

## Hydrogen

### 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.

### Hydrogen knowledge

#### 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  $-253^{\circ}C$ , 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 based 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  $800^{\circ}C$  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 optimise 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 produce pure hydrogen, but the price will be acceptable only when technological innovations allow to produce 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 physicist 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 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

### How it's transported

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 simplest and cheapest way to stock up hydrogen is to use it as compressed gas at 200-250 bar pressure (or more). Compressed gas bottles are the simplest way to transport it, although they are limited by the fact that hydrogen needs very big containers, up to three times bigger than the ones used for methane and ten times as big as those for petrol. Therefore this technology is not suggested for traditional cars, due to the weight and the size of tanks, which represent a limit for the autonomy and load capacity of the vehicle.

Recently big progress has been made with the introduction of metallic tanks or reinforced thermoplastic tanks with carbon fibre, glass and other materials, that weigh 3-4 times as much as ordinary tanks and allow to overcome many problems linked to the use of traditional bottles.

These tanks are able to operate until 350 bars (potentially until 700 bars) and allow to obtain suitable hydrogen densities according to the use on board of the vehicle. Safety is normally very high thanks to the robustness of tanks and the introduction of anti-blast fuses in case of fire, and circuit interruption valves in case of crash.

### **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  $-253^{\circ}\text{C}$  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 times 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 ( $\text{CH}_4$ ) and methanol ( $\text{CH}_3\text{OH}$ ).

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 borohydride, is being tested, as it is able to bind with plenty of hydrogen. A aqueous solution, composed of half of sodium borohydride and half of water, supplies hydrogen with an energy ratio that is similar to petrol, in terms of volume. Sodium borohydride 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 space ships.

## Uses

### Using hydrogen

The annual production of hydrogen amounts to 500 billion cubic metres, corresponding to 44 million tons, that are obtained as follows: 90% is obtained from the reforming chemical process of light hydrocarbons (mainly methane) or from the cracking of heaviest hydrocarbons (oil) and 7% from coal gasification. Only 3% comes from electrolysis.

Hydrogen can be used to produce other compounds or as a fuel to produce energy.

In particular, the hydrogen produced is used in the chemical industry, to produce ammonia, methyl alcohol (methanol), fertilizers for agriculture and oil products, as well as being used in the metallurgic industry for metal treatment.

Hydrogen is also an excellent fuel. It can be used to produce energy in two ways. The first method is by burning hydrogen alone, or added to other fuels. The second method is based on a chemical reaction between hydrogen and oxygen (without burning it), obtaining electric energy directly through a device called fuel cell.

## Directly as a fuel

The combustion of hydrogen does not provoke particular problems and produces emissions that are much less polluting than other fuels. Combustion in the air produces water, un-burnt hydrogen and traces of ammonia. Thus, using this gas to supply a household boiler or a car engine, energy would be produced avoiding the emission of toxic substances. For a few years now, hydrogen vehicles have been circulating experimentally. Moreover, any other fuel mixed with hydrogen improves its combustion and efficiency. Therefore, in the United States the use of methane to which hydrogen is added in the tune of 15% of the weight – commercially known as Hythane – is being assessed.

## Fuel cells

The devices that use hydrogen to directly produce electric energy are called “fuels cells”. Hydrogen fuel cells are electrochemical generators where electric energy is produced from the reaction between a fuel (hydrogen) and a gaseous oxidizing compound (oxygen and air). Together with electricity, heat and water are produced.

A fuel cell is made up of two electrodes of porous material, namely the cathode (negative pole) and anode (positive pole). Electrodes act as catalytic sites for the cell reactions that mainly consume hydrogen and oxygen, with water being produced and electric power running in the external circuit. Between the two poles there is an electrolyte, that has the task to drive the ions produced by a reaction (the one occurring in the anode) and consumed by the other reaction (the one occurring in the cathode), closing the electric circuit inside the cell (see image).

The electrochemical transformation is accompanied by the production of heat, which has to be extracted in order to keep the cell functioning temperature constant. This structure is completely similar to the structure of ordinary electric batteries but, differently from them, hydrogen fuel cells consume substances that come from outside and therefore can work without interruptions as long as they are supplied with fuel and oxidant.

The cell has a flat three-layer structure: the central layer, between the cathode and the anode, is made up of or contains the electrolyte. Individual cells overlap and are connected in such a way to obtain the desired voltage. A pile of cells is called stack.

Usually a fuel cell plant includes, as well as the electro-chemical part, a power converter and a transformer that convert continuous power generated by the stack into alternated power.

Fuel cells are different according to the chemical nature of the electrolyte and their functioning temperature. Those cells that release temperatures between 60 and 200°C are called low-medium temperature cells, while high temperature cells release a temperature up to 1000 °C. The latter are often used for applications that require both electricity and heat. Low-medium temperature cells cause fewer technological problems than high temperature ones, but have a worse performance.

The technology that exploits hydrogen as an energy source is now rapidly developing both for stationary applications (which do not move, like industries, households) and moving systems (transport).

Fuel cells are extremely interesting as far as electric energy production is concerned, as they have advantageous energy and environmental characteristics:

- high electricity performance, with values between 40-48% (referring to the minimum calorific value of the fuel) for low-temperature cell plants, up to 60% for high temperature cell plants
- extremely low environmental impact, both with regard to gaseous emissions and acoustic emissions. Therefore plants can be located in residential areas, making the system particularly suitable for the production of the electric energy to be distributed

- cogeneration possibility (associated production of electric energy and vapour): co-generated heat can be available at different temperatures, as vapour or hot water, and used for sanitary aims, air conditioning, etc. One of the biggest “fuel cell” electric power plants is located in Bicocca, Milan (1.3 MW power).

## Hydrogen vehicles

In this sector both internal combustion engines and fuel cell engines are being developed. The latter are essentially important in order to obtain a transport system with a minimum environmental impact.

In the first case, the engine has cylinders and pistons, it burns hydrogen instead of petrol or gas oil and does not force to review the internal combustion engine technology. In the second case, fuel cells produce power and supply electric engines.

One of the advantages in the use of fuel cells for vehicle propulsion is their energy performance. In fact, 50% of the energy produced by the fuel can be used to move the vehicle, while with petrol engines the maximum percentage amounts to 40%. Moreover, in urban traffic, energy performance of hydrogen vehicles is twice as much as traditional cars. Finally, exhaust materials only consist of aqueous vapour, therefore with no environmental impact.

Hydrogen is supplied to the vehicle cells from a tank where it is kept in liquid or gaseous state. As an alternative, it can be extracted from hydrocarbons, such as methane or methanol, directly on board, through a reformer. At present the possibility to use sodium boronhydride and sunflower oil is being evaluated.

The characteristics of fuel cells allow to build vehicles of different dimensions (from bicycles to cars, buses, locomotives) by using the same technology and with a similar performance, consumption and environmental impact.

At the moment many car manufacturers are making experimental models of hydrogen cars and buses (see image). Some prototypes are already circulating in several Italian and foreign cities.

The problem related to the development of hydrogen vehicles, as well as the production of this fuel, is that there is no distribution network and there is a lack of refuelling stations for this gas. Today hydrogen refuelling stations are very rare. The only two are in Berlin and Munich, and a third one is being built in Milan, close to Bicocca “fuel cell” plant.

Among technological problems, one of the most critical difficulties is the storage of hydrogen on board, as it heavily affects the autonomy of the vehicle due to the excessive weight and tank volume.

## Prototypes of hydrogen vehicles

An advanced prototype, which is already on the market, is the vehicle that uses a 250- atmosphere tank of pure hydrogen, with a speed of more than 150 km/h, but with a limited autonomy.

Another advanced vehicle is based on the “integrated system” concept: it consists of high pressure cylindrical tanks made of carbon fibre that provide a good autonomy also using compressed hydrogen, which is not possible with other prototypes that use metal tanks for the same type of fuel.

One of the most recent vehicle prototypes use a salt ( $\text{NaBH}_4$  = sodium boronhydride, and incorrectly called sodium borate hydroxide) as a fuel: this salted “water” (not toxic and not inflammable) passes through a catalytic system, releases hydrogen “on request”, i.e. the hydrogen is produced only when it is necessary, therefore the hydrogen is rarely free in the system. In this way the risk of fire and/or explosion is significantly reduced. The “processed” fuel is recovered in another tank as borax, that is a chemical compound very similar to soap, which is also not toxic and can be industrially recycled into a new fuel (only by adding hydrogen). This technology may be extremely useful if a cheap system is created. The vehicle has more than 500 km autonomy and a speed of more than 150 km/h.

## Safety

There are still many doubts about the safety of this energy carrier, mainly because it is still scarcely known. Anyhow, a more careful analysis reduces the concept of hydrogen dangerousness.

This gas is less inflammable than petrol (it has a higher self-ignition temperature). Hydrogen is the lightest element and

therefore can be rapidly diluted and dispersed into the open space.

It is almost impossible to make it explode, unless in a closed space (in order to find potentially dangerous concentrations, sensors are used to easily control suitable safety systems). Moreover, when it burns, hydrogen burns out very rapidly, always producing vertical flames.

Instead materials like petrol, gas oil, LPG or natural gas are heavier than the air and, as they do not disperse, they remain dangerous for much longer. It was calculated that a petrol vehicle on fire burns for 20-30 minutes, while a hydrogen vehicle does not burn for more than 1-2 minutes. Moreover, with hydrogen flames, the surrounding materials may also be set on fire. In this way the duration of the fire is reduced even more, and the danger of toxic emissions is also reduced.

Hydrogen, differently from fossil fuels, is not toxic, nor corrosive and any losses from the tanks do not provoke pollution on the soil or in aquifers.