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Hydrogen in energy balance – selected issues

Abstract: Energy from different sources is fundamental to the economy of each country. Bearing in mind the limited reserves of non-renewable energy sources and the fact that their production from new deposits is becoming less economically viable, attention is paid to alternative energy sources, particularly those that are readily available or require no substantial financial investment. One possible solution may be to generate hydrogen, which will then be used for heat (energy) production using other methods. At the same time, these processes will be characterized by low emission levels compared to conventional energy sources. In recent years, more and more emphasis has been placed on the use of clean energy from renewable sources. New, more technically and economically efficient technologies are being developed. The energy use worldwide comes mostly from fossil fuel processing. It can be observed that the share of RES in global production is growing every year. At the end of the 1990s, the share of renewable energy sources was at 6–7%. Global trends indicate the increasing demand for renewable energy due to its form. Global hydrogen resources are practically inexhaustible, but the problem is its availability in molecular form. The article analyzed the use of hydrogen as a fuel. The basic problem is the inexpensive and easy extraction of hydrogen from its compounds; attention has been paid to water, which can easily be electrolytically decomposed to produce oxygen and hydrogen. Hydrogen generated by electrolysis can be stored, but due to its physicochemical properties, it is a costly process; therefore, a decision was made that it is better to store it with natural gas or use it for further reaction. In addition, hydrogen can be used as a substrate for binding and converting the increasingly problematic carbon dioxide, thus reducing its content in the atmosphere.

Keywords: hydrogen, energy balance, power-to-gas

Wodór w bilansie energetycznym – wybrane zagadnienia

Streszczenie: Energia z różnych źródeł ma zasadnicze znaczenie dla gospodarki każdego kraju. Mając na uwadze ograniczone zasoby nieodnawialnych źródeł energii oraz fakt, że ich produkcja z nowych złóż staje się mniej

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opłacalna, zwraca się uwagę na alternatywne źródła energii, szczególnie te, które są łatwo dostępne lub nie wymagają znacznych inwestycji finansowych. Jednym możliwym rozwiązaniem może być wytwarzanie wodoru, który będzie następnie wykorzystywany do produkcji ciepła (energii) za pomocą innych metod. Jednocześnie procesy te będą charakteryzować się niskim poziomem emisji w porównaniu do konwencjonalnych źródeł energii. W ostatnich latach coraz większy nacisk kładzie się na wykorzystanie czystej energii ze źródeł odnawialnych. Trwają prace nad nowymi, wydajniejszymi technicznie i ekonomicznie technologiami. Ogólnoświatowe zużycie energii pochodzi głównie z przetwarzania paliw kopalnych. Można zaobserwować, że udział OZE w globalnej produkcji rośnie z każdym rokiem. Pod koniec lat dziewięćdziesiątych ubiegłego wieku udział odnawialnych źródeł energii kształtował się na poziomie 6–7%. Wskazują na to globalne trendy, zwiększając zapotrzebowanie na energię odnawialną ze względu na jej formę. Globalne zasoby wodoru są praktycznie niewyczerpane, ale problemem jest dostępność w postaci molekularnej. W artykule analizowano wykorzystanie wodoru jako paliwa. Podstawowym problemem jest tania i łatwa ekstrakcja wodoru z jego związków; zwrócono uwagę na wodę, którą można łatwo rozłożyć elektrolitycznie w celu wytworzenia tlenu i wodoru. Wodór generowany przez elektrolizę może być przechowywany, ale ze względu na jego właściwości fizykochemiczne jest to kosztowny proces; dlatego zdecydowano, że lepiej jest przechowywać go za pomocą gazu ziemnego lub użyć go do dalszej reakcji. Ponadto wodór może być stosowany jako substrat do wiązania i przekształcania coraz bardziej problematycznego dwutlenku węgla, zmniejszając w ten sposób jego zawartość w atmosferze.

Słowa kluczowe: wodór, bilans energetyczny, power-to-gas

Introduction

Energy from different sources is fundamental to the economy of each country. This is due to the fact that it is essential for human life, transportation, and industrial production. Bearing the limited reserves of non-renewable energy sources and the fact that their production from new deposits becomes less economically viable in mind, attention is paid to alternative energy sources, particularly those that are readily available or require no substantial financial investment. The proper development of the economy of any country depends on an efficient system for the acquisition and processing of energy. That is why renewable energy sources, such as wind farms, solar power plants, hydroelectric power plants, and geothermal power stations, begin to play a special role. Particular attention is paid to issues related to the processing and storage of energy obtained in this way. One possible solution may be to generate hydrogen, which will then be used for heat (energy) production using other methods. At the same time, these processes will be characterized by low emission levels compared to conventional energy sources.

The increasing prices of oil and its derivatives along with ecological constraints associated with carbon dioxide emissions attract consumers towards more cost-effective and environmentally friendly solutions. The ones that do not use oil derivatives or burn less fossil fuels are becoming increasingly popular.

Historical background

One of the first studies on hydrogen was carried out in the 16th century by Swiss physician and scientist T. Paracelsus. By reacting zinc with hydrochloric acid, he produced a flammable gas, calling it “flammable air”. Hydrogen as an element was discovered by Henry Cavendish in 1781. Another discovery was the formation of water by the combustion of hydrogen (hence the name: in Greek, hydrogène means "water-former"). In Poland, the name "wodór" probably derives from the Russian word "wodorod" (Nowacki 1983).

Hydrogen (Latin *hydrogenium*) is the most common element in the universe and is also the simplest element known to man. A hydrogen atom has only one proton and one electron. In gas form, hydrogen is the most abundant in space; it is the source of all the energy that we receive from the Sun.

Hydrogen, in the gaseous form, is not found on Earth. It is naturally found only in complex forms. The reaction of hydrogen with oxygen produces water (H_2O). In combination with carbon, organic compounds, such as methane (CH_4), coal, petroleum, and many others, are formed. It is also found in all plant and animal organisms, which can be described as biomass. Hydrogen is one of the most abundant elements in the earth's crust.

Physical properties of hydrogen

Hydrogen is found on Earth almost exclusively in chemical compounds[1]: in the form of water, hydrocarbons (crude oil, natural gas), and all the organic compounds found in living organisms.

The Net Calorific Value of hydrogen is very high and amounts to 119.6 MJ/kg (for comparison – in the case of methane it amounts to 50 MJ/kg, for gasoline: 45 MJ/kg, while for coal it is 25 MJ/kg).

Hydrogen as an energy carrier appears in three forms: gas, liquid, and solid.

Hydrogen in a gaseous state – The density of hydrogen gas H_2 (273 K, 1013 hPa) is 89.86 g/m^3. It is therefore easy to calculate that under these conditions 1 kg of hydrogen has a volume of 11.1 m^3, while in the case of methane this value is only 1.4 m^3. Therefore, hydrogen in gas form is stored under high pressure.

Hydrogen in a liquid state – The density of liquid hydrogen LH_2 (the prefix 'L' stands for liquid) is 70.8 kg / m^3 at 20.4 K; it is also the boiling point of hydrogen. Liquid hydrogen is stored in stationary or mobile insulated tanks, but the costs of condensation and storage are high. The energy needed for hydrogen condensation is about 10 kW h/kg LH_2, while, for example, losses of well-insulated spherical tanks with a capacity of 225 to 650 m^3 amount to 0.1% H_2/day (Kabat and Sobański 1998).

Hydrogen in a crystalline state – The density of hydrogen in a crystalline state is 86.6 kg/m^3 at 14.0 K (the melting point of hydrogen). Hydrogen is not produced for storage or transport in this form.

Hydrogen in any form is the lightest element in the universe. The thermal conductivity of hydrogen of 0.1745 W/(m K) and the specific heat of 14.195 kJ/(kg K) (at 273 K) are the largest among all gases. Hydrogen diffuses through rubber, porous materials, and, at elevated temperatures, steel. Hydrogen dissolves well in palladium, niobium, platinum, nickel (870 volumes of hydrogen in one palladium volume, 850 volumes of hydrogen in one vo-

[1] As a gas in its free state, hydrogen is only found in trace amounts. It is produced by some marine algae and algae under extreme conditions for these organisms (lack of oxygen).

lume of niobium), while very poorly in water (0.021 volume of hydrogen in 1 volume of water). Table 1 summarizes the hydrogen properties.

TABLE 1. Properties of hydrogen

TABELA 1. Właściwości wodoru

Property	Unit	Value
Melting point	K	14.0
Boiling point at 0.1013 MPa	K	20.4
Critical temperature	K	23.2
Critical pressure	MPa	1.33
Critical density	g/cm^3	0.0301
The relative density of hydrogen to air	–	0.0695 1:14.4
Specific heat at p = const Gaseous state at 298 K Liquid state at 17 K Crystalline state at 14 K	 J/g·K J/g·K J/g·K	 14.3 8.1 2.6
Enthalpy of fusion at 14 K	J/g·K	58.6
Enthalpy of vaporization at 20.4 K	J/g·K	447.9
The dynamic viscosity coefficient at 288 K	mPa·s	0.00892
Net Calorific Value	kJ/m^3_n kJ/kg	10 760 119 600
Gross Calorific Value	kJ/m^3_n kJ/kg	12 770 142 000

Source: Kabat and Sobański 1998.

The combustion of the hydrogen-air mixture can be carried out in a relatively wide concentration range (between 4.1 and 72.5%) of hydrogen in air. Other fuels have significantly lower flammability ranges, e.g. natural gas: 5.1–13.5%, propane: 2.5–9.3%. The most important parameters of hydrogen, methane, and propane combustion are summarized in Table 2.

Hydrogen at room temperature can form an explosive mixture only with fluorine, with chlorine only under the influence of light at 480 nm, and with oxygen at 450°C. The reaction with oxygen is a highly exothermic reaction. Safe hydrogen combustion can be carried out in a Daniell burner (oxyhydrogen burner) where it burns up to 2600°C.

TABLE 2. Properties of hydrogen, methane, and propane

TABELA 2. Właściwości wodoru, metanu i propanu

Parameter	Unit	H_2	CH_4	C_3H_8
Net Calorific Value	kJ/kg	119 972*	150 020	46 350
	kW·h/kg	33.33	13.90	12.88
	$MJ/m^3{}_n$	10.783	35.882	93.215
	$kW·h/m^3{}_n$	2.995	9.968	25.893
Gross Calorific Value	kJ/kg	141 890	55 530	50 410
	kW·h/kg	39.41	15.42	14.00
	$MJ/m^3{}_n$	12.745	39.819	101.242
	$kW·h/m^3{}_n$	3.509	11.061	28.123
Lower Wobbe Index	MJ/m^3	40.898	48.170	74.744
	$kW·h/m^3$	11.361	13.381	20.762
Upper Wobbe Index	MJ/m^3	48.340	53.454	81.181
	$kW·h/m^3$	13.428	14.848	22.550
Ignition temperature in air	°C	530	645	510
Limits of flammability in the air	% vol.	4.1–72.5	5.1–13.5	2.5–9.3
Maximum flame speed	cm/s	346	43	47

Source: Zittel 1996.

1. Hydrogen in the energy balance

Since the industrial revolution in the 18th century, the development of civilization on Earth has been based on fossil energy resources. The basis for the industrial revolution of the 18th century was the energy obtained from coal. In the late 19th and early 20th centuries, crude oil enabled the development of the automotive industry, the development of which continues to this day. A rapid increase in the use of natural gas, which turned out to be a versatile raw material widely used not only in the energy sector but also in the chemical industry, took place after the Second World War (Mokrzycki et al. 2008).

In the second half of the 20th century nuclear power was considered to be highly prospective for the further development of the power industry, but at the same time, in a certain sense, it was considered a threat. There is no doubt that the Chernobyl nuclear power plant disaster has contributed to perceiving nuclear power in this light. Recent technical solutions aimed at the construction of safe and economical nuclear reactors should gradually change the traditional, now outdated image of nuclear energy.

In recent years more and more emphasis has been placed on the use of clean energy from renewable sources. New, more technically and economically efficient technologies are being developed.

Energy balances summarize both the amount of produced and imported energy in a given country and the demand for this energy in economic sectors in economic terms. Fossil energy carriers (natural gas, coal, and crude oil) play a key role in the structure of raw materials.

Hydrogen production, e.g. by the use of renewable energy sources and its further use (conversion to electricity, heat, or chemical energy), is characterized by a cyclical nature. Hydrogen conversions during the following stages: production – transport and storage – consumption – natural environment are presented in Fig. 1. Oxygen is a byproduct of hydrogen production, which is then required for hydrogen combustion. Thus, a closed oxygen cycle can be observed. In addition, a closed water cycle is also reported, which is, on the one hand, the result of hydrogen combustion and the substrate for its production on the other (Koroneos et al. 2004).

The current energy use worldwide comes mostly from fossil fuel processing. However, it can be observed that the share of RES in global production is growing every year. At the end of the 1990s , the share of renewable energy sources was at 6–7%. Global trends indicate (Table 3) increasing demand for renewable energy due to its form – in many cases it is considered as "clean energy" and has inexhaustible resources. The disadvantage of renewable energy sources which are currently most used (solar and wind energy) is their instability over time.

Global hydrogen resources are practically inexhaustible, but the problem is its availability in molecular form (hydrogen is not a primary energy carrier). To use hydrogen as a fuel, it should first be produced (recovered). Financial expenditures, depending on the technology used and the amount of energy needed to produce hydrogen, have so far reduced its attractiveness compared to cheap fossil fuels. The increased share of unstable RES forces the use of energy storage systems. One of the solutions that have been proposed for several years is the use of surplus electricity in the power sector for the production of hydrogen, followed by its injection into the gas network and methanation (Fig. 2).

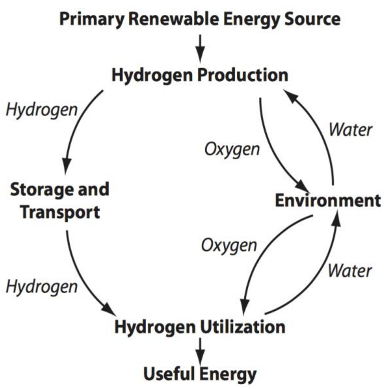

Fig. 1. Life cycle of hydrogen produced from renewable sources
Source: Koroneos et al. 2004

Rys. 1. Cykl przemian wodoru wytwarzanego za pomocą źródeł odnawialnych

TABLE 3. The increase in installed capacity worldwide and energy production by source in the years 2004–2014

TABELA 3. Przyrost mocy zainstalowanej na świecie oraz produkcja energii według źródeł w latach 2004–2014

Source:	The installed capacity in 2004 [GW] and its share in total installed capacity [%]		The installed capacity in 2014 [GW] and its share in total installed capacity [%]		The average annual growth rate [%]	The energy production in 2014 in [TWh] and its share in total production [%]	
Hydropower	715	18.8	1.055	17.1	4	3.898	16.6
Wind power	48	1.3	370	6.0	23	728	3.1
Biomass	39	1.0	93	1.5	9	423	1.8
Solar power	3	0.1	181	2.9	51	211	0.9
Geothermal energy	9	0.2	13	0.2	4	94	0.4
Total RES	814	21.4	1.712	27.7	8	5.353	22.8
Total conventional energy carriers (oil, gas, and coal) and nuclear energy	2.986	78.6	4.468	72.3	4	18.127	77.2
Total	3.800	100	6.180	100	5	23.480	100

Source: based on WEC 2016.

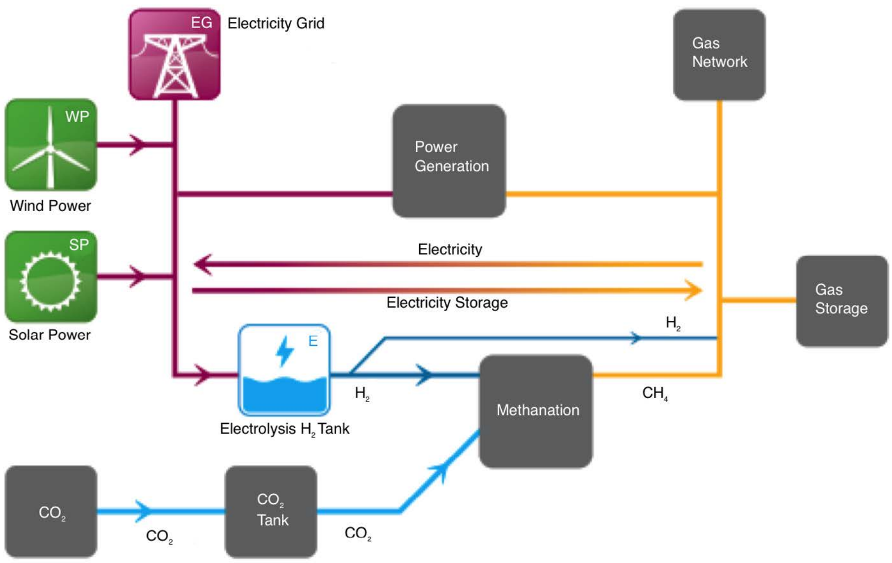

Fig. 2. Methods of hydrogen and energy generation
Source: ITM Power 2017

Rys. 2. Metody wytwarzania wodoru i energii

It is believed that hydrogen will be one of the basic energy carriers in the near future. Different technologies for hydrogen production are currently being developed. The studies are focused on the use of renewable energy sources. All possible methods of hydrogen and energy production are presented in Figure 2.

Hydrogen is most commonly obtained with the use of the following technologies: the reforming of natural gas, electrolysis of water, biochemical methods, gasification of coal, and the separation of hydrogen from gases industry with particular reference to coke oven gas.

Currently, most of the hydrogen is produced from natural gas, but the hydrogen production with the use of water, wind, radiation, and biomass energy is increasing every year. It is also possible to obtain hydrogen by water electrolysis in nuclear plants. The problem is the introduction of hydrogen as a mass-produced fuel, which requires the solution of problems related to storage and distribution.

In the majority of highly developed countries, reference hydrogen stations are already operating. It cannot be forgotten that hydrogen can be obtained from biomass by pyrolysis thermochemical processes. This process takes place without the access of air or by gasification with oxygen or water vapor. The thermochemical conversion of biomass and its waste to hydrogen, which involves the reaction of biomass with water at 700°C and a pressure of 350 bar, is a specific case. The current applications of hydrogen are presented in Fig. 3.

The best way to use hydrogen for energy purposes is to use fuel cells for electricity generation. In the case of methane fuel cells also give better results than direct combustion.

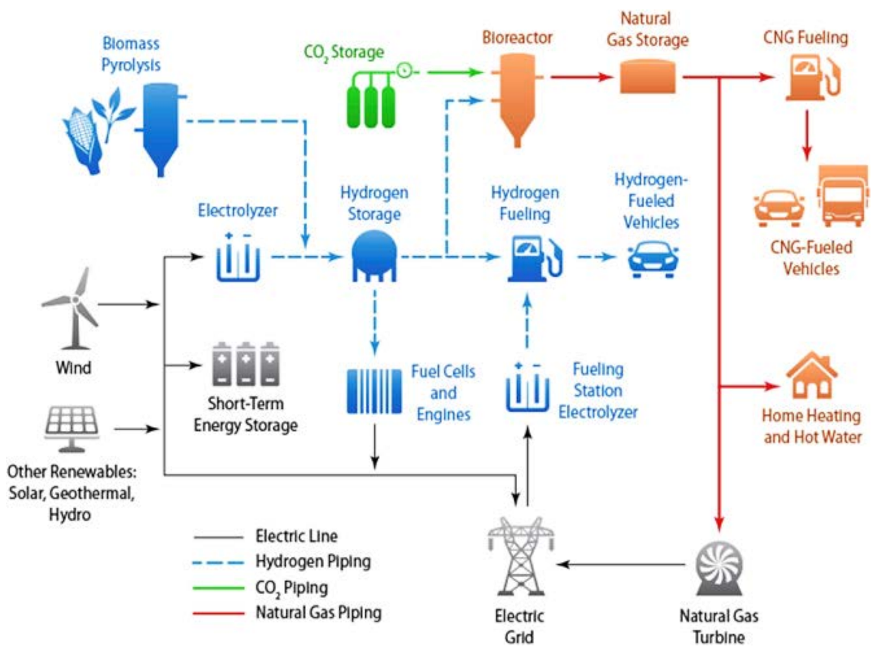

Fig. 3. Applications of RES and hydrogen
Source: Mostafaeipour et al. 2016

Rys. 3. Możliwości wykorzystania OZE i wodoru

When it comes to the abovementioned methods of hydrogen production, it should be noted that the electrolysis of water is economically effective, provided that cheap electricity is available locally. Here, the use of wind power as a source of constant and "cost-free" energy required for the electrolysis process can be a factor of great importance.

In the United Kingdom, hydrogen is produced in wind farms located along the coastline and (mainly) at sea. In North Africa, hydrogen production is to be carried out using photovoltaic cells in the desert (Kabat and Sobański 1998: 119 600 kJ/kg). The existing pipelines of natural gas will be used for transport to Europe. Initially, hydrogen will be injected into existing natural gas pipelines, which will increase the energy value of natural gas. This method is used in the United States.

Natural gas enriched in this way is to be burned in an existing installation. In the future, the transmission and distribution network, after appropriate modernization, will also be used to transport hydrogen. Other solutions, including the mechanism where only hydrogen is transported, while electricity and heat are generated locally in fuel cells in cogeneration, are also possible. The capacity of hydrogen-based cogeneration systems can range from 1 kW to 100 MW.

From the point of view of electricity generation, it is essential to immediately transfer the received energy to the grid, if possible (therefore, the highest efficiency is obtained). However, in the case of problems in the power sector (such as network congestion, negative electricity prices, or physical damage to the grid) or there is no electricity infrastructure at the place of electricity generation, it is believed that the generated energy should be converted to hydrogen. The obtained hydrogen can be injected directly into the gas network, used in the chemical industry, or transferred and stored to be re-converted into electricity at a later time or converted to methane. Conversion into methane requires the appropriate level of hydrogen injection into the gas network.

Another reason for the use of Power-to-Gas (PtG) may be the need to overcome power transmission capacity limits or transport energy over long distances. In such a case, the current "will be converted" into hydrogen or hydrocarbon.

The ways of using electricity to obtain the final products referred to above are shown in Fig. 4. In the technology that is currently used, the first step in converting electricity into hydrogen is the process of water electrolysis.

The amount of hydrogen that can be added to natural gas in the gas infrastructure is limited due to the Wobbe index, the behavior of the gaseous mixture, and the impact on the materials used.

Due to the limitations associated with the introduction of hydrogen into the natural gas network, the potential of hydrogen storage capacity in the gas infrastructure is considerably less than the total storage capacity of methane. For this reason, the process of converting the obtained hydrogen to methane (methanation) is more and more often carried out immediately.

Power-to-Gas is a characteristic technology of storing energy contained in the gas (hydrogen or methane), while the obtained gas is produced as an intermediate product. This gas can then be processed in the form of gas or reconverted into electrical energy. In the case of re-conversion, two methods can be used:

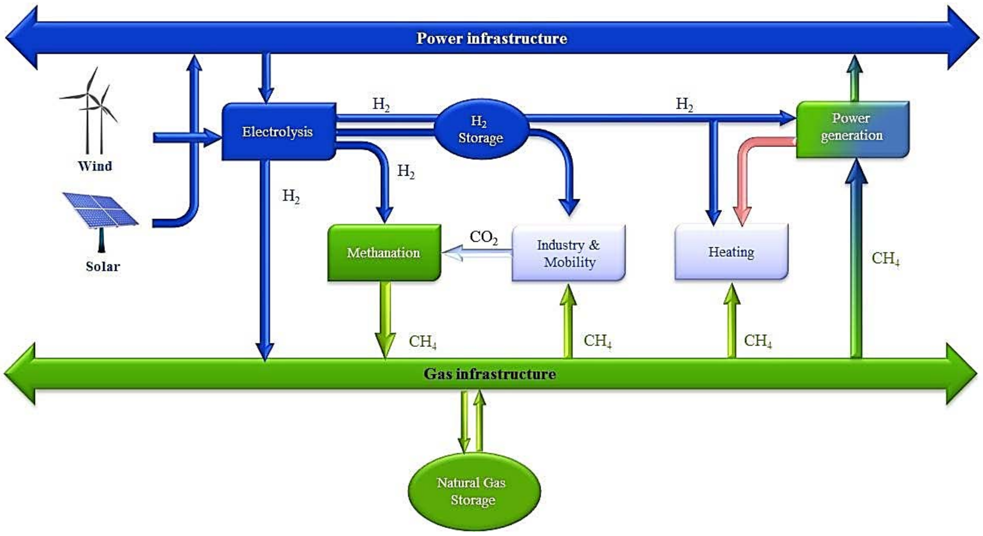

Fig. 4. The scheme of Power-to-Gas installation
Source: Grond et al. 2013

Rys. 4. Schemat instalacji *Power-to-Gas*

- hydrogen from electrolysis is stored and processed by a fuel cell,
- hydrogen/methane is added to the gas infrastructure (pipeline) and re-converted into energy using conventional (existing) gas power plants.

The above mentioned conversion paths are shown in Fig. 5. The first option is preferred for the production of energy generated in the same place where a disproportion (physical limitation) occurs or where there is no gas infrastructure. This, however, requires the PtG system to be equipped with a hydrogen buffer and fuel cell technology. The second option requires less investment and is usually suitable for market applications (Grond et al. 2013).

Fig. 5 clearly shows that the PtG should be distinguished from dedicated storage technologies. By using the PtG technology, electricity can be converted into hydrogen and methane and used in the chemical industry as raw material (directly) or indirectly as fuel in transport.

There are currently around 30 PtG demonstration plants in Europe, most of which were implemented in Germany (Schneider and Kotter 2015). Most of the activities related to PtG technology is focused on the problem of hydrogen production, and, in a further step, on the production of methane (Study on... 2014). In the majority of the demonstration projects, hydrogen is produced to be injected into the gas network, stored, or for direct use (Goetz et al. 2016). All the actions are aimed at making the applied solutions economical. However, this problem has not yet been solved, although the results of ongoing research are promising: and allow for an optimistic outlook, as shown in Fig. 6.

The largest PtG installation, commissioned by Audi AG and built in Werlte, Germany, is currently being developed by Solar GmbH. The plant, with a capacity of 6.3 MW, produces

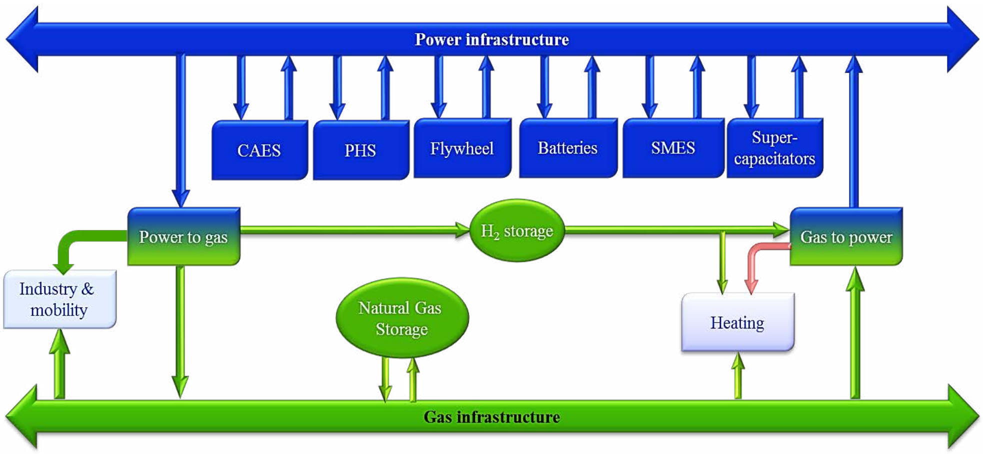

Fig. 5. Methods of energy storage
Source: Grond et al. 2013

Rys. 5. Metody magazynowania energii

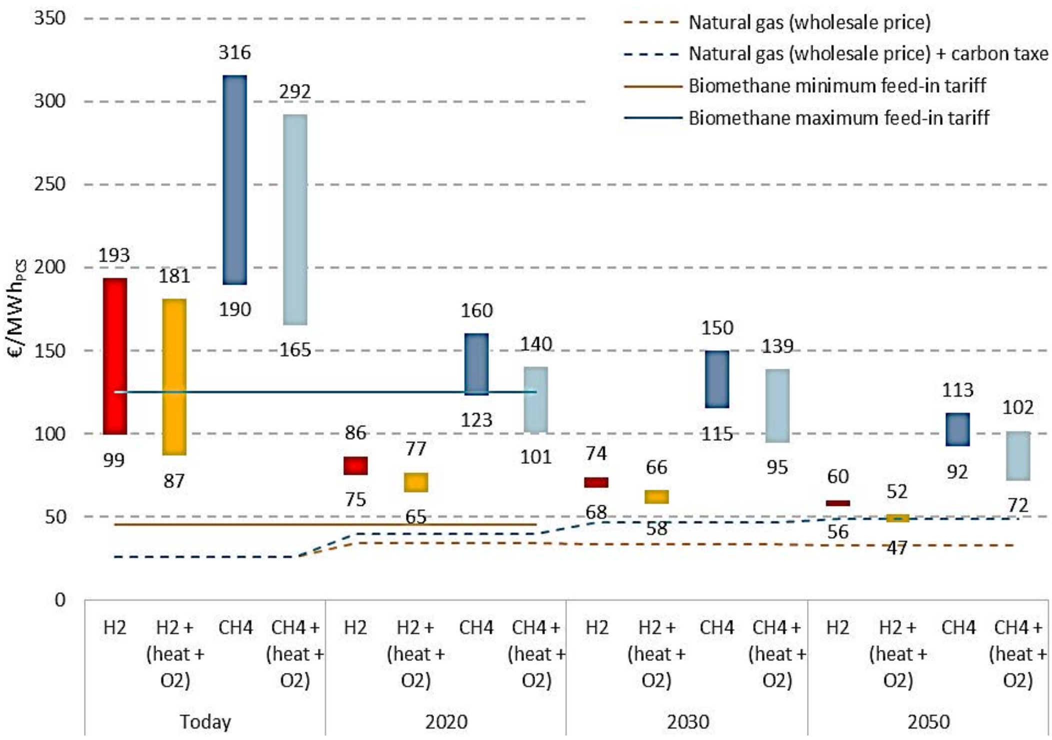

Fig. 6. The economic efficiency of PtG today and in the future
Source: Study on... 2014

Rys. 6. Efektywność ekonomiczna PtG dziś i w przyszłości

360 m^3/h of methane, which is then injected into the local gas distribution network. The source of CO_2 emissions during the process of methanation is the carbon dioxide from the sewage treatment plant of the nearby biogas plant (Grond et al. 2013).

This is in line with the general assumptions where, for a better efficiency of the whole PtG process, a solution based on the production of hydrogen by electrolysis followed by CO_2 methanation is applied.

One cannot forget that the use of the PtG technology stems from the fact that it shows the highest capacity and efficiency of storage, as shown in Fig. 7.

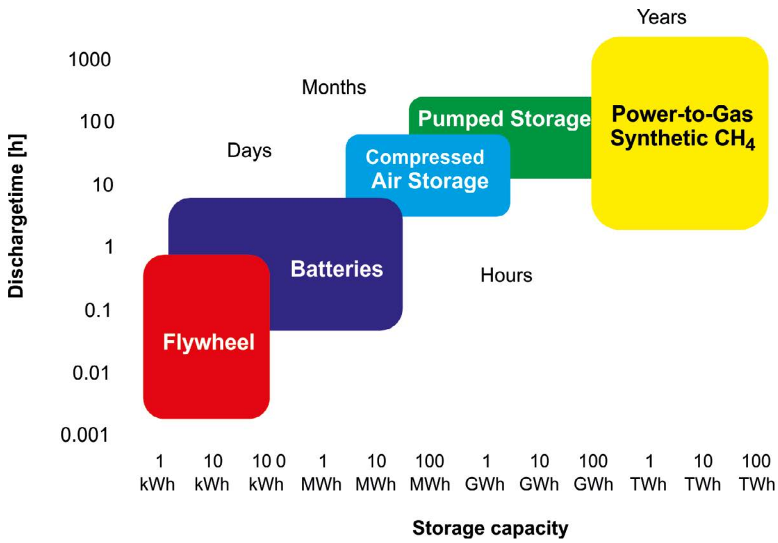

Fig. 7. The relationship between the energy capacity and discharge time for different technologies
Source: Kuhn et al. 2014

Rys. 7. Zależność pomiędzy pojemnością energii i czasem rozładowania dla różnych technologii

It should also be noted that if the current level of electricity demand is lower than the level of production from renewable resources, the surplus is used to produce hydrogen (H_2) by the electrolysis of water.

Hydrogen is then used as the reactant in the methanation of CO_2 originating from one of the two underground storage facilities installed for this purpose. The resulting methane is introduced into the second tank and can be extracted and re-converted to electricity when needed using a Combined-Cycle Gas Steam Turbine Power Plant to provide the maximum conversion efficiency.

Summary and conclusions

The presented discussion on the use of hydrogen as an energy source is not new, as studies on fuel cells focusing, among other things, on hydrogen, have been ongoing for many years.

The fact that hydrogen, as the most abundant element, can be an excellent material for various chemical syntheses has been observed in the world. This is further propelled by the fact that conventional sources of hydrogen are not only less abundant, but also their processing is energy intensive.

The basic problem is the inexpensive and easy extraction of hydrogen from its compounds; attention has been paid to water, which can easily be electrolytically decomposed to produce oxygen and hydrogen.

The electrolysis process requires electric energy; therefore, a decision was made to use alternative energy sources to supply electrolyzers. The combination of these solutions has not only helped to reduce the emissions of fossil fuels, but also to show the potential use of these sources.

Wind energy is also important; however, due to the specificity of wind, non-stop operation of this source of electricity is not possible. Often, the amount of energy generated by the windmill making it economically viable from an industrial point of view can be obtained only for part of the year (seasonally).

Hydrogen generated by electrolysis can be stored, but due to its physicochemical properties, it is a costly process; therefore, a decision was made that it is better to store it with natural gas or use it for further reaction.

It was noted that the problem is the emission of greenhouse gases, including CO_2, which can easily be deposited. However, a question arises: what next? The use of hydrogen from water electrolysis using renewable energy to convert carbon dioxide into synthesis gas allows for the easy disposal of the excess carbon dioxide.

Power-to-gas is a technology that is increasingly being developed in the world; it allows for the use of inexpensive energy sources for hydrogen production, which can be a great material for further chemical synthesis as a substrate.

In addition, hydrogen can be used as a substrate for binding and converting the increasingly problematic carbon dioxide, thus reducing its content in the atmosphere.

The existing solutions have their advantages and disadvantages. Initially, they generate costs, but later, as zero emission technologies, they allow for, among othrs:

- making full use of the excess energy to produce hydrogen, which can be used for clean-energy storage;
- the conversion of energy stored in hydrogen to methane through the methanation process while reducing the content of man-made carbon dioxide;
- the accumulation of excess energy in the gas network system of the country at a given time;
- the development of modern zero emission technologies.

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