# HYDROGEN AS AN ALTERNATIVE FUEL, ENERGY SOURCE AND AN INDUSTRIAL GAS

Pavel KUČERA

*VÍTKOVICE CYLINDERS a.s., Technical department, Ostrava, Czech Republic, EU,*
*pavel.kucera@cylinders.cz*

https://doi.org/10.37904/metal.2019.665

## Abstract

Hydrogen is a well-known chemical element for centuries however its use was highly limited as mainly industrial gas applied in metallurgy, chemical industry, glass industry and others. Within last two decades, hydrogen became significantly more popular thank to its use also as an alternative fuel and source of an energy. Beside hydrogen storage e.g. in hydrides and/or hydrocarbons hydrogen can be also compressed up to 1100 bar and then stored at the same pressure level thanks to the development of compression units and storage units. Regarding the on-board car storage, hydrogen is stored at 700 or 350 bar in composite pressure vessels and is being filled from mentioned 1100 or 1000 storage unit made of steel. The storage in full steel pressure vessel (Type I) is highly demanding task to fulfill all mechanical properties, pressure, SSC, cycle and hydrogen embrittlement requirements etc. Presented paper describes the background, advantages, disadvantages and issues related to the hydrogen storage and transport. Also, a comparison of hydrogen mobility and electro mobility is briefly submitted.

**Keywords:** Hydrogen, energy, storage system, high pressure vessels, hydrogen embrittlement

## 1. INTRODUCTION

Hydrogen is a widely used gas in a variety of industrial fields for more than hundred years due to its positive characteristics such as high combustibility, fairly wide flammability range (4 - 75 %) and low ignition energy. Regarding positives of hydrogen, it must be mentioned that there is almost an infinite source, which is water. And during the electrolytic production of hydrogen, the oxygen of high purity is being produced and can be subsequently used for a variety of applications. It is necessary to also mention a few negatives of hydrogen gas such as it high volatility which, short fire suppression distance, very low liquification temperature (- 253 °C) and also due to its molecular size, the potential issues regarding pressure cycles, SSC and hydrogen embrittlement requirements [1-3]. During last two decades, hydrogen became also highly common as energy carrier as its energy capacity is shown in **Table 1.**

**Table 1** Energy capacity of hydrogen compared other fuels and batteries

| **Fuels and energy sources** | **(kWh/kg)** |
|---|---|
| Hydrogen | 39.72 |
| CNG | 13.3 |
| Petrol | 13.11 |
| Diesel | 12.01 |
| LPG | 12.89 |
| **Batteries** | |
| Lithium-air | 1.33 |
| Zinc-air | 0.89 |
| Lithium | 0.36 |
| Lithium-iont batteries | 0.2 |

With the development of renewable energy sources such as wind power turbines, solar energy plants, flood tide power plants, the new approach took place. This approach is based on the minimization of the reliability on the fossil fuels using the surplus energy from renewable sources for the water electrolysis to create hydrogen, then to compress hydrogen to special pressure vessels and when there is an excessive need of the electricity supply, the electricity is created using fuell-cells system. This can be applied in large industrial scale, but also as a household application. The only side product of this catalytic reaction is a high purity water that can be used for any purpose.

Regarding the hydrogen production and its subsequent use, two main approaches are globally used. The first one, so called power to gas (P2G) is the most environmentally friendly and efficient attitude how to approach to hydrogen. It is based on the direct water electrolysis as it is depicted in **Figure 1**. Main benefit of this method is low initial investment costs, high efficiency of hydrogen production, favorable side product (pure oxygen). Hydrogen produced by this method can be directly used as a fuel for personal vehicles, busses, trains or to be injected directly to the natural gas grid. Second approach of hydrogen use so called power to methane (P2M) is a method based also on the water electrolysis combined with a subsequent mixture with carbon dioxide during the process of methanation, see **Figure 2**. This procedure can be used for certain purposes where methane is needed for fueling of vehicles, for heating purposes or to be injected to the natural gas grid. However initial investment into the equipment is significantly higher compared with P2G equipment. Another negative parameter is the low efficiency of entire process. Highly positive aspect of this method is the large volume of water as a side product

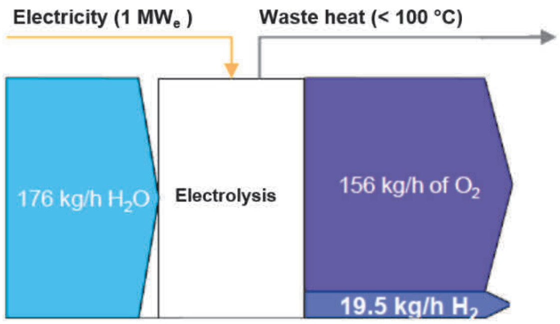

**Figure 1** Power to gas principle

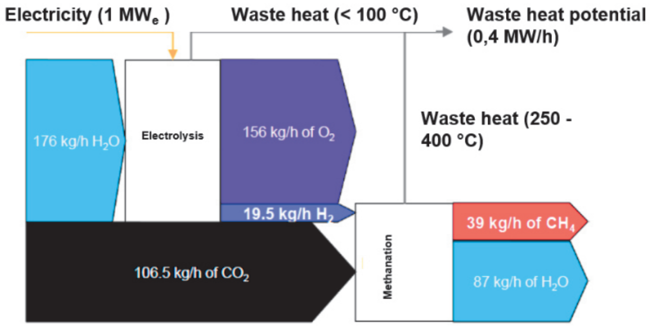

**Figure 2** Power to methane principle

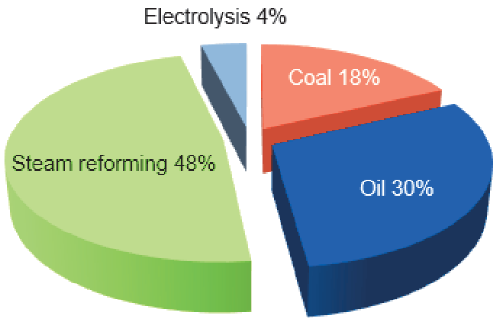

**Figure 3** The global division of hydrogen production methods

As it was already above mentioned, there are generally most common two ways of hydrogen production the first one is based on the production from the fossil fuels so called “grey hydrogen” and the second one based on the electrolysis of water producing so called “green hydrogen”. As the most common method for the grey hydrogen production, the steam reforming method is being used, where the side product of this type of hydrogen production is carbon dioxide which is nowadays exhaled to the atmosphere, instead of its purification and subsequentially compression for further use. Therefore, the process is energetically highly demanding and is also producing an unfavorable (for now) side product. The second method is an oxidation of oil fractions and the third most common type of production from fossil fuels is the production of hydrogen from coke production, based on the method of coal gasification. This last mentioned method is still the one that is giving the most promising results resulting in the energy needed vs amount of obtained hydrogen since the coke gas can contain up to 30 % of hydrogen. Unfortunately, the most ecological and energetically positive method of green hydrogen but least globally used (applied) production is electrolysis of water using either alkaline electrolyte or polymer electron membrane (PEM) or the steam electrolysis. The comparison of all hydrogen production methods division globally is shown in **Figure 3**.

One of the most challenging areas is the storing of hydrogen produced either grey or green. There are four basic technologies of hydrogen storage. The most common one used in the mobility (on-board stored tanks) and also in the storage field, is the hydrogen storage in gaseous state. This is most commonly used under several most common pressure levels … 350 bar storage is most commonly used in the field of the heavy-duty transportation (trucks, buses, trains), the 700 bar increased pressure storage tanks are typically used in the personal vehicles due to the limited space, therefore an increased pressure takes place. The on-board installed tanks are most commonly of the composite construction so called Type III or Type IV according to [4]. The gaseous state storage systems are also commonly used as the source of hydrogen for the filling of mentioned vehicles or can be used as storage of hydrogen for further use (injection to the natural gas grid, source of hydrogen for electricity production using fuel-cells, use as an industrial gas). These storage systems work usually under extremely high pressures, e.g. 500, 1000 or 1100 bar. The reason of this is the need of significantly higher storage pressure than the filling pressure for busses, trains or personal vehicles is. However, these storage systems do not have to contain composite pressure vessels or tanks due to its stationary purpose. Therefore, the construction of such pressure vessels or tanks is usually as Type I according to [5-8] sometimes in special cases, usually due to manufacturer´s production limit can be used also a version called Type II. All 4 basic standardized types of pressure vessels and tanks are depicted in **Figure 4**.

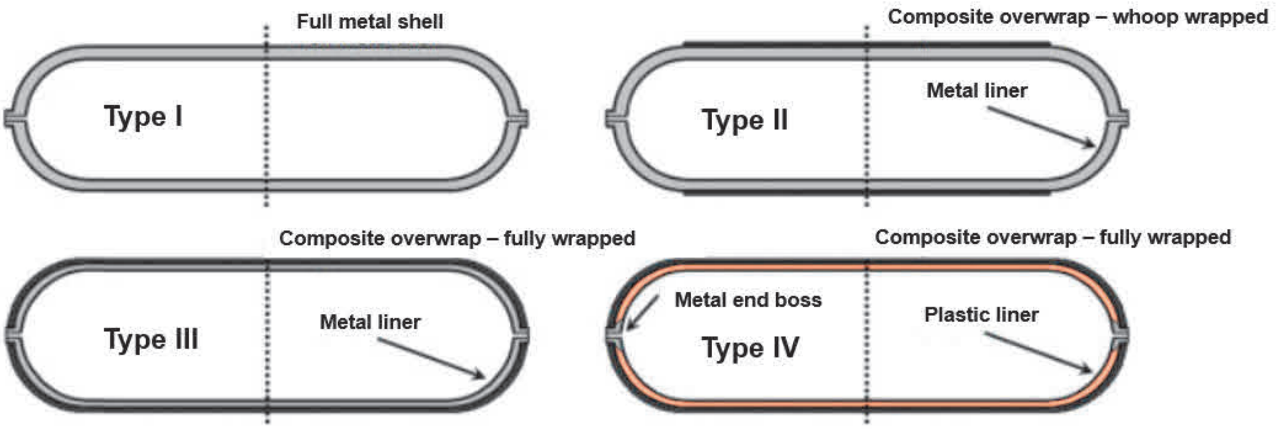

**Figure 4** Four basic types of pressure vessels and tanks

Storing of hydrogen in gaseous state provides favorable ratio of energy needed for storage vs the stored energy (approx. 20 - 30 %). Another benefit of this method is also it almost full standardization and long-lasting history of us together with a lot of global experience.

The second type of hydrogen storage system is the liquification, which is intended for mainly transportable applications. This brings significantly worse ratio of energy needed for storage vs energy stored energy, which is in this case approx. 40 - 50 %. This is caused by the significantly low liquification temperature of hydrogen. There is also a need of such hydrogen state storage in highly complex pressure vessels consisting of multilayered stainless and well insulated continuously cooled system which is working under max. 20 bar.

Absorbed hydrogen storage is the third most common method. Even thou this system provides the best ratio (approx. 15 - 20 %) of energy storage need for storage and very low storage pressure only up to 10 bar, it still has some major disadvantages, e.g. high temperature of desorption (150 + °C) and very long hydrogen availability response and finally just a partial standardization. This method is suitable only for the stationary applications due to heavy metal hydrides tanks.

Quiet new approach to hydrogen storage is the adsorbed state. This can provide favorable ratio of energy storage need for storage on the level of approx. 20 - 30 %, similar to gaseous state, but with the much larger amount of storage hydrogen up to 1.8 times. There is a huge potential but also are significant obstacles, e.g. high production costs of adsorbents like carbon nanostructures (tubes and others). This approach would be suitable for both, stationary an also transportable applications, but there is no standardization done so far.

## 2. EXPERIMENTAL PROCEDURE AND RESULTS

The entire experimental procedure has several basic steps (Reversed extrusion, neck forming and heat treating process). It begins with the production of pressure vessels as it is shown in several steps (see **Figure 5**) and subsequent calculation using finite element method (FEM) of the tangential loading stress for given pressure amplitudes that finally indicates the stress at every set pressure level**.** As the next step, test specimens are extracted from a cylindrical part of the pressure vessel and are precisely machined, see **Figure 6** according to the [9-10].

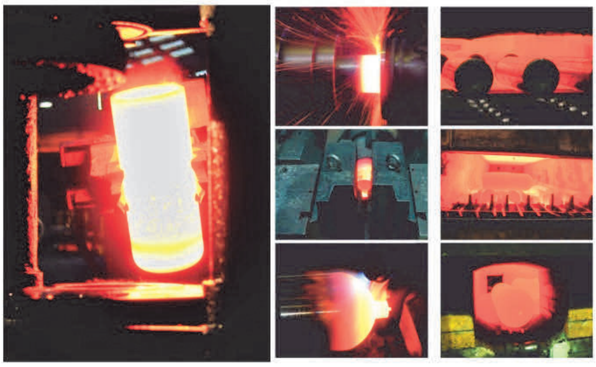

**Figure 5** Pressure vessels manufacturing steps

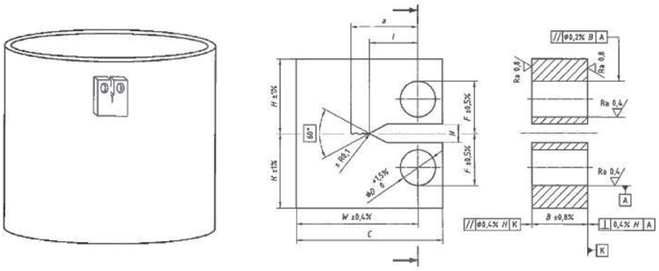

**Figure 6** Test samples extraction extraction scheme and shape

The test procedure is based on the samples cycling in the hydrogen environment using the servo hydraulic testing machine MTS 100 kN in the range of pressure amplitude (lower and upper cycling pressure) recalculated to the stress in the wall thickness. An example of test parameters of cycling in the range of 600 to 950 bar in case of the 1000 bar pressure vessel is given below:

Max. tangential stress in the pressure vessel from calculation $P_{max}$ = 346 MPa (outcome of the FEM analysis)

Corresponding $K_{max.}$ (max. stress intensity factor) = 27 $MPam^{1/2}$

Expected R (ratio) = 0.95 $P_{max}/0.6\ P_{max}$ = 0.63

$K_{95\%}$ (stress intensity factor for 95 % of working pressure) = 25.7 $MPam^{1/2}$

$K_{60\%}$ (stress intensity factor for 60 % of working pressure) = 16.2 $MPam^{1/2}$

$\Delta K$ = 9.5 $MPam^{1/2}$

$\Delta P$ (force amplitude for testing) = 2000N

f (test frequency) = 7Hz

Test gas = hydrogen

The pre-cracked specimen is then measured including the length of the initiated crack ($a_0$). The crack length is also measured ($a_t$) after the achieving desired number of cycles. Results of the testing are given in **Table 2**. Results of the test are based on the achieving or not achieving the maximum allowable defect size according to the [10] after requested number of cycles (N).

**Table 2** Test parameters and results

| Specimen N. | Thickness | Width | Crack length at the start | Crack length at the end | Number of cycles | Note |
|---|---|---|---|---|---|---|
| | B | W | $a_0$ | $a_t$ | N | |
| | (mm) | (mm) | (mm) | (mm) | (1) | |
| 1 | 12.5 | 25 | 11.01/11.01 | 11.01/11.01 | 50 000 | Not failed |
| 2 | 12.5 | 25 | 11.01/11.11 | 11.15/12.07 | 50 000 | Not failed |
| 3 | 12.5 | 25 | 10.93/10.78 | 10.93/10.78 | 50 000 | Not failed |

## 3. DISCUSSION

Achieved results clearly show that the developed method using the [10] as the basis can reveal the hydrogen embrittlement affect during the cycle loading in the high-pressure hydrogen environment. So far, all presented results with the requirement of the 50 000 cycles are satisfactory, however presented data in **Table 2** show that the crack growth length is clearly distinguishable. The crack growth differed in case of each tested specimen therefore, there it can be estimated that the most significantly affecting parameter will be preciseness of machined notch and the shape of pre-cracked flaw. This is estimated because samples were extracted from the same area there no materials differences could take place.

## 4. CONCLUSIONS

Hydrogen is the one of the most ecological and economically beneficial sources of energy that can be used in the transportation, energy, industrial and many other areas. It can be produced in a highly ecological approach, however its majority is still worldwide produced in non-ecologically. But with a progressive development of renewable source of energy, more options for ecological “green” hydrogen are available. The challenging tasks such as hydrogen storage under high and extremely high pressures are being solved and deeply investigated mainly in the field of high pressure storage systems using Type I pressure vessels and tanks. So far obtained results are showing highly positive hydrogen response that is directly linked with the desired as long as possible lifetime. Despite this, the deeper materials research has to be carried out to understand exact hydrogen embrittlement process in 300 bar and higher hydrogen pressures.

## REFERENCES

[1] KUČERA, P. and MAZANCOVÁ, E. Resistance of AISI 4135 steel to sulphide stress cracking after the accelerated cooling process under the Ar3 temperature. In 13th Conf. Degradácia konštr. Materiálov 2013. Žilina: Strojnická fakulta Žilinské university v Žilině, 2013, pp. 64-69.

[2] KUČERA, P. and MAZANCOVÁ, E. 34CrMo4 steel resistance against the SSC after controlled cooling process. Mat. Eng. 2014. vol. 21, no. 2, pp. 61-67.

[3] MOLI-SANCHEZ, EL., MARTIN, F., LEUNIS, E., CHENE, J. and WERY, M. Hydrogen transport in 34CrMo4 Martensitic steel: Influence of microstructure defects on H diffusion. Defect and Diffusion forum. 2012. pp. 323-325.

[4] ISO 19881: 2018 Gaseous hydrogen - Land Vehicle fuel containers, 2018.

[5] EN 13445-2: 2014 Unfired pressure vessels, 2014.

[6] EN 13445-3: 2014 Unfired pressure vessels, 2014.

[7] ISO 11120: 2015 Gas cylinders - Refillable seamless steel tubes of water capacity between 150 l and 3000 l - Design, construction and testing, 2015.

[8] ASME Sec. VIII Div. I: 2017 Rules for Construction of Pressure Vessels, 2017.

[9] KANDER, L, ČÍŽEK P. and STEJSKALOVÁ Š. Effect of high pressure hydrogen environment on fatigue crack growth rate properties of structural steels used for cylinders, In METAL 2017: 26th International Conference on Metallurgy and Materials. Ostrava: TANGER Ltd., Ostrava, 2017, pp. 826-831.

[10] ČSN EN ISO 11114-4: 2019 Láhve na přepravu plynů - Kompatibilita materiálů lahve a ventilu s plynným obsahem - Část 4: Zkušební metody pro výběr ocelí odolných proti vodíkovému křehnutí.