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## THE TECHNICAL AND ECONOMICAL PERSPECTIVES FOR THE PRODUCTION AND STORAGE OF HYDROGEN IN POLAND

### Abstract

This article presents the potential of hydrogen production and storage technology in Poland. The decomposition of fossil fuels (methane reforming using steam, partial methane oxidation, autothermal reforming and coal gasification), decomposition of biological material (biological and thermochemical methods) and nuclear technologies as possible key methods of hydrogen production in Poland are discussed. The total estimated technical potential of hydrogen production was set at 37 million Mg per year nationally. Coal gasification was the most prospective technology. The methods of hydrogen storage in porous materials and polymers were also analyzed. The possibilities of using hydrogen in transport were also presented.

### Key words

hydrogen economy, hydrogen production and storage, hydrogen technical potential

### Introduction

The first postulates of the development of hydropower date back to the 1970s. In many countries around the world, primarily in the member countries of the International Hydropower Association, which brings together more than 85% of the world's GDP, efforts are being made to develop hydrogen-based energy markets. This is primarily done by guaranteeing "the practical possibility of buying a competitive hydrogen-powered car the necessary fuel near consumers' homes and workplaces" [1]. Unlike the world economic powers such as the USA, China and India, so far no national hydrogen development program has been developed in Poland. The use of

hydrogen as a source of energy remains in the background of discussions on the future of the Polish power industry, which has been dominated by renewable, nuclear, and shale power plants in recent years. Despite this, considering the important advantages of hydrogen as a fuel of the future, such as cleanliness, versatility and high calorific value, the analysis of the possibilities for hydrogen production and storage remains an interesting area of the debate on the vision of the Polish power sector in the perspective after the year 2050.

Assuming the time of exhaustion of domestic coal reserves by 2150 and the natural gas reserves by 2050, the estimated technical potential of hydrogen production in Poland is about 37 mln Mg per year. The structure of the identified H<sub>2</sub> production sources (see: Fig. 1). Taking into account the long time horizon of energy investments, as well as the existing hydrogen production potential in Poland, it is worth starting the discussion on the technical and economic perspectives of hydrogen production and storage today.

### Methods of hydrogen production

The key technologies for hydrogen production now include decomposition of fossil fuels, decay of biological material, and nuclear technologies. In Poland, from the point of view of the concept of development of low-carbon economy, the anaerobic hydrogen production by decomposition of fossil fuels is characterized by the greatest technical potential.

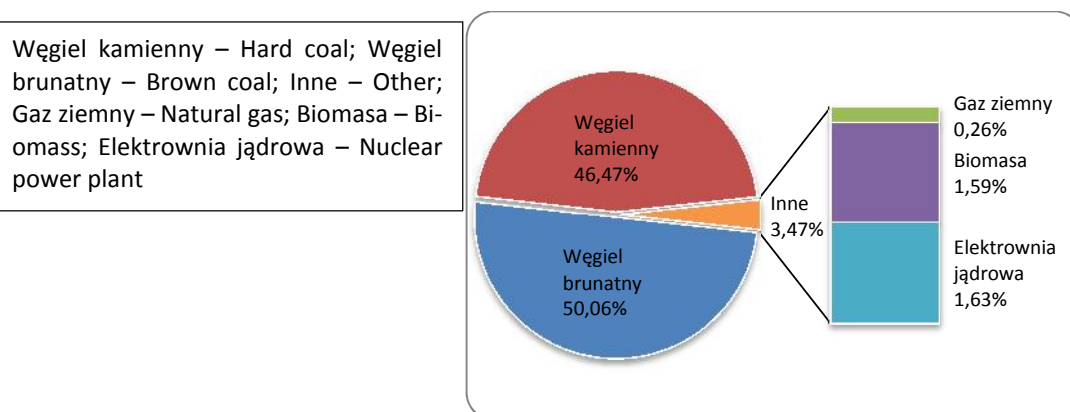


Fig. 1. The estimated technical potential of hydrogen production in Poland (100% = 36.88 million Mg annually)

Source: the author's own study.

### Decomposition of fossil fuels

At present, decomposition of fossil fuels is one of the main sources of hydrogen. It is estimated that 98% of the total annual hydrogen production in the world is generated this way (about 0.1 Gtons) [2]. The main area of application of this process are oil refineries and plants producing ammonia and methanol [3].

The most popular and most cost-effective method of producing hydrogen from fossil fuels is Steam Methane Reforming (SMR), which converts methane in ceramic tubes at a temperature of 700-1100 °C with a catalyst, such as nickel, following the reaction:

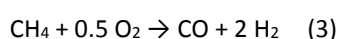


In the technological process, after the SMR, there is the Water-GasShift (WGS), following the reaction:



Separation of hydrogen produced from carbon dioxide is most commonly performed through Pressure Swing Adsorption (PSA). The final result of steam reform is hydrogen that is pure enough to use for fuel cells or ammonia production, and carbon dioxide for industrial use. The first reaction (water gas production) is strongly endothermic (it absorbs 206 kJ/mol), and the second reaction is exothermic (it releases 41 kJ/mol). The final energy balance is negative (165 kJ/mol). With perfect efficiency, producing 1 kg of hydrogen (containing 142 MJ of energy) requires the supply of 82.5 MJ of energy from the outside [4].

Another way of producing hydrogen is the partial oxidation of methane (Catalytic Partial Oxidation, or CPO), which runs under high pressure and temperature [5], in the presence of metallic catalysts (mostly nickel), following the reaction:



As in the case of methane reforming using water vapor in the hydrogen production process, the CPO is followed by the Water-Gas Shift (WGS), following the reaction (2), and then pressure swing adsorption.

In turn, Auto-Thermal Reforming (ATR) is a combined reaction of hydrocarbon fuel with water vapor (1) and oxygen (3) under thermal equilibrium conditions.

From the point of view of the Polish fuel system, the key process to produce hydrogen can be the coal gasification process, in which the primary product is syngas, resulting from the reaction:



Particularly interesting from Poland's perspective are the research works on unconventional technologies for obtaining hydrogen from coal, and its conversion into gas directly in the deposit, along with the recovery of a part of the heat [6]. The gas produced during underground coal gasification is suitable for incineration in gas turbines of much higher efficiency than in conventional coal-fired power plants, while the ash mostly stays underground, which eliminates the problems with its transport and disposal. It is expected that in the case of the widespread use of underground coal gasification, the gas from this source, including hydrogen and carbon monoxide, will become one of the world's major energy sources.

The data included in Table 1 shows that the efficiency of hydrogen production from decomposition of fossil fuels ranges from 63% to 83% and is higher than the efficiency of other possible ways of producing hydrogen. Reforming methane using water vapor, partial methane oxidation and coal gasification are also characterized by higher economic efficiency than other technologies.

Table 1. Efficiency and cost of hydrogen production using different technologies

Technology		Efficiency	Price of 1 kg of hydrogen [€]
Decomposition of fossil fuels	Steam Methane Reforming (SMR)	83%	0.75
	Catalytic Partial Oxidation (CPO)	70-80%	0.98
	Autothermal Reforming (ATR)	71-74%	1.93
	Carbon gasification	63%	0.92
Other processes	Direct gasification of biomass	40-50%	1.21
	Electrolysis powered by nuclear fission	45-55%	1.95
	PV cell-powered water electrolysis	10-14%	4.98

Source: own study based on [7]

The basic advantages of the technical processes of hydrogen production through the decomposition of fossil fuels include the possibility of easier storage of energy carriers than in the storage of pure hydrogen. This may allow for the development of a hydrogen-based vehicle technology with a mobile fossil fuel reforming system that will replace high-pressure hydrogen tanks with lower thermodynamic capacity, such as those containing liquid ethanol [8].

One of the most important disadvantages of the processes of hydrogen production through the decomposition of fossil fuels is its emissivity. The pursuit of large-scale use of SMR, CPO or ATR, while reducing greenhouse gas emissions, would be inseparable from the need for CO<sub>2</sub> capture and sequestration technologies. Another problem is the limited resources of fossil fuels on which the analyzed technologies are based. An interesting alternative may be the production of hydrogen from biogas in the process of oxyreforming [9].

The possibilities of hydrogen production from fossil fuels in Poland are primarily related to existing coal reserves, estimated at 29,814.7 million Mg of hard coal and 40,148.6 million Mg of brown coal [10]. Assuming a content of 75% of elemental coal in hard coal and 60% in brown coal, and assuming 63% of gasification efficiency, the

maximum amount of hydrogen to be obtained is 4,877.2 million Mg, which corresponds to about 50 times the current annual hydrogen production worldwide.

Much less hydrogen can be produced from Polish natural gas, the documented reserves of which amount to 98 billion m<sup>3</sup>, remaining at the disposal of Polskie Górnictwo Naftowe i Gazownictwo SA (Polish Oil and Gas Company) [11]. In addition to the domestic gas extraction, an important source of methane in Poland is its release in coal mines, the industrial resources of which are estimated at 5.6 billion m<sup>3</sup> [12]. Assuming a content of 90% of methane in natural gas and assuming 83% efficiency of steam reforming, the maximum amount of hydrogen to be obtained is 3.4825 million Mg, equivalent to about 3% of the world's current hydrogen production.

### Nuclear technologies

The technology of producing hydrogen by atomic means is a mature technology, used since the middle of last century in many countries of the world. Nuclear reactor development research has received widespread support from the industry and national governments. Significant research into hydrogen production using nuclear energy is funded by the US Department of Energy under the Nuclear Hydrogen Initiative Program [13]. The program's goal is to build and launch a commercial hydrogen production system by 2019.

Nuclear power plants can meet the demand for electricity at the base load for the industrial, service and residential sectors. To be able to recycle nuclear energy in transport and other sectors, it must be converted to a suitable non-carbon carrier, such as hydrogen. Currently, research is being carried out on a variety of methods of producing hydrogen from nuclear energy. Figure 2 shows a division into three classes depending on the range of reactor temperatures for low, medium and high temperatures. Among the methods of hydrogen production using nuclear reactors, we distinguish four basic ones: direct radiolysis of water using nuclear radiation, a combination of a conventional nuclear reactor with a low temperature electrolyzer, a combination of a medium and a high temperature nuclear reactor with a high temperature electrolyzer, and a combination of a high temperature reactor with various thermochemical water splitting cycles. Because of the low efficiency of subsequent processes of converting heat energy into a final product that is hydrogen, electrolysis is not profitable in large-scale use. Therefore, research has begun on the direct use of the thermal energy produced in nuclear processes, analyzing thermochemical water splitting, as well as sulfur-iodine, calcium-bromine and sulfur hybrid cycles. High temperature steam electrolysis, the efficiency of which is greater than that of a conventional one [14], is of great importance.

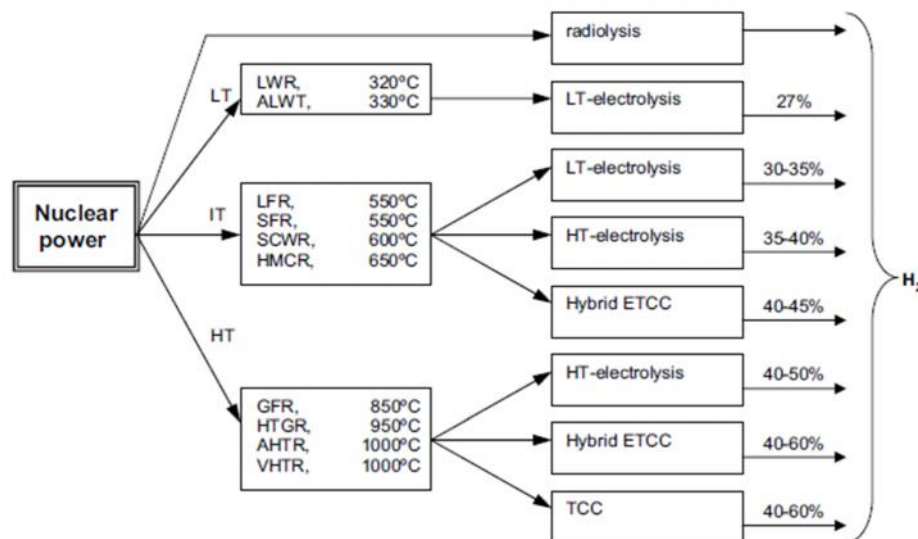


Fig. 2. Methods of using nuclear energy to produce hydrogen

Source: own study based on [15]

Markings in figure 2:

LT – low temperature,  
HT – high temperature,  
TCC – thermochemical cycle,  
ALWT – advanced light-water reactor,  
ALWT – advanced light-water,

IT – intermediate temperature,  
ETCC – hybrid electro-thermochemical cycle,  
LWR – light-water reactor,  
LFR – light-water reactor,  
LFR – lead-cooled fast reactor,

SFR – sodium-cooled fast reactor,  
 SCWR – supercritical water-cooled reactor,  
 HTGR – high temperature graphite reactor,

GFR – gas-cooled fast reactor,  
 HMCR – heavy metal cooled reactor,  
 MSR – molten salt-cooled reactor,  
 VHTR – very high-temperature reactor.

Previous studies have shown that there are 200 possible thermochemical cycles, but only some of them have gone beyond theoretical considerations. S-I cycles and sulfur hybrid cycles have been studied in many countries, including Japan, USA, France and Italy [16]. Canada, South Korea, China and South Africa also have active programs to produce hydrogen by atomic means. Apart from the two primary ones, the coordinators from Nuclear Hydrogen Initiative have described the following cycles as the most promising ones: Cu-Cl, Fe-Cl, Ce-Cl, Fe-Cl, V-Cl, Cu-SO<sub>4</sub> and hybrid-chlorine. Most of these cycles require temperatures higher than 800 °C. Such temperature ranges are only available in reactors of the fourth generation, which are not widely available for the time being due to material and design challenges. The Cu-Cl cycle has the advantage over the other ones in that it requires a temperature of 530 °C and lower. As a result, it can be combined with ultra-super-critical thermal stations and SCWR (Super-Critical Water Reactor) fourth generation generators.

The greatest emphasis is put on the development of the fourth-generation reactors in terms of cost, reliability and safety. Of the nearly 100 different concepts of this type of reactor, six have gained priority in research: VHTR (very-high temperature range, 1000 °C, efficiency 50%), SCWR (supercritical water reactor, 400-600 °C, efficiency 38-45%), GFR (fast gas-cooled reactor (850 °C, efficiency 48%), HMCR SCR (fast sodium-cooled reactor (550 °C, unspecified efficiency), MSR (molten salt-cooled reactor, 700-850 °C, efficiency 44-50%). These reactors are designed to operate at much higher temperatures than conventional light-water reactors, resulting in higher efficiency of converting heat into electrical energy. In 2002, the Department of Energy planned to improve their technology by 2025 [17]. In a broader perspective, the planned target seems unattainable in the assumed time horizon.

Assuming that the amount of hydrogen that can be obtained from a 3,000 MW nuclear power plant and the working time of 8,000 hours per year will be similar to that of existing installations in Japan [18], the maximum hydrogen mass obtained using the nuclear method will amount to approximately 0.6 million tons, which would account for about 0.6% of current annual H<sub>2</sub> production in the world.

#### **Radiolysis and conventional and high temperature electrolysis**

Under the influence of ionizing  $\alpha$ ,  $\beta$ , and  $\gamma$  radiation, dissociation of water takes place into atoms of hydrogen (H<sup>+</sup>) and oxygen-containing components, such as the hydroxyl group (OH<sup>\*</sup>), ozone (O<sub>3</sub>) hydrogen peroxide H<sub>2</sub>O<sub>2</sub>. These components, after the sequence of intermediate reactions, are converted to oxygen and hydrogen. This method has attracted interest among researchers because of the potentially wide-ranging access to radioactive waste energy from nuclear reactors. Although water splitting through radiolysis has several advantages over other indirect methods of hydrogen production, it is still a technology with limited application possibilities not only in Poland but also in the world.

The implementation of hydrogen production methods as a result of the combination with a conventional low temperature electrolytic cell is possible, inter alia, in modern LWR light-water reactors. Russian scientists Ryzantsev and Chabak have proposed using electricity produced outside the peak of nuclear reactors and conventional electrolysis for this purpose [19]. During the dips in electricity demand, the overproduction of energy can be used to produce hydrogen. According to the results of their research, a small installation with a capacity of 30 MW and a production power of 14,500 kg of hydrogen per day can be located near a working nuclear power plant. Over time, it will be possible to increase the power to 300 MW. In the example installation, it is possible to produce 8,000 t hydrogen per year using waste energy. The results of this analysis indicate that without building new nuclear units, hydrogen can be efficiently produced using the off-peak power surplus of the working units.

High temperature electrolysis is potentially more effective than traditional low temperature electrolysis, primarily because of the better kinetics of the reaction and the reduction of over-potential at the anode and cathode [15]. The conceptual design of the HTE high temperature electrolysis cycle was presented by a researcher from General Atomics in San Diego, M. Richards, who recommended the MHR (Modular Helium Reactor) as a source of heat and power. This reactor operates at a temperature up to 850 °C, which is 500 °C higher than the current operating temperature of light-water reactors. Higher temperatures allow for higher thermal efficiency in conventional electricity generation and provide the temperature required for high temperature electrolysis [20]. In the HTE installation model, a 600 MW MHR reactor was used, helium-cooled, which propels the gas turbine and

generates electrical power with an efficiency of 48-52% [20]. In the high temperature electrolysis process, nearly 11% of the heat output is used to generate superheated steam, and the rest to generate electricity for Solid-Oxide Electrolysis Cells modules. The total estimated efficiency of the installation is 55%, based on the heat of hydrogen combustion [21]. Considering, however, the relatively low peak power surplus over the electricity demand in the KSE, conventional electrolysis does not seem to be the optimal technology for hydrogen production in Poland.

### Thermochemical processes

Thermochemical decomposition of water is an emerging technology for large scale hydrogen production. In the second cycle, with the use of two chemical compounds, the water is separated into hydrogen and oxygen by a sequence of thermal and chemical processes, without discharging any impurities into the atmosphere [22]. Thermochemical cracking is a complex process in which water is separated into hydrogen and oxygen using heat energy. The most efficient is the sulfur-iodine (SI) process, carried out using waste heat from a nuclear power plant [22]. Schulz's conceptual design is based on four MHR (Modular Helium Reactor) reactors with a total heat output of 2,400 MW, which produces 800,000 kg of hydrogen per day in the S-I process. The process begins with decomposition of sulfuric acid at a high temperature. Then the acid hydrates with water. In the Bunsen reaction, sulfuric acid and hydrogen iodide are formed when heat is generated below 120 °C. Sodium is recycled so it can be used repeatedly. Hydrogen is produced by splitting hydrogen iodide into hydrogen and iodine at 300 °C. Hydrogen is produced with a total efficiency of 45% relative to the hydrogen combustion heat [20].

The Cu-Cl thermochemical cycle is also worth mentioning. Its advantage over the other ones is the lower operating temperatures mentioned in the introduction, the possibility of utilizing low temperature waste heat to achieve higher efficiency and the potentially lower cost of construction materials. Another advantage is the relatively low voltage required at the electrochemical stage, the commonly known chemical agents and no side reactions. The overall efficiency of the Cu-Cl cycle is much higher than the conventional electrolysis of water in the thermal power stations, as heat is used directly for hydrogen production, not indirectly through the production of electricity and then hydrogen. Aspen Plus simulations of the Cu-Cl cycle indicated an efficiency of up to 54% [22]. Although the value 43% is more realistic, still the performance of this technology is significant, exceeding by more than 1/3 the value of the energy conversion efficiency using electrolysis.

Nuclear energy is seen by many as a future carbon-free energy source and one that can potentially address climate change [23]. It should be noted, however, that the CO<sub>2</sub> emission, amounting to about 24.2 g / kWh, although negligible, crops up during the considerations of the fuel supply to nuclear power plants [23]. This is a negligible value compared to traditional fossil fuel-based thermal stations (600-951 g / kWh), but it increases exponentially with the decrease in uranium content in the ore [24]. As in the case of fossil fuels, nuclear fuel is non-renewable, but its resources are much higher than other resources like coal.

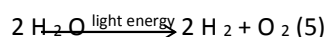
### Decomposition of biological material

Basing the production of hydrogen on fossil fuels such as crude oil or natural gas will increase Poland's dependence on foreign supplies. Improved energy security can be provided by biomass and organic waste processing technologies. These raw materials are generally available, and waste management is currently an important trend for the development of power engineering.

Biomass is widely used in the world as fuel. Its resources cover 9 to 13% of the world's energy demand [25]. In Poland, 30 million tons of biomass are produced annually [26]. In 2010, the technical potential for energy applications amounted to 13 million tons, and by 2020 it will increase to 18.5 million tons [27]. It is considered that biomass combustion does not produce CO<sub>2</sub> emissions, but emissions of other pollutants: i.a. SO<sub>2</sub>, NO<sub>x</sub> and dust cannot be ignored. Obtaining hydrogen from biomass and the subsequent use of this fuel for energy purposes only involves CO<sub>2</sub> (in the production process) and steam emissions. Hydrogen is therefore a fuel with little environmental impact. There are two groups of methods of production of hydrogen from bio-mass: thermochemical and biological. The thermochemical methods are pyrolysis and gasification. Among the biological methods, we can distinguish direct photolysis, indirect photolysis, bacterial fermentation and photofermentation.

### Biological methods

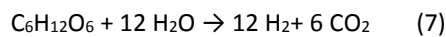
One of the basic biological methods for obtaining hydrogen from biomass is biofotolysis, which consists in the photosynthetic production of hydrogen from water, as observed in microscopic algae. Examples are *Chlamydomonas reinhardtii*, *Chlorella fusca*, *Scenedesmus obliquus*. The only substrate is water, and the reaction requires light as a source of energy:



In this case, the formation of an anaerobic environment for the incubation of algae, lasting from a few minutes to several hours, with an oxygen content of less than 0.1% is the condition required for obtaining hydrogen [28]. It is only in such conditions that they induce hydrogenases, the proteins responsible for the direct production of hydrogen. This is accomplished by grading the process. Firstly, oxygen and plastochinol are obtained, which then releases hydrogen under the influence of hydrogenases. In the presence of oxygen, hydrogen reduces CO<sub>2</sub>. To do this, it is necessary to place the culture in an environment with little sulfur content. Biofotolysis can also take place indirectly. Cyanobacteria are used in this process. This is a two-stage process, requiring, apart from water and light, CO<sub>2</sub> and N<sub>2</sub> from air and mineral salts. The first stage is the formation of carbohydrates from carbon dioxide by photosynthesis, following the equation:

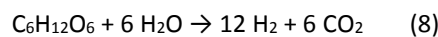


Then nitrogenase and two hydrogenases contribute to the production of hydrogen. It is important here to reduce nitrogen to ammonia while simultaneously releasing hydrogen. The production of hydrogen takes place in the fermentation process, taking place in the presence of cyanobacteria (e.g. *Cyanobacterium gloeocapsaalpicola*, *Cyanobacterium anaerobium*), following the reaction:



The advantage of biophotolysis-based methods is the negligible contribution of substrates. This may be another method of converting solar energy, alongside the generation of electricity in photovoltaic cells and heat in collectors. However, these methods are not efficient enough.

The second biological method of obtaining hydrogen from biomass is bacterial fermentation, which results from the anaerobic respiration carried out by some bacteria. The reaction products are hydrogen and carbon dioxide. Hydrogen production with this method is particularly promising due to the substrates of the reaction and the production efficiency. The substrates can be biofuel waste (glycerol), as well as substances containing glucose or other simple sugars. The maximum theoretical capacity of glucose fermentation is 12 mols of hydrogen per one mole of glucose, pursuant to the equation [29]:



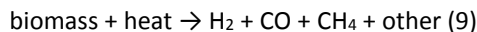
The glycerol processing capacity oscillates around 0.49 dm<sup>3</sup>H<sub>2</sub>/g<sub>glycerol</sub> [30]. The rate of such process is 10.6 m<sup>3</sup> H<sub>2</sub>/m<sup>3</sup> of the medium\*d, and in the case of sucrose fermentation, it even reaches up to 14.1 m<sup>3</sup>/m<sup>3</sup>\*d [31]. These processes do not require high temperatures - it is the range 25-80 °C, depending on the type of fermentation. Temperatures of around 100 °C are only required in the short term to eliminate acetogenic bacteria that contribute to the production of acetic acid from hydrogen, and carbon dioxide. This procedure improves the efficiency of the process. Hydrogen production is carried out in bioreactors containing a microbial culture and with feed applied cyclically. The organisms used for hydrogen fermentation can be obtained even from anaerobic sludge from sewage treatment plants, after prior elimination of methanogens. The main research is currently focused on improving the efficiency of hydrogen production so that it can obtain a solid economic justification. One way to increase the efficiency of this process is to extend it with a subsequent step - photofermentation, using unnecessary reaction products.

The bacteria that participate in the photofermentation process are green and purple sulfur bacteria and green and purple non-sulfur bacteria. Compared to plant photosynthesis, bacterial photosynthesis does not lead to oxygen production and substrates include CO or organic acids and alcohols (fermentation products). Photofermentation can be a cost-effective complementation to fermentation, and under optimum conditions it is possible to achieve a maximum yield of 12 moles of H<sub>2</sub> per 1 mole of glucose.

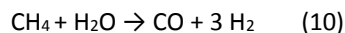
The energy input in the biological methods is solar energy and heat with temperatures slightly above 100 °C. The temperatures required by these technologies may be provided, for example, by geothermal energy.

### Thermochemical methods

Pyrolysis consists in heating biomass up to the temperature of 650-800 K under the pressure of 0.1-0.5 MPa in anaerobic conditions [28]. The products of this process are charcoal, coal, tar, acetone, acetic acid and the gases: hydrogen, methane, carbon monoxide and carbon dioxide. Catalysts are required for the reaction. For this purpose, one utilizes nickel compounds, Y type zeolites and potassium, calcium and sodium carbonates. The reaction follows the equation:



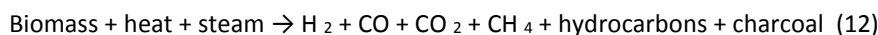
Methane is then reformed with steam to carbon monoxide and hydrogen form:



Carbon monoxide further provides as a substrate for the conversion of aqueous gas to provide an even greater hydrogen yield:



Another thermochemical method is gasification, a process in which biomass particles are partially oxidized, resulting in gas and charcoal. Charcoal is then reduced to gaseous form: hydrogen, carbon monoxide, carbon dioxide and methane. The reactions follow the equation:



The process occurs at a temperature of 975-1225 K and at atmospheric pressure [32]. The process efficiency is 40-50% vol [33]. The limitation for the gasification process is the moisture content of the biomass. The moisture content cannot be higher than 35% [28]. When this condition is not met, it is possible to conduct the process in supercritical conditions, such as using water with a temperature above 647 K and a pressure of 22 MPa.

At present, only laboratory tests on thermochemical methods (e.g. at National Renewable Energy Laboratory US DOE) are being conducted. It is anticipated that in the future, large-scale production of hydrogen from biomass using thermochemical methods will be possible.

Studies have shown that the maximum yield of hydrogen from biomass in the gasification process is 45.16 g H<sub>2</sub>/kg of biomass [34]. This will vary depending on the type of biomass, but due to the low mass percentage of elemental hydrogen in the different types of biomass, the difference will be negligible. Utilizing the entire technical potential of biomass for power generation in Poland, it is possible to obtain 5.87\*10<sup>8</sup> kg of hydrogen per year, which is 0.59% of the current global annual production of this fuel. With the increase in the biomass production potential, it is possible to reach the level of 0.84% in 2020.

### Methods of hydrogen storage

Due to the very low hydrogen density compared to other energy carriers, and at the same time the highest combustion heat per kilogram of mass, a storage method is needed that would gather the largest mass (number of particles) of hydrogen in the smallest volume of space. For example, in a liquid hydrogen tank, the liquid density is 0.07 kg/l, and in the fly state at a pressure of 700 bar it is only 0.03 kg/l, whereas the density of gasoline is about 0.7 kg/l.

One of the basic parameters associated with energy storage is its accumulative repository. In this respect, hydrogen as a fuel with very low density loses the match against the currently popular gasoline (see: Fig. 3) [34].

Gęstość objętościowa wodoru –  
Volumetric density of hydrogen;  
Gęstość masowa wodoru – Mass  
density of hydrogen

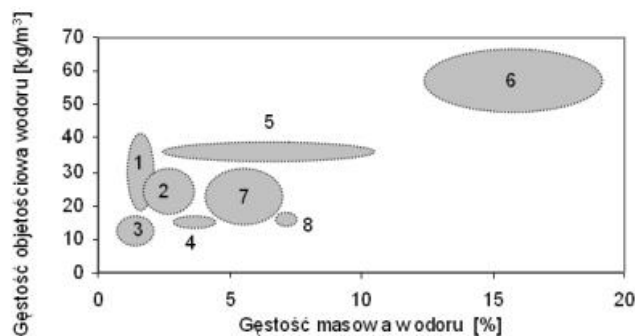


Fig. 3. Hydrogen storage density graph  
Source: own study based on [34]



Markings in figure 3:

1. metal hydrides, 5. hydrogen compressed in cryogenic containers,
2. microbeads, 6. liquid hydrogen in super insulated tanks,
3. hydrogen compressed in metal containers, 7. hydrogen adsorbed under cryogenic conditions,
4. hydrogen compressed in composite containers, 8. composite beads.

The safety and density of the stored energy are critical issues associated with traditional hydrogen storage methods in the form of compressed gas up to a pressure of 150-800 bar or a liquid with a temperature of less than 20 K [35]. The solution to the problems signaled is envisaged in the use of hydrogen accumulating materials. Storage can take place in two ways. First, following the principle of chemical absorption, when hydrogen is stored on the surface of metals and their alloys, intermetallic compounds, borohydrides, nitrides, or amides. Second, following the principle of physical sorption, which involves the adsorption of hydrogen molecules into porous materials, on their surface and in the crevices in their structure.

#### **Porous materials**

Porous materials include all kinds of coal allotropes, such as fullerenes, nanotubes, nanofibers, nanocomposites, carbon nanotubes, as well as clathrates, zeolites and organometallic structures (MOFs). Squeezing and enclosing the hydrogen inside the pores reduces the risk of it seeping through by the walls of the tank to the environment. As a result, the material requirements of storage tanks are not as restrictive as those of gas or liquid hydrogen containers (hydrogen molecules penetrate most materials, including steel).

There is a great interest in the adsorption of hydrogen on carbon nanotubes, which are cylindrical carbon nanotube structures with a diameter of 1.5 nm, admixed with potassium. It is presumed that the mass of hydrogen stored up this way can amount to as much as 65% of the weight of the tank, while the hitherto most effective physical metal hydride technologies have enabled the accumulation of hydrogen in an amount not greater than 5% of the weight of the tank [36]. The mass of hydrogen usually accounts for 14% of the mass of the storage material; an amount of 24% was obtained in laboratory conditions. However, these results cannot be reproduced in the so-called room conditions. Binding of hydrogen molecules in carbon nanomaterial structures is effective at low temperatures (77 K) and at pressures of 30-40 bar.

A similar situation applies to the storage of hydrogen in other porous materials. Hydrogen molecules can penetrate the tetrahedral cavities of  $\text{SiO}_2$  and  $\text{AlO}_4$  complexes, of which zeolites are built, or fill gaps in the crystalline structure of the clathrates, or accumulate in the space of the MOF cubic structures.

#### **Polymer materials**

One of the ideas that is still under study is the storage of hydrogen in polymer foam. The tests performed yield relatively good results due to the amount of the stored hydrogen and its ease of accumulation compared to other methods. For example, to store hydrogen in liquid form, the tank must be cooled to about  $-250^\circ\text{C}$ , which creates a big problem. When hydrogen is stored at high pressures, pressures up to 700 bar are used, where, using polymer materials, hydrogen is injected into the foam at an overpressure of only 100-150 kPa. Thanks to the long transport time of hydrogen, polymeric materials can be used not only as storage but also as buffers to offset the unevenness of hydrogen production by, for example, renewable energy sources such as photovoltaic panels or windmills.

Based on the experiments performed in works [37] and [38], the possibilities of hydrogen storage using polymeric materials have been determined. First, the sample's hydrogen transport time was examined. For this purpose, a polystyrene sample with a porosity of 97% and an estimated porosity of 250 microns and walls with a thickness of 2.5 microns was used. The sample had parallel channels for pumping and receiving hydrogen with diameters of 0.5 mm and 12 cm in length. Their distance was 3 cm. On the outside, the sample was covered with 50 micron gas-tight aluminum foil. Hydrogen in gas form was pumped into the inlet at an overpressure of 150 kPa. After 350 minutes, the steady state was reached and the pumping process was stopped shortly after. The measured parameters are shown in figure 4.

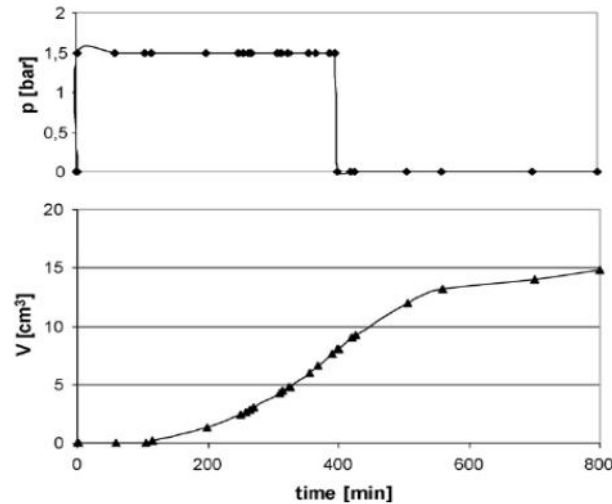


Fig. 4. Transport of hydrogen via polystyrene foam - pumping pressure (up), accumulated volume (down)  
Source: own study based on [37]

In the second part of the experiment, the capacity of the sample was examined. To this end, the channels were connected in parallel and hydrogen was pumped into both. The pumping pressure was set at 100 kPa until equilibrium was reached. It was investigated that after one hour, nearly 100 ml of hydrogen seeped out from one channel. Each channel served as an outlet for a 3.5 cm diameter foam cylinder. The measurement results for this experiment are shown in Figure 5.

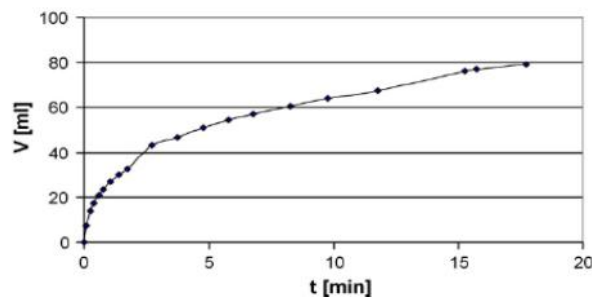


Fig. 5. Release of hydrogen from a single channel, 10 cm in length and 0.5 mm in diameter  
Source: own study based on [37]

The density of hydrogen storage in the polymer foam sample used in the experiment is very good compared to other storage methods. For example, after a simple preparation, activated carbon may store hydrogen with a mass of 1% of the carbon sample mass at a pressure of 10 MPa. When using polymer foam, the same result is achieved at as little as 350 kPa. It is also evident from experiments that in polymeric foams, a clear delay in the recovery of hydrogen with respect to the filling of the sample is apparent. In everyday use, it can therefore serve

as a buffer or offsetting storage so that hydrogen can be received at a constant speed, despite its unstable production. This way, it will be possible to neutralize the problem of high peak and low nightly energy demand in the future.

### **Hydrogen in transport**

Because of the hydrogen properties, it is impossible to use existing transmission installations for liquid and gaseous fuels in Poland. This gas has a high propensity to explode. In addition, hydrogen molecules, which are significantly smaller than all other substances on Earth, penetrate through construction materials [39]. Transmission of hydrogen from the manufacturer to the user requires the design and construction of completely new installations, which is a technical and financial challenge. The main problem of using hydrogen as a fuel in car transport is its storage. For a passenger car to drive 500 km at full load, the capacity of the liquid hydrogen tank would have to be almost three times larger, and hydrogen in gaseous form at 250 atmospheres would be about ten times larger than the traditional gas tank [40]. Large tank sizes entail an increase in investment, and it is worth pointing out that the materials from which hydrogen storage facilities are made are relatively expensive. Apart from the economic aspect, the mounting of large tanks in vehicles is technically unjustifiable. Considering the energy storage process, safety considerations should also be considered, as hydrogen forms an explosive mixture with air.

For a car to have a range of about 500 km, it should be able to store several kilograms of hydrogen. Currently, compressed gaseous hydrogen for use by welders is stored in cylinders that can store 40 liters of hydrogen at 150 atmospheres. This is about 0.6 kg of hydrogen. The use of such cylinders in cars is the simplest solution, but with some disadvantages. To allow a few kilograms of hydrogen to be refilled at one time, more cylinders or tanks that would be able to be filled with gas at significantly higher pressures would be needed. Another downside is the high consumption of energy in the gas compression process. If the gas was compressed to 600 atmospheres, half of the energy of the hydrogen transported in such conditions would have to be used for compression.

Another solution is to store hydrogen in cars in liquid form. In this case, the energy consumption of the process is also significant, as the gas needs to cool to a temperature of  $-253\text{ }^{\circ}\text{C}$  and hydrogen should be maintained in the car at a temperature of  $-250\text{ }^{\circ}\text{C}$  [41]. Two solutions are possible to maintain such a low temperature for the transported hydrogen: liquid nitrogen cooling or vacuum insulation. Hydrogen-absorbing materials such as specially activated carbon or metal hydrides can also be used as a method of storing hydrogen. These materials absorb hydrogen and release it at an appropriately higher temperature. The problem, however, is that these materials absorb only about 5% of hydrogen in relation to their mass, so filling 5 kg of hydrogen would require 50 kg of the material.

Car manufacturers interested in introducing hydrogen as a driving agent have formulated many demands for the implementation of the new fuel economy, i.a. safety of use and mechanical strength of the storage system, as well as:

- maximum storage tank capacity at the level of 200 l;
- mass of the stored hydrogen at the level of 5-7 kg, allowing to drive 500-700 km;
- ratio of the mass of the stored hydrogen to the mass of the storage material exceeding 10%;
- pressure and operating temperature of the storage below 25 bar,  $80^{\circ}\text{C}$  respectively;
- a small amount of heat released during storage (filling the tank) and delivered when the storage is discharged (emptying the tank);
- storage loading time (tank filling) not exceeding 5 minutes.

Current consumption of oil in Poland is 26.3 million tons per year [42], equivalent to 8.52 million tons of hydrogen. Obtaining such an amount of hydrogen through gasification of hard coal would require the consumption of 81 million tons of coal, and if the cheaper brown coal was used for this purpose, 102 million tons of coal would be required, with an assumption of a content of 75% of elemental carbon in the hard coal and 60% of elemental carbon in the brown coal, as well as assuming an efficiency of 63% for the gasification process. The use of such quantities of brown coal for hydrogen production would cause the country's resources to be exhausted after 30 years, and if hard coal was to be used for hydrogen production, its resources would have been exhausted within 116 years. Carbon dioxide emissions alone would increase by 120 million tons annually, or more than 34% of the total Polish emissions from 2011.

### **Conclusion**

Due to the rising prices of gasoline and diesel fuel and the growing trend of pro-ecological and pro-efficiency trends, the use of hydrogen as a source of energy seems to be only a matter of time. The potential of hydrogen

production from fossil fuels, primarily from coal, is very large in Poland. This would, however, require halting the 20-year downturn trend in Polish coal mining, the implementation of new mining technologies and techniques, utilizing the difficult to mine coal deposits, as well as solving the environmental protection problems.

Hydrogen, the most common element in the universe, has long been hailed as the fuel of the future. In particular, the automotive industry pins its faith on it, treating it as a gold mine for rising petrol, diesel fuel and gas prices. However, the tremendous enthusiasm associated with the use of this energy carrier with a calorific value of 120 MJ/kg, unmatched in comparison to conventional fuels, is played down by the problems associated with its safe and efficient storage.

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