http://www.infoplease.com/encyclopedia/science/hydrogen-theisotopes-forms.html

containers. He then put those containers into diluted sulfuric acid and realized that an electrical current flows between electrodes and water is created in the gas chamber. By connecting more of such apparatus, he increased the voltage in this "gas battery". Later, chemists l. Mond and Ch. Langer used the term fuel cell[6].

CHAPTER SUMMARY:

- Hydrogen is the lightest chemical element of protonic number 1;
- Hydrogen isotopes differ in the number of neutrons in the core;
- Henry Cavendish is considered to have discovered hydrogen.

END-OF-CHAPTER QUESTIONS:

1. Define hydrogen as a chemical element, its chemical symbol and its protonic number.
2. How many isotopes are there in hydrogen, and what are they called?
3. At what temperature does hydrogen become liquid?
4. In what year has Henry Cavendish discovered hydrogen?
5. Which French chemist named hydrogen?
6. What colours are used to label hydrogen, and which are acquired from fossil fuels?
7. Describe the process during which green hydrogen is made.

2 HYDROGEN PRODUCTION FROM FOSSIL FUELS

OBJECTIVES:

- To define hydrogen as an energy vector;
- to recognize the differences between steam reformation and partial oxidation technologies for acquiring hydrogen
- to describe the process of acquiring hydrogen from refinery gas
- to name other technologies for acquiring hydrogen from refinery gas.

KEYWORDS:

[6] Historie objevu kyslíku a vodíku, prvků tvořících vodu. In: BŘÍŽĎALA, Jan. EChem. Book: Multimediální učebnice chemie [online]. Available at: http://www.e-chembook.eu/cz/historie-objevu-kysliku-a-vodikuprvku-tvoricich-vodu

Energy vector, steam reformation, partial oxidation, cryogenic separation, absorption, diffusion, plasma reforming

Hydrogen is not traditional fuel; it is an energy vector or carrier. Practically speaking, it means hydrogen is not free to mine and is energetically demanding as it does not occur in its pure form on our planet. Therefore, it has to be produced using a large amount of energy which, on the other hand, can be sourced carbon-free from renewable resources. But unfortunately, it is mainly produced using fossil fuels that cause the greenhouse effect. The most common means of hydrogen production is steam reformation, partial oxidation, and gasification of coal. Coal, oil, natural gas, and methane are used during these processes. Secondary products are CO and CO_2.

2.1 STEAM REFORMATION

During the steam reformation, hydrocarbon (e.g., methane) reacts with water steam in the catalyst. The product of this process is carbon monoxide, hydrogen [1] and in the residual steam, carbon dioxide [2]. If the source used contains a sulphur compound, desulphurisation is necessary.

$$[1]\ CH4 + H2O \longrightarrow CO + 3H2$$

$$[2]\ CH4 + 2H2O \longrightarrow CO2 + 4H2$$

The pressure of 3-5 MPa and temperatures between 750 – 800 °C are applied. Nickel oxide is used as a catalyst. The ratio of steam is 3:1 to avoid carbon settlement in the catalyst. 9 Produced Carbon monoxide undergoes a water-gas shift, and more carbon dioxide and hydrogen are manufactured. This reaction is exothermic and is implemented in two stages. During the first stage, iron oxide and chromium oxide are used as catalysts. It is a less reactive catalyst and is resistant to impurities. The reactor entry temperature is 380°C, and the exit temperature is 500°C. During the second stage of the process, much lower temperatures are used (180 – 230°C). This is allowed by using a highly reactive copper catalyst. This way, the concentration of carbon monoxide is decreased to 0.2 – 0.3%.

$$[3]\ CO + H2O \longrightarrow CO2 + H2$$

Hydrogen used for hydrogenation cannot contain oxygen compounds (CO and CO2) and must be converted back into methane [4,5]. This process is done in a methanation reactor at a temperature of around 400°C. If the amount of CO and CO2 in raw gas exceeds 3%, it is necessary to cool it down as both reactions are exothermic.

$$[4]\ CO + 3H_2 \longrightarrow CH_4 + H_2O$$

$$[5]\ CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

Figure number one shows a simplified diagram of Steam reformation using natural gas. Heated natural gas, after desulphurisation, is mixed with steam in a reformer where reactions [1] and [2] occur. First, products go through a reformer heated to 750°C and then to a shift reactor where they are cooled to 360°C. The following two stages are high-temperature and low-temperature shift converters, where CO is converted to CO_2 [3]. Gases are then led to the absorber, where using ethanolamine or other means, CO_2 is absorbed. Finally, residual CO and CO_2 are converted to methane in a methanation reactor [4,5]. This way, hydrogen of 98% purity is produced, and the remaining 2% is mostly methane.

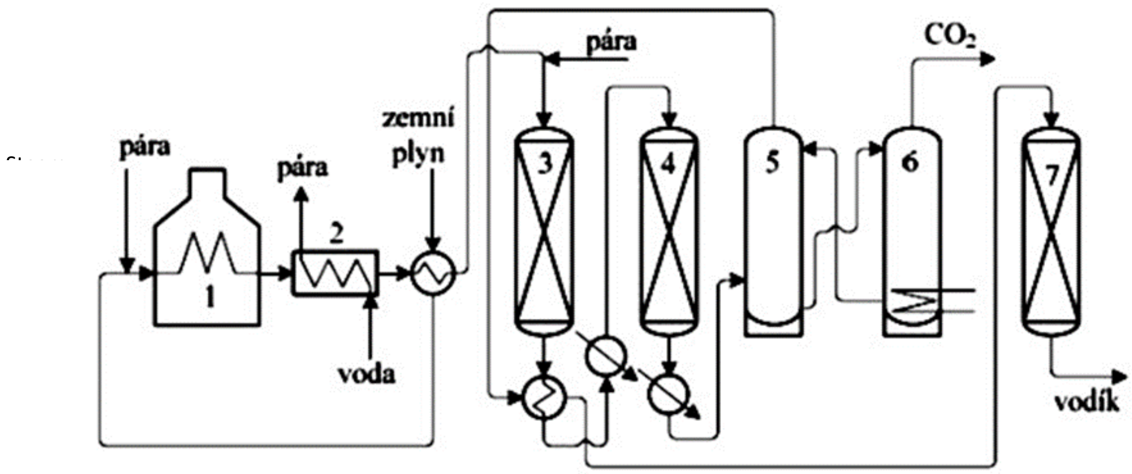

Fig. 1: Steam reforming using natural gas diagram

The effectivity of steam reformation is between 70 – 85% depending on hydrogen purity and the amount of steam to carbon ratio. Carbon dioxide produced during steam reforming or partial oxidation is released into the air, purified, liquidated, or turned into solid (dry ice) and used for cooling in the food industry.[7]

[7] *Výroba vodíku parním reformováním.* Petroleum.cz, [online] Available at: http://www.petroleum.cz/zpracovani/ zpracovani-ropy-43.aspx

2.2 PARTIAL OXIDATION

Partial oxidation is quite common in hydrogen production: gas and liquid materials from primary and secondary oil processing are used. Frequently, heavy oil residue fractions are gasified (Vacuum residuals, propane asphalt and others). The gasification process uses oxygen and steam at 1300-1500 C and 3-8 MPa. A limited amount of oxygen allows partial oxidation. The partial oxidation of hydrocarbon sources (CnHm) uses partly reactions [6] and partly [7]. The product of the reaction is carbon dioxide, carbon monoxide and hydrogen. Both reactions are exothermic and heat the mixture to 1500 C.

$$[6]\ 2C_nHm + nO_2 \longrightarrow 2nCO + mH_2$$

$$[7]\ C_nH_m + nO_2 \longrightarrow nCO_2 + m/2H_2$$

The part of the sources not gasified by oxidation is gasified by endothermic reaction using steam [8]. Steam gasification leads to high hydrogen profit and to lowering process temperatures to 1350 C.

$$[8]\ C_nH_m + nH_2O \longrightarrow nCO + n{+}m/2H_2$$

The product of partial oxidation of different sources is always a mixture of CO, CO2, H2O, H2, CH4 and sulphuric compounds H2S and COS. The harmful byproduct is soot.

Figure 2 shows a simplified diagram of the partial oxidation of heavy oil residue. Warmed heavy oil residue is dispersed into a stream of steam and oxygen mixture. In a generator, the gas of 1350 C is produced and connected to a steam reactor. The gas is rapidly moved through the reactor to avoid soot sediment. The gas is then cooled in the boiler above the temperature of saturated water steam (around 260 C), and at the same time, high-pressure steam of 12 MPa is produced. Some steam is used in the partial oxidation process (20%), and the rest is in other applications. In the next part of the process, generator gas is cooled by water dispersion in a radiator which removes part of the soot. Finally, the gas is completely purified in a gas purifier.

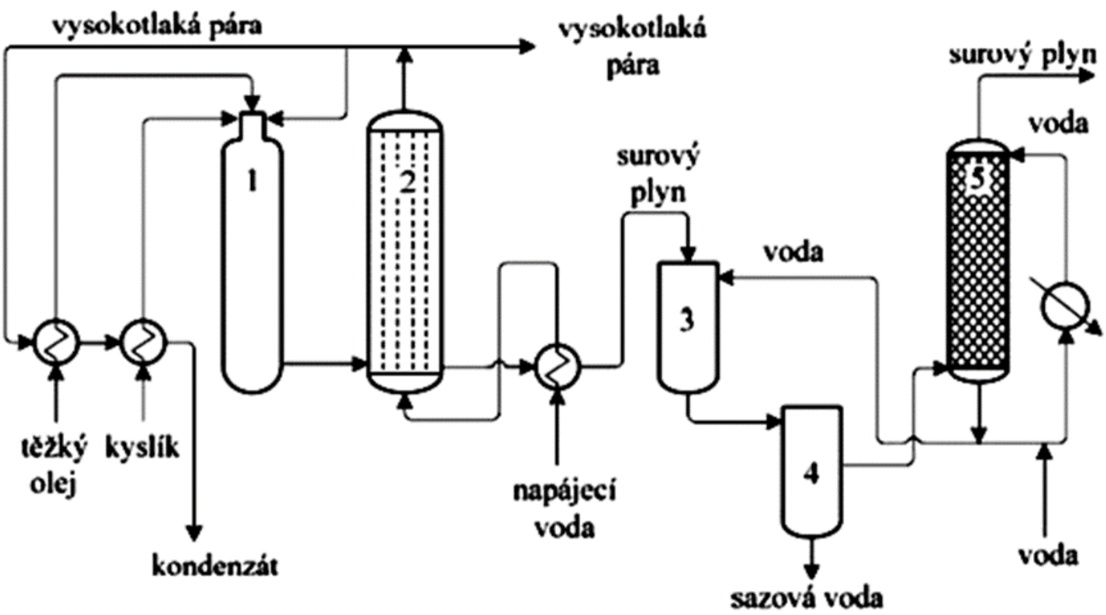

Fig 2: Diagram of partial oxidation of crude petroleum oil (1 – generator, 2 –boiler, 3 – radiator, 4 – separator, 5 – purifier)

Sulphane is removed from the final generator gas. The CO is converted to CO2, which is also removed from the gas. Residual CO and CO2 are then extracted using methanation. Conversion, purification and methanation are processed in the same manner as with natural gas.

The efficacy of partial oxidation of oil fractions is generally lower than steam reformation, usually around 50%. As with steam reformation, the investment demands are very high, but these are not included in my energetic needs compared to 1 m3 of hydrogen. Partial oxidation needs higher pressure and temperature than steam reformation; therefore, the energetic demands are higher. When considering the environment, partial oxidation is not better than steam reformation. A large amount of greenhouse gasses is produced. According to the limited use of heavy oil residue, few selling options and dwindling supplies of fossil fuels, partial oxidation has a higher potential for its use.

2.3 HYDROGEN PRODUCTION FROM REFINERY GAS

Hydrogen is also resourced from gases released during the processing of oil. Among these processes belong hydrocracking and hydrogenation. Hydrogen is usually diluted by gas hydrocarbon, most of all methane. The methods used to capture hydrogen are cryogenic separation, absorption or diffusion.

Cryogenic separation. The first step is to remove acidic gases (CO2, H2O) and water. The next step is, cooling the gas to -150 C at 1.4-3.5 MPa, which causes hydrocarbon condensation. The purity of hydrogen is around 90% of the volume. Since the cooling phase, it is an energetically demanding process raising the cost.

Absorption. The unwanted substances are removed from the gas by trapping them in activated carbon (CO2, CH4, N2) and zeolite molecular sieve (CO, CH4.N2). The moment the one absorbent is replete, the gas stream is led to the second absorbent, and the first regenerates by displacement of hydrocarbons.

Diffusion. The diffusion process separates hydrogen from methane and other gases using semi-permeable membranes. Hydrogen's small molecule diffuses through the membrane while other gases are captured. Membranes are made from palladium or its alloy with silver. The process takes place at 350 C and 2 MPa.[8]

2.4 OTHER TECHNOLOGIES USING FOSSIL FUELS

Coal Gasification

Coal gasification is the oldest method of extracting hydrogen. Coal is heated to 900°C; this way, it is transformed in coke oven gas. It is a gas that contains hydrogen, methane, oxide monoxide and a small amount of unsaturated hydrocarbon. The percentage of hydrogen is almost 60%. The gas is mixed with steam and nickel-based catalysts

Catalytic reforming

Catalytic reforming uses catalytic reactions to process primarily low-octane high-boiling straight-run gasoline into high-octane aromatics. Catalysts (Pt, Rh, etc.) are used in cyclisation and dehydrogenation, where hydrogen is a waste product.

Plasma reforming

There are several procedures using plasma reforming technology. The most known is the Kvaerner process, developed by a Norwegian company of the same name. Owing to new technologies, this is an environment-friendly process. Hydrocarbons are split into carbon and hydrogen in a reactor using a plasma burner at high temperatures (1600 - 2000°C). Compared to the other methods, the greatest advantage of this procedure is transforming carbon into soot without producing harmful CO_2. Plasma

[8] BLAŽEK, Josef a Vratislav RÁBL. Základy zpracování a využití ropy. 2., přepr. vyd. Praha: VŠCHT, 2006, 254 s. ISBN 80-708-0619-2

reforming products are 48% of pure hydrogen, 40% of carbon in the form of soot and 10% of overheated steam. The disadvantage to other methods is high energy demands, 2-2.5 kWh energy per 1 m^3 of H_2.

This chapter described the most common methods of hydrogen production from fossil fuels. With time the efficiency of this methods increases, and energy demands decrease. The underlying problem of using fossil fuels to produce hydrogen is intensive by-production of greenhouse gases. They need to be stored permanently to prevent their release into the atmosphere. For this purpose, empty oil tanks or underground water reservoirs are used. A 1996 study showed that the capacity for storing greenhouse gases in Europe is 806 billion tons of CO_2. Most of this capacity (476 billion tons of CO2) is on the Norwegian continental shelf in underground water reservoirs. This capacity would cover the CO_2 produced by all power plants in western Europe for centuries.[9]

CHAPTER SUMMARY:

- Hydrogen does not belong among traditional fuels, but it is an energy vector;
- During the process of steam reformation, hydrogen compound reacts with water steam in the presence of a catalyst;
- During partial oxidation, heavy oil fractions are gasified using oxygen and water steam under high pressure and high temperatures;
- Hydrogen can be acquired from gases produced during oil processing;
- Another possibility of acquiring hydrogen is from fossil fuels.

END-OF-CHAPTER QUESTIONS:

1. Explain the concept of hydrogen as an energy vector.
2. From which substances is hydrogen acquired during the steam reformation?
3. What chemical substances form in substance transformation during a steam reformation?
4. During partial oxidation, in what temperatures and pressure does hydrogen form?

[9] Hydrogen technologies. Bellona, [online]. Available at: http://www.interstatetraveler.us/Reference-Bibliography/Bellona-HydrogenReport.html

5. Is a steam reformation of partial oxidation more convenient for hydrogen production?
6. What are the three primary processes used to produce hydrogen from refinery gas?
7. Name three other possibilities to produce hydrogen from fossil fuels.

3 HYDROGEN PRODUCTION FROM RENEWABLE RESOURCES

OBJECTIVES:

- to define the principle of water electrolysis;

- to describe the difference between alkaline water electrolysis, high-temperature electrolysis and thermochemical water splitting;

- to name other alternative technologies of hydrogen production;

- to explain the principle of hydrogen production using biotechnological processes.

KEYWORDS:

Water electrolysis, high-temperature electrolysis, Westinghouse sulphur cycle, solar-powered hydrogen powerplant, pee power, biomass, photolysis, fermentation, dark fermentation

More than 70% of the Earth's surface is covered by water. The mass percentage of hydrogen in water is 11.2%. As mentioned previously, hydrogen binds to oxygen during combustion and creates water. Therefore, hydrogen is considered to be renewable resource of energy.

3.1 WATER ELECTROLYSIS

During water electrolysis, water is separated into hydrogen and oxygen. Direct electric current flows through the aqueous solution and splits chemical bonds between hydrogen and oxygen. Water reacts at the anode to form O_2 and at the cathode H_2 (F. 5) $2H_2O \longrightarrow 2\ H_2 + O_2$. Hydrogen produced at the cathode is collected and stored. The process can be done at room temperature, and only electricity is needed. This method produces highly pure hydrogen gas with no need to be further purification. Consequently, this method is suitable where pure hydrogen and oxygen are needed. The apparatus used for electrolysis is called an electrolyser. It consists of a container, electrode, and electrolyte. The efficiency of the process is somewhere between 80 – 92%, and it can be increased

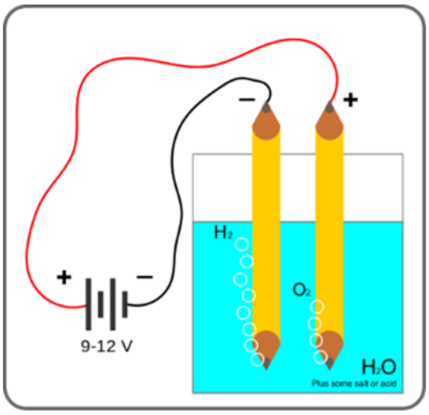

Fig. 3: Diagram of water electrolysis

by the additional electrolyte, which boosts water conductivity. Electrolysis is not used mainly because of the high cost of electricity. The efficiency of electric power production influences the efficiency of electrolysis. Currently, the efficacy of electric energy production it is between 30-40% using available resources; therefore, the efficacy of electrolysis is somewhere between 25-35%. Compared to other methods, electrolysis has a high energy demand. Power consumption is 5.2 kWh per 1m^3 of hydrogen which makes it 57 kWh per 1 kg. Electrolysis is a promising option for carbon-free hydrogen production from renewable resources.[10]

Electrolysis is used where affordable "green" energy is available and where there is a surplus of energy. In addition, oxygen is produced which can also be used.

3.2 ALKALINE WATER ELECTROLYSIS

Acid or Alkaline solutions are used to split water. An alkaline electrolyte is ideal prevention of corrosion which occur when using acids. Highly concentrated potassium hydroxide (KOH 25-30%) is often used. A large contact surface area among electrodes with electrolytes is needed for the correct process. The final product is then separated from the electrodes. Low-carbon steel, sometimes

[10] DOUCEK, A., JANÍK, L., TENKRÁT, D., DLOUHÝ, P. *Využití vodíku k regulaci obnovitelných zdrojů energie* [online]. Chemagazín, 2010, č.3, roč. 20. Available at: http://www.chemagazin.cz/userdata/chemagazin_2010/file/CHXX3_cl1.pdf

covered with a thin layer of nickel, is used for cathodes. Anodes are made of nickel-plated low-carbon steel or nickel steel. Platinum is seldom used as a catalyst. A diaphragm separates electrodes to avoid a reaction between produced hydrogen and oxygen. Earlier, the diaphragm was made of asbestos, but due to the risks it imposes on our health, it was banned, and new materials were tested.

3.3 POLYMER ELECTROLYTE MEMBRANE ELECTROLYSIS

In polymer electrolyte electrolysis the proton exchange membrane (PEM) is used to transfer the. Water is brought in contact with a bipolar plate; it circulates to the anode, where it is split into oxygen. Produced protons are transported through the PEM to the cathode. The electrons exit from the anode through the external power circuit, which provides the reaction's driving force (cell voltage). On the cathode side, the protons and electrons recombine to produce hydrogen. PEM separates produced gases, and electrodes are in direct contact with PEM to avoid undesired reactions. Electrodes are made of platinum, and of their alloys, they must be resilient to acids as PEM has the same properties as an aggressive acid.

3.4 HIGH-TEMPERATURE ELECTROLYSIS (HTE)

High-temperature electrolysis is sometimes called steam electrolysis. It is very similar to water electrolysis. The difference is in the form of provided energy. Some of the energy is brought in the form of electric energy and some in the form of heat. This way, the efficiency of the process is increased. Water and hydrogen enter the electrolyser, forming an enriched mixture (75%hm hydrogen and 25%hm steam). Hydrogen is then dissociated in the condensation unit. The reactions in high-temperature electrolytes are reversed to reactions in solid oxide fuel cells. Energy demands for the process are temperatures between 600 -100°C. In the HTSE process, water is first converted to steam by using nuclear thermal energy rather than electricity, and then dissociated at the cathode to form the hydrogen molecules as well as oxygen ions, which subsequently migrate through the solid oxide electrolyte material, and then form oxygen molecules at the anode surface.[11]

The overall efficiency can reach up to 45 -50%. The energy demands are lower than conventional electrolysis since the higher the steam temperature, the lower the electricity demand. It is a very clean

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[11] https://www.sciencedirect.com/topics/engineering/high-temperature-steam-electrolysis 17.08.2022 [online]

method of hydrogen production and is constantly under development as one of the candidates for the largescale hydrogen production. Nuclear energy is one of the leading electricity sources.[12]

3.5 THERMOCHEMICAL WATER SPLITTING

During thermochemical water splitting, water is separated into oxygen and hydrogen using chemical reactions. These reactions are initiated by heat or by combination of heat and electric energy using hybrid cycles. This process only needs source of water and heat as the rest of the chemical substances are reused. The final products are hydrogen and oxygen.

One of the cycles is the sulphur-iodine thermochemical cycle. It is an inexpensive and efficient method of hydrogen production using nuclear power. The first step of the process is the reaction of water with iodine and sulphur dioxide [9]. The outcomes of this reaction are sulfuric acid and hydrogen iodine. The next step is the endothermic decomposition of sulphuric acid and hydrogen iodine [10 and 11], which requires high temperatures (800 - 1200°C and 450°C respectively).

$$[9]\ I_2 + SO_2 + H_2O \longrightarrow 2HI + H_2SO_4$$

$$[10]\ H_2SO_4 \longrightarrow SO_2 + H_2SO_4 + 1/2O_2$$

$$[11]\ 2HI \longrightarrow I_2 + H_2$$

The efficiency of such a complex process is difficult to establish. Generally, it varies between 40 – 52% (50% at 950°C). Higher temperature means higher efficiency of the cycle. Compared to electrolysis, the energy loss during electric energy production is eliminated. Disadvantages lay in high temperatures and aggressive chemicals such as sulphuric acid and hydroiodic acid. Therefore, containers must be made of – materials with high resistance to these chemicals. Same as electrolysis, theoretically no waste is produced during the thermochemical splitting. However, certain amount of chemical compounds is lost during this process and needs to be regularly refilled. This long-term

[12] *Jak se vyrábí palivo budoucnosti. Vodík pro auta i elektroniku* [online]. Available at http://technet.idnes.cz/ jak-se-vyrabi-palivo-budoucnosti-vodik-pro-auta-ielektroniku p6d/tec_technika.aspx?c=A080127_234744_tec_ technika_vse

technology pathway has potentially low or no greenhouse gas emissions despite the process control in mass production remains challenging to translate this technology into industry.

3.6 PHOTOELECTROLYSIS OF WATER

In the photoelectrolysis of water, hydrogen is produced from water using sunlight and specialised semiconductors similar to the ones used in a photovoltaic cell. The light energy is then used to dissociate water molecules into hydrogen and oxygen directly. In photovoltaic, the principle is such that two semiconductors (p-type and n-type) are joined to form a p–n junction. The collection of light-generated carriers by the p-n junction causes a movement of electrons to the n-type side and holes to the p-type side of the junction. Under short circuit conditions, there is no charge build-up, as the carriers exit the device as light-generated current. [15] For photoelectrolysis, the semiconductor is immersed in a water-based electrolyte, where instead of electricity production the solar energy is used for the water-splitting process.[13,14]

3.7 OTHER TECHNOLOGIES

Westinghouse sulphur cycle

The Westinghouse sulphur cycle developed by Westinghouse company in 1975 is a hybrid thermochemical process using sulphuric acid. The raw material input consists of water sulphur dioxide. These are reacted electrolytically to produce hydrogen and sulphuric acid. Sulphuric acid is then decomposed into oxygen and raw material. It is the simplest of sulphuric processes, and the efficiency is around 40%. The most significant advantage is 3 – 4 times lower electricity demands compared to the electrolysis of water. The main disadvantage is the highly corrosive properties of sulphuric acid.

Solar Powered Hydrogen Power Plant

SolarLab research is focused on solar energy. The hydrogen power plant concept developed by this company works on a simple principle. Solar tiles will be placed offshore, and the hydrogen production

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[14] HADRAVA, Jan, Roman VOKATÝ, HLINČÍK a Daniel TENKRÁT. Porovnání kvality vodíku z různých technologií výroby. *Paliva* [online]. 2013, roč. 5, č. 3, 79 – 83. Available at> http://paliva.vscht.cz/download.php?id=95

efficacy could be raised by up to 30% due to the cooling properties of seawater. The electric energy sourced by solar panels will then be used for water electrolysis. Hydrogen will be stored in tanks on the sea floor, eliminating the risk of explosion and distributed to shore through a pipeline, resulting in relatively safe and cheap hydrogen production process.[15]

Pee Power

Gerardine Botte, a professor of chemical and biomolecular engineering at Ohio University, has developed a technology to generate hydrogen fuel from urine. Urine contains two compounds that could be a source of hydrogen: ammonia and urea. The technology is based on the principles of water electrolysis with a difference in energy demands since hydrogen bond in ammonia and urea is weaker than in water. Botte's technology has certain potential in settings where large numbers of people gather like airports and sports stadiums. It can also be used when dealing with environmental pollution associated with large animal farms. According to Professor Botte, urine produced by a thousand cows could generate 40-50 kW of energy, and harmful ammoniac could be eliminated through the process.[16]

3.8 BIOLOGICAL PRODUCTION OF HYDROGEN

Biomass belongs to most prospective renewable resources. Its energetic use including hydrogen production is versatile. Its content in biomass (6-6.5% mass fraction) is lower compared to natural gas (25% mass fraction) but equal to the content of hydrogen in coal (5% mass fraction).

Dry Biomass

Dry biomass is a name for wooden or dry plant waste. If can be further processed by burning and gasification.

Thermochemical processes

Thermochemical processes include steam reformation of biomass. This two-step process consists of pyrolysis, where gas products are generated (methane, hydrogen, carbon monoxide) and the second step where high-temperatures (600°–1.000°C) are used. During the second step a series of chemical

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[15] HORČÍK, J. *Výroba vodíku s pomocí solárních elektráren* [online]. Ekologické bydlení. Available at: http://www.ekobydleni.eu/energie/vyroba-vodiku-s-pomocisolarnich-elektraren

[16] DeWEERDT, S. *Pee power could fuel hydrogen cars* [online]. Conservation Magazine. Available at: http://www.guardian.co.uk/environment/2011/mar/09/peepower- fuel-hydrogen-urine

reactions, the residual solids and methane are transformed into hydrogen and carbon dioxide using water stem and the total yield of hydrogen is further increased by transforming carbon dioxide into hydrogen and carbon monoxide. The chemicals used in the process can be reused within each cycle, creating a closed loop that consumes only water and produces hydrogen and oxygen. Materials that can be processed by this method range from a general waste, food industries waste, farm waste to coal. The process can then vary based on the raw materials used, temperature or type of catalysts.

High-moisture content biomass

Compared to dry biomass, high-moisture content biomass is due to economic reasons unsuitable for traditional thermochemical processes. Instead, it undergoes biotechnological processes catalysed by microorganisms in water environment under low temperature and pressure. These biological processes usually use algae or anaerobic bacteria that are found in environment with no atmospheric oxygen. The effect of microorganisms then differs based on the feedstock and process conditions used.

An overview of the most common methods of hydrogen production using biotechnological processes:

Direct photolysis

Direct photolysis uses sunlight and enzymes produced by microorganisms to split water into oxygen and hydrogen. The process uses the photosynthetic microalgae system to harness solar energy and convert it into a chemical energy needed for water splitting. These processes are possible only under anaerobic conditions where the oxygen content is a maximum of 0.1 % as the enzymes are highly sensitive to free oxygen presence. The entry substance of direct photolysis is just water which is free and easy to access. The disadvantage of direct photolysis is the low efficiency of 5%, which can be increased under laboratory conditions up to 15%. Another option is indirect photolysis, a more complex method consisting of several steps: biomass production through photosynthesis, concentration of biomass, anaerobic fermentation and acetate conversion (acetic acid salts). Indirect photolysis uses cyanobacteria.

Fermentation

Fermentation is a conversion of substances using microorganism enzymes due to metabolic activity. Organic substances (carbohydrates) are converted into low-energy compounds (ethanol, carbon dioxide). The most suitable resources are potatoes and sugarcane. There are two main types of fermentation. The first one is hydrogen fermentation (dark fermentation) and the second one is photofermentation.[17]

Dark Fermentation

Dark fermentation is carried out by obligate anaerobes and facultative anaerobes in the absence of light and oxygen. Organic compounds are the primary source of energy and hydrogen. Different types of bacteria use the proton reduction to hydrogen for storing the electrons produced during oxidation of organic compounds. Theoretical yield from 1 mol glucose is shown in the following equation. The maximum amount of direct hydrogen yield is 4 mol and 206kJ of energy is released. Another producing 2 mols of acetate are produced which can be further used for gaining another 4 mols of H_2.

$$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 2CO_3^{2-} + 6H^+ + 4H_2$$

$$\Delta H_r^0 = -206 \frac{kJ}{mol}$$

Photofermentation

Similarly to dark fermentation photofermentation leads to production of hydrogen and CO_2 using bacteria and organic matter. The difference is that the processes are carried out using sunlight. One of the groups of microorganisms with the ability of photofermentation is purple non-sulphur bacteria that, under anaerobic conditions, use simple organic acids. The process is described by the following equation: [18]

$$CH_3COOH + 2H_2O \xrightarrow{solar\ power} 4H_2 + 2CO_2$$

The advantage of using bacteria is their ability to adapt the metabolic process. Meaning they can be used in various conditions. Both types of fermentation are combined with increasing economic profit, and the acetate by-product of dark fermentation is used for photofermentation. It is a two-step bioproduction of hydrogen. In the first step, hydrogen is produced from organic matter via hydrogen

[17] BRANDEJSKÁ, E.; PROKEŠ, O.; TENKRÁT, D. *Získávání vodíku z obnovitelných zdrojů* [online]. Energie z biomasy, Brno. Dostupné z: http://oei.fme.vutbr.cz/konfer/biomasa_v/papers/08-Brandejska.pdf

[18] BIČÁKOVÁ, O. *Možnosti výroby vodíku biologickými procesy* [online]. Paliva 2, 2010, s. 103-112. Available at: http://paliva.vscht.cz/data/clanky/29_moznosti_vyroby_vodiku_biologickymi_procesy.pdf

fermentation, and in the second step, biogas is resourced, or hydrogen is produced via photofermentation. It is also possible to produce energy by burning residual biomass. [19]

The efficacy of the process is influenced by materials and technology used. On its own, fermentation has low efficiency (around 10%) but using a combination of fermentations; the efficiency can reach up to 40%. Energy demands of the process depend on the amount of heat needed to warm up the entry materials and can be relatively high. A small amount of NOx and CO emissions are released into the atmosphere during the two-step fermentation process. However, due to its low concentrations, the emissions should not significantly affect the environment. There is great potential in fermentation as it is constantly under development, and extensive research is focusing on the genetic modification of microorganisms to increase the efficiency of the process. The greatest asset of fermentation is contributing to waste management as the waste production worldwide keeps increasing.

CHAPTER SUMMARY:

- When direct electric current flows through the aqueous solution, it splits chemical bonds between hydrogen and oxygen–water electrolysis;

- Overall electrolysis efficacy is between 25-35%;

- Electrolysis is energetically very demanding. Around 5,2 kWh if used to produce 1m3 of hydrogen;

- Hydrogen gas of high purity is produced during electrolysis due to the clean process;

- Electrolysis is used where cheap green energy is available;

- Acid or Alkaline solution is used as an electrolyte during alkaline electrolysis;

- Polymer electrolyte electrolysis uses a membrane to carry ions;

- Some of the energy is brought in the form of electricity and some in the form of heat during the high-temperature electrolysis;

- During thermochemical water splitting,chemical reactions are initiated by heat and the rest of the chemical substances are recycled in the process;

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[19] DOUCEK, A., *Výroba vodíku z biomasy* [online]. Česká vodíková technologická platforma. Dostupné z: http://hytep.cz/?loc=article&id=17

- In Photoelectrolysis, electrodes are merged in electrolyte, but instead of producing an electrical current, water is split into hydrogen and oxygen;

- The Westinghouse sulphur cycle uses electrical energy, water, and sulfur dioxide to produce hydrogen and sulphuric acid;

- Solar panels placed onto the sea level can be used for water electrolysis;

- ammonia and urea contained in urine are used to produce hydrogen using Pee Power technology;

- Energy produced during the burning or gasification of biomass can be used to produce hydrogen, e.g. steam reformation.

END-OF-CHAPTER QUESTIONS:

1. Describe the main principles of water electrolysis.
2. What chemical substance is used as an electrolyte during alkaline water electrolysis?
3. What chemical substance is used as an electrolyte during polymer membrane water electrolysis?
4. What are the operating temperatures during high-temperature electrolysis?
5. What energy is used during thermochemical water splitting?
6. What is the Westinghouse sulphuric cycle?
7. Where is the use of solar-powered hydrogen powerplants most common?
8. Explain the term Pee Power.
9. Name and explain the most known technologies used to produce hydrogen from biomass.

4 FUEL CELLS

OBJECTIVES:

- To explain the principles of fuel cells;
- to divide cells by their operating temperatures;
- to define cells by the electrolyte type;
- to name other components of a vehicle with fuel cells.

KEYWORDS:

Fuel cell, electrolyte

There are different types of fuel cells that can be differenciated mainly by the electrolyte type and process temperature. The systems use different chemical reactions happening on electrodes and the efficacy of electrochemical conversion.

The principle of electricity production is based on chemical reactions between hydrogen and oxygen. This reaction produces energy and water. The energy comes in the form of an electric current. Function of all fuel cells is based on the identical principle Fig. 14. If we look back at the electrolysis hydrogen production, we will see that the fuel cell works similarly. In this case, the input substance is hydrogen, and the outcome is electric current. Hydrogen is pumped to the anode. The process splits hydrogen into anions and cations [12].

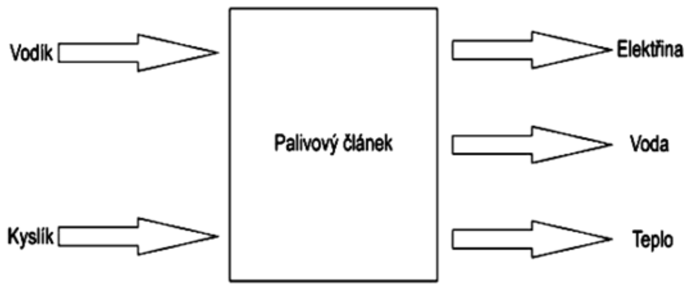

Fig. 3: Functional principle of fuel cell

$$[12]\ 2H_2 \longrightarrow 4H^+ + 4e^-$$

The electrolyte allows the flow of protons but prevents the flow of electrons from the anode to the cathode. Electrons have to access the cathode through an external circuit. The flow of electrons via this circuit produces an electric current. Afterwards, the air is led to a cathode, where it is combined with hydrogen ions, and together they produce water and heat Fig. 13.

$$[13]\ 4H^+ + 4e^- + O_2 \longrightarrow 2H_2O$$

The overall reaction in a fuel cell is shown in Fig. 14.

$$[14]\ 2H_2 + O_2 \longrightarrow 2H_2O$$

The voltage in a fuel cell is very low, around 1 V. It has to be much higher to be used in practice. To achieve that serial connecting of multiple fuel cells is used.

4.1 BASIC ORGANISATION OF FUEL CELLS

Types of fuel cells differ mainly by the electrolyte type and process temperature. The systems use different chemical reactions happening on electrodes and the efficacy of electrochemical conversion.

Organisation of fuel cells by process temperature:

- Low temperature 60 – 130 °C
- Medium temperature 160 – 220 °C
- High temperature 600 – 1050 °C

Organisation of fuel cells by electrolyte type:

- Alkaline fuel cells (AFC's) in which the electrolyte is mainly diluted potassium hydroxide (KOH)
- Polymer electrolyte membrane fuel cells (PEMFC's) in which the electrolyte is solid organic polymer
- Phosphoric acid fuel cells (PAFC's) in which the electrolyte is phosphoric acid (HPO_3)
- Molten carbonate fuel cells (MCFC's) in which the electrolyte is a mixture of melted carbonates
- Solid oxide fuel cells (SOFC's) in which the electrolyte are oxides of chosen metals[20]

Hydrogen-powered cars with fuel cells must include other substantial parts without which they could not run.

Fuel tank: One or more cylinders store compressed hydrogen under a pressure of 30 to 70 MPa.

Battery: Stores electric energy and supports the car when accelerating. Energy collected by recuperation changes kinetic energy when braking or deceleration to electric power.

Electric engine: An engine with high torque drives the front or back axle. Energy is sourced directly from the fuel cell or the battery. It needs less maintenance than a combustion engine.

[20] Vlk, F. Alternativní pohony motorových vozidel, Brno: Vlastním nákladem, 2004. 234 s. ISBN 80-239-1602-5

CHAPTER SUMMARY:

- The principle of electricity production is based on the chemical reaction between hydrogen and oxygen;

- By their operating temperature, fuel cells are divided into a low-temperature, medium-temperature and high-temperature groups;

- By their electrolyte type, fuel cells are divided into Alkaline, polymer, phosphoric acid, molten carbonate and solid oxide fuel cells

END-OF-CHAPTER QUESTIONS:

1. What chemical reactions take place in a fuel cell?
2. What voltage value is generated by fuel cells?
3. In what temperatures are high-temperature fuel cells operating?
4. What chemical substance forms the electrolyte of alkaline fuel cells?

5 SAFETY AND HYDROGEN STORAGE

OBJECTIVES:

– To define safety guidelines when handling hydrogen and its biological effects;

- To explain the differences between hydrogen storage in liquid form and as a gas;

- to explain the principles of storing hydrogen as a hydride;

- to explain the terms absorption and adsorption.

KEYWORDS:

Hydrogen storage, cryogenic chambers, hydrides, absorption, adsorption

This chapter is devoted to hydrogen storage technologies which are the main limiting factor for wider use of hydrogen. Hydrogen of all fuel types has the lowest density and boiling point which makes its storage challenging. The main storage methods are divided into well-known and used and new alternative methods.

5.1 SAFE USE OF HYDROGEN

As inexpert use of hydrogen led to several severe accidents significantly influencing the perception of its usage by the public. It is considered to be significantly dangerous. However, these accidents were caused mainly by technical issues and service failure. Therefore, it is crucial to consider the hazards when working with hydrogen and increase the awareness for operational conditions in hydrogen facilities.

Fig. 4: Safety sign– extremely flammable

Hydrogen creates a combustible compound when mixed with oxygen, fluor and chlorine. The most important safety rule is to avoid contact of hydrogen with air while this mixture is highly flammable. It can be easily ignited with cigarettes, electric charge, sparks, or even hot objects. Therefore, it is necessary to follow the strict safety, technical and fire regulations, and guidelines in all areas where hydrogen is used or stored.

Hydrogen has a negative Joule Thomson coefficient at standard temperatures and its temperature therefore rises with decreasing pressure. This leads to risk of spontaneous combustion during fast expansion of compressed hydrogen. Areas for storing and using hydrogen must therefore be well ventilated.

Since hydrogen is lighter than air, it can also accumulate under the roof increasing the risk of an explosion. In pressure cylinders with compressed gas, the pressure rises with temperature. Therefore, the pressure cylinders' storage conditions should not exceed 50˚ C, otherwise danger of mechanical damage to the collection system (valve, regulator, distribution boards). [21]

5.2 BIOLOGICAL EFFECTS OF HYDROGEN

High concentration of hydrogen in closed arear can be harmful for people as it lowers the amount of oxygen in the air. However, the concentration of hydrogen needed to create an environment with insufficient oxygen is much higher than the point of flammability; hence the danger of explosion is greater. Liquid hydrogen and cool gas released from the liquid can cause burns when in contact with the skin. Skin can stick to insufficiently isolated hydrogen containers and be torn from flash afterwards. Inhalation of pure hydrogen causes loss of consciousness and nearly immediate death.

5.3 COMPRESSED GAS STORAGE

Storing hydrogen as a compressed gas is less energetically demanding compared to storing it in its liquidated form. Vessels for stationary hydrogen storage are made of low-carbon or chrome steel alloy without a weld. The pressure in these tanks is around 200 bar. In the Czech Republic, 61 kg and 50 l volume vessels are mostly common. Cylinders of 1 l or 2 l volume are used for high purity hydrogen. To increase the capacity, small containers are grouped and joined. There are usually ten cylinders in

[21] TUČEK, Vít, Ludmila DVOŘÁKOVÁ a Jiří HANZAL. Česká asociace technických plynů: vodík[online]. Available at: http://www.catp.cz/publikace2.php?download=catp_03-04-cz.pdf

the bunch. Composite cylinders are used for hydrogen transportation. These are made in 10 l to 300l volumes and are coated with a thin layer of metal or special polymer. This layer prevents leakage. The pressure in the cylinders is between 350 – 700 bar, and the technological limit of these containers is 1000 bar. In the case of large volume applications, it is more suitable to use fuel cell vehicles. The fuel cell vehicles are equipped with numerous 50 l volume cylinders or nine horizontal pressure tanks. The gas is then transferred to stationary pressure tanks when delivered to the customer. The stationary pressure tanks are standardised cylindrical vessels operated under 50 bar pressure. They are manufactured in 25, 50 and 90 m^3 volumes.

Fig 5: Cross-section of hydrogen cylinder

Another method is underground storage. For such method, cavities in salt mines and empty gas deposits are used. This way hydrogen can be stored at pressures up to 110 bar. Higher pressures can exceed the capillary force that is keeping water in micropores and result in hydrogen leakage.

Hydrogen in its gaseous form can be stored in hollow glass microspheres (HGM). This method is still under development. It should be a safe form of hydrogen storage for mobile applications. The HGM are filled with hydrogen under the 350-700 bar pressure and 300°C using diffusion. The gas is then trapped when cooling down to room temperature. To release the gas, HGM needs to be heated to 200 - 300°C. [22]

[22] RIIS, Trygve, Gary SANDROCK, Oystein ULLEBERG a Preben J. S. VIE. Hydrogen Storage: Gaps and Priorities. [online]. Available at: http://ieahia.org/pdfs/HIA_Storage_G&P_Final_with_Rev.pdf

5.4 CRYOGENIC LIQUID HYDROGEN STORAGE

Liquefying hydrogen increases its storage density; hence it is possible to store more energy than when stored as a gas. LH_2 (liquid H_2) is stored at the temperature of -253°C, and the main concern is the energy-intensive process of liquefying using 30% of energy sourced by burning liquid hydrogen. Another problem represents a 3% volume loss of stored hydrogen daily. Therefore, it is crucial to develop new methods of liquefying to decrease energy demands and increase the efficacy of the process.

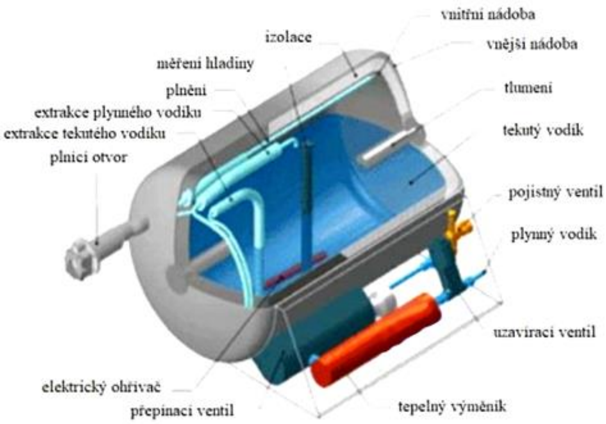

Fig. 6: Hydrogen cryogenic container

The energy demands mainly lye in ortho-form (o-H_2) to para-form (p-H_2) conversion. Ortho-form is a hydrogen molecule where the atoms have spin symmetry and para-form molecules atoms have spin asymmetry. The p-H_2 is more stable in lower temperatures and has a lower enthalpy. Due to this characteristic, heat is released during the conversion increasing the energy demand of the process. The other factor is the purity of the gas; all gases except helium need to be removed, especially CO_2, CO, CH_4 and O_2. Oxygen concentration above 1 mg per kg can cause explosion.

LH_2 is stored in multilayer containers with superior insulation properties equipped with overpressure protection. The overpressure protection releases the evaporated LH_2 to avoid pressure build-up in the tank. Usual daily losses of LH_2 are 3% of the volume per day. Sometimes, the evaporated LH_2 is captured and stored in additional pressure cylinders.[23]

[23] DLOUHÝ, Petr a Luděk JANÍK. Skladování vodíku I. *Česká vodíková technologická platforma*[online]. 2007. Available at: http://www.hytep.cz/cz/vodik/informace-o-vodiku/transport-a-skladovanivodiku/ 495-skladovani-vodiku-i

Comparison of conventional methods

The following table shows the comparison of weight and volume characteristics for a full fuel tank of a C-segment car with a 500 km range representing the equivalent of 6 kg H_2 to 45 l of petrol.

Container type	Container weight [kg]	Container volume [l]
Fuel tank	55	45
Cryogenic tank	100	180
Steel tank 350 bar	360	290
Composite tank 350 bar	120	290
Composite tank 450 bar	130	230
Composite tank 700 bar	140	200

Fig. 7: Common storage methods comparison

A hydrogen-powered car with 500 km range would be equipped with almost four times larger and 2-3 times heavier fuel tank compared to a petrol-powered car (in case of steel tank up to 7 times heavier than fuel tank).

5.5 HYDROGEN STORAGE IN HYDRIDES

Hydrogen storage in metal hydrides

This storage method is based on bonding hydrogen to metal-based materials under convenient temperature and pressure conditions. The reaction of hydrogen with metal is called the hydrogen absorption. Hydrogen is absorbed directly into the material volume. The atomic hydrogen is incorporated into the interstitial space in the crystal lattice of simple crystalline metal hydrides. Hydrogen bonding is an exothermic reaction and heat is released during filling of the tank; therefore, it must be cooled down. During the reverse process when releasing hydrogen, the heat must be supplied externally. Hydrogen is released in the form of gas, and the process can be repeated without any losses of the storage capacity. Reaction thermodynamics, hydrogen adsorption and desorption kinetics, the volumetric and gravimetric capacities, the price, and complexity of the process are investigated. The potential of hydrogen storage in metal hydrides lies in cars and other means of transport use where reversible storage is needed. Hydrogen desorption operates under low temperature and pressure ranges. The optimal operating conditions for fuel cells with polymer membrane are pressure 1–10 atm and temperature 25-120°C. The residual heat of a fuel cell is considered. A simple metal hydride such as $LaNi_5H_6$ can be used in this setup. The disadvantages are low gravimetric capacity (cell capacity to cell weight ratio) of hydrogen storage (approximately 1.3 %) and too high expenditure for the automotive industry.

Other materials for hydrogen storage include magnesium-based materials. Their gravimetric capacity is 5-6 % at 260-280°C experimental conditions. Complex hydrides also provide better gravimetric capacity (18%for $LiBH_4$) than simple hydrides, but the reversibility (hydrogen release) is worsened.[24]

Hydrogen storage in chemical hydrides

Hydrogen storage in chemical hydrides is a label for other hydrides that do not contain metals. These hydrides are mainly compounds of boron and nitrogen. Hydrogen is derived by a chemical reaction between hydrides and water or alcohol. This reaction is less reversible than metal hydrides; therefore, its use in vehicles is complicated. The bunt fuel and by-products are withdrawn from the vehicle and for further reprocessing.

Hydrolysis

Hydrolysis is a reaction between chemical hydrides and water to produce hydrogen. One example is a reaction between water and sodium borohydride.

$$NaBH_4 + H_2O \longrightarrow NaBO_2 + 4H_2$$

To prevent the reaction (initiated by water) during fuel manipulation, stabilising liquid is used. When the fuel is needed, the stabilising liquid is mixed with water, producing very pure hydrogen. The gravimetric capacity is around 4%. Another material suitable for hydrolysis is MgH_2. Its gravimetric capacity in laboratory conditions is up to 11 %.

$$MgH_2 + H_2O \longrightarrow Mg(OH)_2 + H_2$$ [25]

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[24] EUROPEAN COMMISSION, Directorate General. *Hydrogen storage: state-of-theart and future perspective* [online]. Luxembourg: Office for Official Publications of the European Communities, 2003. ISBN 92-894-6950-1.

Available at: http://publications.jrc.ec.europa.eu/repository/bitstream/111111111/6013/1/EUR%2020995%20EN.pdf

[25] ENERGY.GOV: OFFICE OF ENERGY EFFICIENCY & RENEWABLE ENERGY [online]. Dostupné z: http://energy.gov/eere/fuelcells/fuel-celltechnologies-office

Hydrogenation/Dehydrogenation Reactions

Hydrogenation is a chemical reaction during which a molecule of hydrogen is added to the compound. The reversed reaction is dehydrogenation, during which hydrogen is released from the compound. Hydrogenation and dehydrogenation as a possibility of hydrogen storage have been studied for many years. One of these reactions is the decalin-to-naphthalene reaction, which can release 7.3% of the mass is released as hydrogen at 210 ºC via the reaction. The advantage of this method is that no water is needed.

$$C_{10}H_{18} \longrightarrow C_{10}H_8 + 5H_2$$

New studies focus on the reaction between light metals with methanol or ethanol. Deliberate hydrogen production should be possible at room temperature. The disadvantage is the same as hydrolysis; reprocessing the by-products is complicated. The disadvantage for automotive industry's lies in need for alcohol, which increases the weight and price of the whole process.

The sorption of hydrogen

The investigation of hydrogen storage using sorption has been an important scientific topic past few years. Sorption is a process in which one substance (absorbate) becomes attached to the surface of another (absorbent). The absorption capacity of a substance grows with the size of its surface. Two known methods are physical absorption which uses attraction force, and chemical sorption, which uses chemical bonds.

Carbon Nanotubes

New studies show that the capacity to store hydrogen in carbon nanotubes (CNT) at room temperature and pressure of 8MPa does not exceed the value of 0.42% of mass fraction. CNT bundle storing a large amount of hydrogen in cryogenic conditions. Many theoretical and experimental studies confirmed that hydrogen storage capacity in carbon nanostructures is mediated by weak interaction between H_2 and CNT at room temperature. [26,27]

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[26] FROUDAKIS, George E. Hydrogen storage in nanotubes & nanostructures. *Materialstoday*[online]. 2011, vol. 14, issues 7-8. Available at: http://www.sciencedirect.com/science/article/pii/S1369702111701626

[27] Hydrogen storage in nanotubes & nanostructures, online, Available at: https://www.sciencedirect.com/science/article/pii/S1369702111701626

Boron nitride nanotubes

Another material suitable for storing hydrogen is nanotubes based on carbon and boron nitride (BNNTs). By importing heteroatoms of boron nitride into CNT, interaction of the materials with H_2 is stronger than with CNT alone. Studies have shown that the capacity of BNNTS at room temperature is up to 2.6% and can be increased to 4.2% of mass fraction of hydrogen when BNNTs structure collapses.

Pillared graphene

Carbon-based materials have a great potential for hydrogen storage in industry. One of the issues slowing its spread is the storage capacity. It is crucial to increase the number of absorbed hydrogen molecules. It was proved that absorption depends on the material porosity; therefore, a new material (pillared graphene, Fig. 23) was designed. It combines two allotropes of carbon (CNTs and graphene sheets) creating a 3D material with tunable pores.

Small pores in materials prevents hydrogen insertion; large pores, cause residual spaces in the material. Therefore, only ideal-sized pores create efficient hydrogen storage conditions. The variation of pore size can be achieved through the freedom to vary the tube length or diameter, together with the intertube distance.[28]

Overview of alternative technologies

In the previous chapter, the leading alternative hydrogen storage technologies were described. There is a large number of methods under development. In addition, experiments with hydrogen compounds (hydrocarbon, ammonia) are conducted. Currently used methods are improved. Fig.24 shows the principles of conventional and alternative methods.

[28] George E. Froudakis, Hydrogen storage in nanotubes & nanostructures,

Materials Today, (https://www.sciencedirect.com/science/article/pii/S1369702111701626)

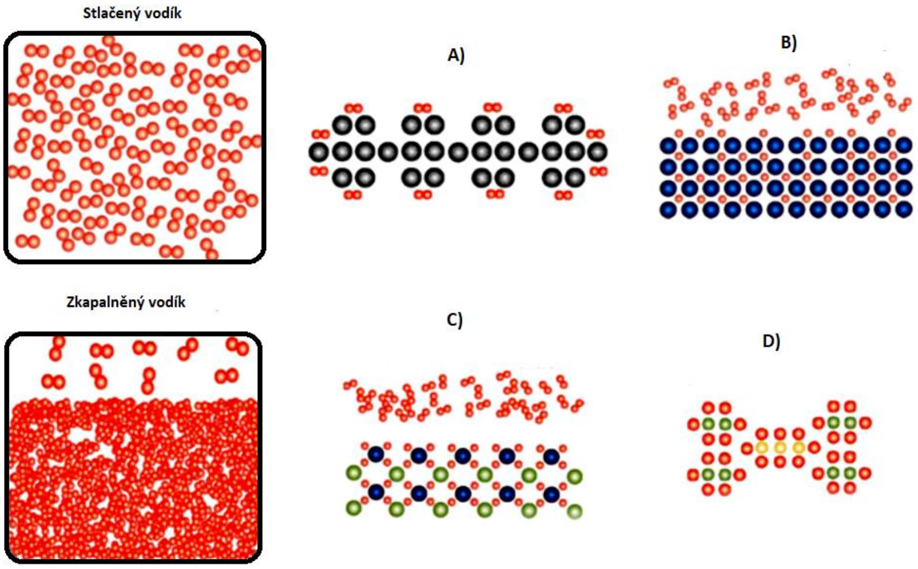

Fig. 8: Different methods of hydrogen storage and its principles

Figures in the first column show compressed and liquified hydrogen. Picture A shows hydrogen storage by absorption on the surface of solid substances, where hydrogen is bound in hydrogen molecules H_2 or atoms H. Picture B represents the absorption of hydrogen atoms that are inserted into the material grid (this method shows a large amount of storage in small volumes, at low pressure and almost room temperature). Pictures C and D show complex hydrides, where hydrogen is tightly bound in molecule structures in the form of chemical compounds. The density increases from A to D.[29]

5.6 SAFETY IN AUTOMOTIVE INDUSTRY

All fuels contain a high concentration of energy and therefore are, under certain conditions, dangerous. Hydrogen should be considered similarly or even safer than any other fuel. Hydrogen tanks are tested not only in standard crash tests but also to endure fire from a rifle. The tanks can resist twice the pressure that would typically affect them. Similar safety is achieved at the filling stations containing different types of safety systems focused on high-pressure conditions.

[29] *Fuel cell technologies program* [online]. Published: January 2011. At http://www1.eere.energy.gov/ hydrogenandfuelcells/ pdfs/fct_h2_storage.pdf

The safety advantage of hydrogen lies in its low density. Therefore, when the tank is punctured, it rises quickly into the atmosphere avoiding accumulation at the place of the accident. Also, during a fire, the flame will rise vertically above the vehicle avoiding its flare as is common with liquid fossil fuels.

Hydrogen production has been here for decades, and there have not been any exceptional tragedies. Hydrogen is also a gas that is not harmful to health, and possible leakage would not endanger people. In addition, hydrogen systems in modern vehicles are designed so that they would be isolated in case of an accident to avoid sudden flares.

CHAPTER SUMMARY:

- Hydrogen forms explosive compounds with oxygen, fluoride and chlorine that are very flammable;
- The fast expansion of compressed hydrogen can lead to spontaneous combustion;
- Direct contact with hydrogen causes burns, and its direct inhalation causes loss of consciousness and death;
- Storage of hydrogen as a gas is less energetically demanding, and 50 l cylinders and 200 bar pressure are used;
- Another method of hydrogen storage as a gas is underground storage;
- Gaseous hydrogen can also be stored in glass microspheres;
- Liquifyed hydrogen is stored in a temperature of - 253˚C;
- Up to 30% of energy acquired from liquefied hydrogen is needed for its liquifying;
- Under the influence of surrounding heat, LH2 evaporates and increases the pressure in the tank;
- The crystal grid of metal and nonmetal materials can absorb hydrogen;
- Hydrogen can be bound to the surface of different materials by adsorption and stored;

END-OF-CHAPTER QUESTION:

1. What chemical substances can cause combustion when mixed with hydrogen?
2. Describe the states in which hydrogen can be stored.
3. Explain the term hydrogen storage in the form of hydrides.
4. What is absorption?
5. What is adsorption?

6 CONCLUSION

Hydrogen as an energy source is an important current topic. It is referred to as the fuel of the 21st century. Hydrogen production is a crucial process coming from various resources. Currently, 48% of hydrogen is produced from natural gas, 30% from oil, 18 % from coal, and 4% from electrolysis. It is evident that fossil fuels dominate hydrogen production, and only a small fraction is produced by electrolysis. Thermochemical, biochemical, and photochemical production processes are still at the beginning and without industry use. In the automotive industry, only hydrogen produced by alternative methods makes sense as fossil fuels can be used as a fuel directly. That is the main reason to search for alternatives.

Water electrolysis recently cannot challenge traditional methods due to its high energy demand. Its use is suitable for countries with an abundancy of water and inexpensive electricity. Island is such country, sourcing its energy from geothermal springs. Another interesting method for hydrogen production is generators of the fourth generation. A heated cooling medium has a high enough temperature to conduct chemical cycles or high-temperature electrolysis. The most relevant method that could challenge fossil fuels in near future is hydrogen production using biomass. Biomass belongs to promising renewable sources of energy. Except for hydrogen production, it also holds large-scale energy use. The remaining issue of hydrogen use lies in its storage. Storage capacity needs to be improved for the global spread of hydrogen use due to its high weight and large volume. The cost of hydrogen still over-exceeds the cost of fossil fuels. The energetic efficiency (high energetic demand on compression, liquifying or reprocessing of chemical compounds) is another aspect needing to be increased.