HYDROGEN KNOWLEDGE

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Introduction

The hydrogen used for the production of energy is gas molecule hydrogen, identified with the formula H_2. It is a molecule that has been known for over 200 years, and when it burns it frees energy, producing only water. However, on the Earth there are no molecule hydrogen deposits, as in the case of fossil fuels. It is a molecule that is found in great quantities in nature, but only in combination with other atoms to form, for example, water or methane. Due to the simple fact that on the Earth there are none, hydrogen is not a primary source of energy, in order to use it, it must be produced, using energy. In any case, only when it will be produced in a sufficiently economic manner will it be used as an energy vector, and only after having solved the problems tied to the fact that it is a gas that is difficult to transport, store and use.

What it is

Natural hydrogen is a colourless, odourless and non-toxic gas. It is very light, 14.4 times lighter than the air. Consequently, natural hydrogen alone cannot be found on the Earth since it disperses into the outer space. Researchers say that hydrogen only represents 0.9% of the Earth's crust components. It can be found in elementary state in volcanic emissions, fumaroles, and oil springs. However, it is present combined with other elements in many compounds such as water, mineral substances, hydrocarbons such as oil and methane, coal, animal and vegetal organisms, and organic substances. Therefore, if natural hydrogen is to be found, it will be necessary to consume much energy to extract it from the substances that contain it. This is why hydrogen is not a primary energy source, but an "energy carrier", i.e. a form of energy that is not naturally available (as the case is with natural gas, oil or coal).
In the gaseous state it is a good fuel, albeit less dense than natural gas. When it is burnt, it produces a quantity of heat expressed in Joules per kilogram 2.6 times greater than the energy produced by burning natural gas. Another feature is that it tends to form hydrides, i.e. solid compounds, when it gets in contact with most of elementary metals, thus making them more fragile. If it is cooled at a temperature of –253°C, hydrogen becomes liquid and in that state it does not react chemically with metals. This is the reason why it is difficult, in the gaseous state, to use pipelines to transport it, whereas it is easier to transport it when it is liquid.

Production from fossil sources

The technologies for the production of hydrogen from fossil fuels are mature and widely used, even though they should be improved from an economic, energetic and environmental point of view.
These processes are bases on the production of hydrogen through different refining stages and fractioning of hydrocarbon molecules until the complete elimination of carbon is obtained. In this way a huge quantity of hydrogen is currently produced, for example all the hydrogen consumed by

the chemical sector to produce synthesis fertilizers and by the metallurgic sector, for steel production.

From oil and methane. To extract hydrogen from oil or methane water steam is used at a temperature of 800°C along with a material that speeds up the process (catalyst): carbon oxidizes, hydrogen is freed from the molecule and carbon dioxide (CO_2) is released. Through this operation, called reforming, impure hydrogen is obtained, i.e. it is mixed with another gas, carbon monoxide.

To obtain pure hydrogen also this gas needs to be eliminated. This procedure is technically well experimented and is carried out at industrial level with large reactors, with a capacity of 100,000 cubic metres per hour. Another system to produce hydrogen is cracking, which consists of breaking the methane molecule through thermal systems. This system does not produce carbon monoxide, but coal and it is not among the most efficient systems.

From coal. To obtain hydrogen from coal a procedure called gasification is carried out: coal is made to react with water steam at 900°C, and then at 500°C with another catalysing compound. The resulting gas, formed of hydrogen and carbon monoxide, was once used as city gas. In the United States, over the last few years efforts have been made to carry out this operation directly in the mines, where waste could be confined, thus preventing the pollution of other areas.

Production from biomass

With regard to the production of hydrogen from biomass, no process has yet reached a mature level from an industrial point of view. One of the most used techniques to obtain hydrogen from biomass is pyrolysis, that is a process based on thermal decomposition, which breaks complex molecules of organic substances into simple and separate elements. Pyrolysis consists of heating the substance at 900-1000°C, in the absence of air, with adequate equipment, in order to obtain volatile substances and a solid residue.

Very small organisms, called photosynthetic micro-organisms, produce hydrogen with the aid of solar energy. Many researchers are now trying to understand how it is possible to obtain quite large quantities of hydrogen by using these micro-organisms. This is called photo-biological technique, and it is based on the use of solar energy combined with biological systems like algae, micro-organisms, organic waste. In particular, the studies are involving genetic engineering in order to optimize hydrogen production with the use of photosynthetic micro-organisms.

Some researchers are testing the production of hydrogen from “wet waste”, or waste water of food-processes through anaerobic bioreactors, which exploit fermentation phenomena: these techniques are called biochemical techniques. This is a promising technology and, even though it is still at an experimental stage, researchers think they will be able to obtain commercial systems in the medium-short term. All the above-mentioned alternatives require a significant commitment to research, development and demonstration, even if at different levels. However, they are all promising alternatives, also considering the different materials that need to be used.

Production from water

Hydrogen can be produced from water by splitting the molecule into its components (hydrogen and oxygen) through different processes, among which the most consolidated is electrolysis. Electrolysis is the scission of water through the use of electric energy according to the following reaction: water plus electric energy equal hydrogen plus oxygen. Electric energy could be produced in plants that exploit renewable sources. In order to obtain a cubic metre of hydrogen in the gaseous state 4-5 kW/h of electric energy are needed. The main problem is still the cost. It is true that water electrolysis produces pure hydrogen, but the price will be acceptable only when technological innovations allow to produced electric energy from renewable sources at extremely low costs.
An experimental system to separate water is thermo-electrolysis: by applying the electrolysis on high temperature vapour (900/100°C) the result is hydrogen with 2.4 kW per cubic metre. However, electrolysis efficiency is directly proportional to temperature: at 15-20°C, in order to separate water, 83% of the reaction energy must be electric energy, while at 1000 °C the percentage is reduced to 65%. High temperature vapour could be obtained from geothermal fumaroles or concentration thermo-solar power plants.
Other experimental processes are:

- photo-conversion that separates water by using biological organisms or synthetic materials;
- photo-electrochemical techniques that generate electric power;
- by using catalysing systems or semi-conductors that, associated to the sunlight, are able to separate water molecules;
- thermolysis that separates water molecules by using heat. It requires very high temperatures, i.e. around 3000°C (with many problems deriving from such temperatures).

A bit of history

The use of hydrogen as fuel was already known around the 1950s. At that time in big Italian cities, and still today in some European cities, the so-called “city-gas” was distributed for household heating purposes. That gas was a mixture of hydrogen (approximately 50%) and carbon oxide, achieved through the reaction of carbon and water steam.
Many people still associate hydrogen to the memory of the first German airships, the mythical Zeppelins, “filled” with hydrogen (lighter than the air) and very famous thanks to their transatlantic routes. Unfortunately, tragic memories emerge too. To highlight the dangers of hydrogen, the tragedy of the Hindenburg airship is often mentioned, which exploded and fell on the ground in 1937. A more accurate analysis actually showed that the presence of hydrogen was not the main cause of the tragedy. Recent studies tend to give the responsibility for the accident to the very flammable airship cover.
Over the years, the sector stimulating most research projects has been the transport sector. For decades, for example, the use of hydrogen has been proposed to replace the fuel currently used in airborne transport, mainly because hydrogen is much lighter. The first experiments in this field date back to 1957, when the United States built a hydrogen-propelled B-57 bomber (a military plane).

In the road transport sector, at the beginning of the 1970s an engineer from Turin, Massimiliano Longo, developed a system to use hydrogen in cars. This possibility became strategic with the development of fuel cells over the last decades.
Actually, in 1939 the British physic William R. Grove had already shown that the electrochemical combination of hydrogen and oxygen generates electricity. During an experiment, he managed to generate electric energy in a cell that contained sulphuric acid. Inside the cell, two electrodes, made up of two thin platinum layers, respectively attracted hydrogen and oxygen.
Nevertheless, fuel cells based on this principle remained a lab prop for over 50 years, i.e. until the ‘60s, when NASA started implementing light (and very costly) versions thereof as energy source for spaceships. At the beginning of the 1950s, the U.S. financed research on a new type of bomb characterised by greater destructive potential than the atomic bomb. The project was entrusted upon a group of scientists headed by Edward Teller and led to the implementation of a new generation of bombs, called “H” bombs or “hydrogen bombs”, the destructive power of which was astonishing, as shown by the first experimental explosion on the 1st of November 1952 on the small island of Eniwetok, one of the Marshall Islands (South Pacific). The 65-tonne bomb dug a 3 km wide and 800 m deep hole, virtually annihilating the whole island. Such bombs were never used during a war, but many experimental tests were carried out with undesired effects.
In particular, the radioactive fall-out can contaminate food and cause serious diseases such as cancer. Partly to reduce such dangers in August 1963 the United States, the Soviet Union and Great Britain signed a treaty to ban any experiment with any kind of nuclear weapon in the atmosphere (including the hydrogen bomb), in the space or underwater. Since then, many nations signed the treaty. However, some countries have not signed it yet and still carry out experiments in the atmosphere.

Storage and transport

Hydrogen not only needs to be produced, but it also needs to be transported and stored in the place of consumption. Such activities are particularly difficult due to the characteristics of hydrogen. It is flammable, has a low density and is easily dispersed into the air. Preservation and transport still make a widespread use of hydrogen quite difficult. In the last few years different storage systems have become more and more efficient and suitable for many applications. Hydrogen can be built-up and transported in gaseous, liquid state or absorbed by special materials. Each way has some pros and cons. Anyhow it is necessary to make significant progress in terms of R&D in order to make hydrogen more reliable and economically competitive (i.e. to build a suitable network for car supply).

Storage of compressed hydrogen

The easiest and most economical way to accumulate hydrogen, and use it, is in the form of compressed gas at a pressure of 200-250 bar (and over). Tanks containing compressed gas are the simplest mode of transportation, however this method is limited by the fact that hydrogen needs very large containers, up to three times the size of the tanks used for methane and ten times the size of those used for petrol. Therefore, this technology is not so suited for use on traditional cars, due to the weight and volume of the tanks that are currently used, which can provide a limited range besides a limited loading capacity of the vehicle. Recently, remarkable progress has been made with the introduction of metal structure tanks, or thermoplastic structure tanks reinforced with carbon fibre, glass fibre and other materials, whose weight is 3 to 4 times less than the common tanks, so that it has been possible to overcome most of the inconveniences of using the traditional tanks. These tanks can reach pressures up to 350 bar (potentially up to 700 bar) and therefore it is possible to obtain a hydrogen accumulation density that is suitable for vehicles. The safety specifications are usually very high due to the robust nature of the tanks and due to the introduction of explosion-proof devices in case of fire, and circuit breaker valves in case of impact.

Storage of liquid hydrogen

In order not to use big containers, it is possible to make use of liquid hydrogen, which occupies less volume than methane. But also, this method causes some difficulties: hydrogen becomes liquid at –253°C and in order to keep it in this state special tanks and lots of energy are needed. Moreover, there are many problems related to safety (losses during refuelling or in case of accident). For this reason, the most modern tanks for cars are made up of two very resistant steel layers with an empty space in between.
Storage in liquid state is probably the best technology as it satisfies car requirements. However, it also has some cons, for example: the system is much more complex, not only on board of the vehicle but also on earth, when dealing with the distribution and refuelling, as well as higher costs connected to it. Also, the energy cost for liquefaction is high, as it amounts to 30% of the energy content of the fuel, while cost for compressed hydrogen is between 4% and 7%.

Chemical storage

Other technologies exploit the ability of hydrogen to bind to chemical compounds or metals in order to facilitate its storage and transport. Hydrogen can chemically bind to different metals and metal alloys by forming hydrides, i.e. compounds that are able to trap the hydrogen at relatively low pressures (the gas penetrates inside the crystal lattice of the metal) and release it at high temperatures. This technology allows to reach energy densities that are potentially higher than compressed hydrogen and can be compared with liquid hydrogen. Storage volume could be reduced by 3-4 times, making its use in cars possible, while specific energy depends on the specific gravity of the basic metal. The percentage of hydrogen weight as compared to the total metal weight varies from 1% to 12.7% (lithium hydride), while for ordinary bottles that percentage is slightly higher than 1%.
Despite all these positive characteristics, there are still many problems to be solved in order to have a competitive storage. For example, it is necessary to work better to improve the structural and thermal stability of the material, to make pressure and temperature compatible with the expected applications, etc. Anyhow, at present, the available materials provoke a very heavy storage: with the

same weight, the vehicle has three time less autonomy than what would be obtained with liquid or compressed hydrogen and advanced tanks.
Instead, there are clear advantages in terms of convenience, compact shape, and safety. As an alternative, it is possible to transport molecules rich in hydrogen from which the gas can be extracted only where and when it is needed by means of a device called reformer (but in this way a certain quantity of waste will be obtained, too). There are different molecules that could be used in order to reach this objective, like methane (CH_4) and methanol (CH_3OH). These chemical procedures are advantageous as they allow to use already-existing transport and storage facilities. Although they are very promising, these technologies have many negative characteristics: methanol, for example, is toxic. At the moment a chemical compound, sodium boronhydride, is being tested, as it is able to bind with plenty of hydrogen. An aqueous solution, composed of half of sodium boronhydride and half of water, supplies hydrogen with an energy ratio that is similar to petrol, in terms of volume. Sodium boronhydride without hydrogen converts into borax, a substance that is present in ordinary detergents and that can be used again.

Storage in carbon nanostructures

An extremely recent experimental technology for hydrogen accumulation consists of using carbon nanostructures (carbon nanotubes and nanofibres), i.e. microscopic structures made of carbon fibres inside which it is possible to store a certain quantity of hydrogen. Discovered at the beginning of the ‘90s, they are showing a good capacity to absorb hydrogen, with sometimes impressive results. Several research groups are working on these materials, but the results obtained so far are still contrasting and difficult to compare, since the tests were made on samples of different materials, at very different pressure and temperature conditions.
Storage in crystal micro-spheres. A new promising technology to store hydrogen is based on the use of crystal micro-spheres with 25-500 micron diameter (a micron corresponds to a thousandth of a millimetre) and with walls that are a micron thick. When heated up to 400°C, the crystal wall of the micro-spheres becomes permeable to hydrogen. In this way it is possible to “trap” the gas inside them and transport it as fine dust in low-pressure micro-spheres. The extraction of hydrogen is obtained by heating the micro-spheres that, after being emptied, can be filled again. Hydrogen can be released also by breaking the spheres, although in this case they could not be recycled.

The distribution

According to the quantities, hydrogen can be transported through tankers and hydrogen pipelines. The two possibilities significantly differ in costs and therefore only technical-economic assessments can determine the best solution for each case. The long experience in the gas sector can be directly used to create hydrogen distribution networks, which are quite similar to natural gas existing networks. The main differences include the materials used (some types of steel are more compatible with hydrogen) and the design criteria for pumping stations. In fact, hydrogen requires three times as much pumping pressure as methane due to its lower density. Moreover, if the ideal diameter of

a gas pipelines is 1.4 metres, the ideal diameter for hydrogen pipelines is 2 metres. However, although it has a lower energy density than natural gas, hydrogen is less viscous than natural gas.
As a consequence, the energy needed for its pumping is similar to the energy required for the same quantity of natural gas. Large hydrogen pipelines are present in several countries. In northern France there is a network of around 170 km, while in Europe the total length amounts to more than 1500 km. North America has more than 700 km of pipes for the hydrogen transport.
The distribution networks for liquid hydrogen result to be particularly expensive and difficult to manage. They were created only for highly specialized applications, like the refuelling of spaceships.

Text updated to August 2022