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MODERN METHODS OF PRODUCING HYDROGEN FOR THE NEEDS OF HYDROGEN ENERGY

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The article examines some modern methods of obtaining hydrogen for the needs of hydrogen energy, especially using RES, conducts a comparative analysis, and offers practical recommendations.

Keywords: *hydrogen, electrolysis, pyrolysis, thermolysis, steam conversion of methane, copyrolysis.*

Abstract. The growing interest in the use of energy from alternative sources is due to the predicted reduction in reserves of traditional resource and energy carriers. Moreover, the transition to hydrogen energy using renewable energy sources will allow oil-importing countries to be less dependent on oil and gas suppliers, as well as solve environmental problems [1].

Hydrogen energy also corresponds to global trends in autonomous and local energy consumption. The main obstacle to the widespread use of hydrogen energy today is the high cost of hydrogen power plants [1]. As a result, the search for modern methods of obtaining raw materials for hydrogen energy is a relevant and in-demand task.

The purpose of this article is to compare currently available technologies for obtaining hydrogen, analyze the state of the technology for obtaining hydrogen from renewable energy sources and offer recommendations for further developments.

Methods of article. To make the article, the following methods were used: searching for information on the Internet, a systematic approach, analysis, comparison, analogy, and synthesis.

Results and discussion. Today, several main technologies for producing hydrogen are known: steam reforming of methane and natural gas, coal gasification, water electrolysis including high temperature electrolysis of steam, pyrolysis, partial oxidation, biotechnology [1, 2, 3]. In this case, the following are used for industrial applications: electrolysis of water and aqueous solutions of alkalis and salts, passing water vapor over hot coal at 1000°C, steam and steam-oxygen conversion of methane, coal gasification, use of nuclear energy, use of alternative energy sources [1]. Let's consider some of them in details.

Fossil-fuel based technologies*. Steam conversion of methane* is the most widespread industrial technology for producing hydrogen – up to 85% of all hydrogen is obtained using it. And at the same time, its efficiency reaches 80% and the resulting hydrogen is characterized by the lowest cost price [1].

Coal gasification is the oldest method of producing hydrogen. The first gas generator was built in Great Britain in the 1840s. Hydrogen production from coal is associated with the thermal decomposition of water, and coal is used as an energy resource and a chemical reagent; coal is simultaneously exposed to steam and oxygen – steam-oxygen reforming. All these industries are characterized by large unit capacities of the units and the absence of restrictions on energy flows [1]. Processes based on conventional partial oxidation and coal gasification are two to three times more expensive than steam reforming of natural gas [3].

But the main disadvantages of producing hydrogen from natural fuels are the emission of large amounts of CO_2 into the atmosphere, the utilization of which requires significant capital expenditures and operating costs, thereby significantly increasing the cost of the final product. In addition, while ideal for large-scale production, the method is poorly adapted to small-scale installations required for decentralized hydrogen production (e.g., filling stations, autonomous power systems, etc.) [1]. Another disadvantage of the method is the presence of CO and CO_2 impurities in the final product, which imposes additional requirements on hydrogen purification when it is used in a number of devices [1].

Electrolysis. The water electrolysis is an expensive, but is well developed and available commercially and environmentally friendly and highly efficient technology for producing hydrogen – the efficiency reaches 90% [1, 2]. In addition, the raw material – water – is practically publicly available. Another advantage is the possibility of creating installations with a wide range of productivity (from several liters to hundreds of m^3 of hydrogen per hour), ease of operation and convenience in work, high purity of the produced hydrogen and the presence of a valuable by-product – gaseous oxygen. The method has found wide application in a number of countries with significant resources of cheap hydropower. The largest electrochemical complexes are located in Canada, India, Norway, Egypt [1].

Hydrogen production from water electrolysis and from renewable energy sources is characterized by zero emissions of CO_2, and this is their main advantage [4].

Currently, approximately only 4% of hydrogen worldwide is produced by this process [2]. However, in comparison with the foregoing methods described, electrolysis is a highly energy-demanding technology.

Electrolysis is a leading hydrogen production pathway to achieve the Hydrogen Energy Earth shot goal of reducing the cost of clean hydrogen by 80% to $1 per 1 kilogram in 1 decade ("1 1 1") till 2030 [4].

Advanced electrolysis technologies. Proton exchange membrane (PEM) electrolyzers, favored for reduced operating and capital expenditures, cater to both industrial and residential needs. Other prevalent electrolyzers include solid oxide electrolyzers (SOE), which avoid the use of precious metal catalysts due to low operating temperatures, and anion-exchange membrane (AEM) electrolyzers, which utilize hydroxide ions [5, 6].

US-based startup Alchem roffers AEM electrolyzers to produce hydrogen. Its AEM technology allows for low electrolyte degradation with the use of thin durable membranes, resulting in optimal hydrogen production. These electrolyzers do not require noble metals as catalysts, thus reducing capital expenditures. The AEM electrolyzers are connected to RES power inputs or scaled up for large-size hydrogen production, with a capacity of up to 100 MW [5, 6].

Spanish startup H2B2 develops scalable electrolyzers for both residential and industrial use. *EL580N* is the startup's large-scale electrolyzer, with the capacity to produce 1 251 kgs of hydrogen per day. The startup custom-builds the electrolyzer according to regional standards while integrating it into a 40 ft container. It comes with CE marking as well as hazard and operability studies (HAZOP) conducted, along with an option for ETL stamps [5].

Nuclear technology has virtually unlimited resources of cheap energy for hydrogen production, and in producing electricity, heat and hydrogen, nuclear energy has the least impact on the environment compared to the use of carbon resources [1]. The concept of atomic hydrogen energy (AHE) is proposed to be defined as "water at the input + clean nuclear energy => hydrogen => oxygen = clean energy + water at the output." in [1].

Strictly speaking, a nuclear reactor is a source of inexpensive electrical energy, which can then be used to produce hydrogen using the same electrolysis. In the same way, thermal energy obtained from a nuclear reactor can be used to reduce the cost of thermochemical methods for producing hydrogen [1]. In this case, special attention must be paid to the safety of the reactor operation and maintenance, especially if thermal energy from the reactor, rather than electrical energy, is used to produce hydrogen. Thus, despite its very high potential efficiency, the use of nuclear energy to produce hydrogen requires significant financial costs at the stages of development, installation, and commissioning.

Obtaining hydrogen from alternative energy sources also implies obtaining alternative electrical or thermal energy to intensify the already known electrolytic and thermochemical methods of producing hydrogen.

Renewable energy sources (RES) such as wind power, upper ocean heat, hydropower, geothermal energy and tidal energy can be used to produce hydrogen after converting primary energy into electricity [1]. Green hydrogen, produced using renewable energy systems, eliminates carbon emissions common in traditional hydrogen production. Options for hydrogen production include photocatalytic and thermochemical water splitting using solar energy [5].

Hydrogen could be also produced by the ***biomass-based approaches*** (e.g., gasification, pyrolysis, and aqueous phase reforming) along with production of hydrogen from water (e.g., electrolysis, photoelectrolysis, and thermochemical water splitting) is described later [4, 6].

Direct solar water splitting, or photolytic, processes use light energy to split water into hydrogen and oxygen. These processes are currently in various early stages of research but offer long-term potential for sustainable hydrogen production with low environmental impact [2, 4].

A solar concentrator project consisting of a parabolic dish, a steam turbine (Stirling engine), and an electric generator has been successfully implemented in the USA. A parabolic concentrator with a diameter of 3 meters produces 4–5 kW; 6.4 meters – 25–30 kW. The efficiency of such installations is 28–30%. In the state of Arizona, in the summer you can get 1.2 kW h/m^2 using such installations; in the winter – 0.62 kW h/m^2. Operating costs are $ 5.00 / kW [1].

The Swiss company Clean Hydrogen Producers (CHP) has developed a technology ***for producing hydrogen from water using parabolic solar concentrators***. The area of the mirrors of the installation is 93 m^2 [1]. At the focus of the concentrator, the temperature reaches

2200 ° C. Water begins to separate into hydrogen and oxygen at a temperature of more than 1700 °C. During a 6.5-hour daylight period (6.5 kW h/m^2), the CHP plant can separate 94.9 litersof water into hydrogen and oxygen. Hydrogen production will be 3800 kg/year (about 10.4 kg/day) [1].

German startup HY2GEN utilizes solar energy to produce green hydrogen. The startup's project, *SUNRHYSE*, powers a 30 MW electrolysis plant using green electricity via solar panels. In the process, HY2GEN supplies hydrogen for the mobility and maritime sectors. The startup is involved in several other projects, like HYNOVERA, which synthesizes e-fuels through biomass gasification through green hydrogen [5].

Wind. The US Department of Energy (DOE) and the National Research Energy Laboratory (NREL) have been conducting research work ***"Hydrogen from Wind"*** since 2006. A hydrogen filling station with a 100 kW wind generator has been built. The wind-hydrolysis system is installed at the National Wind Technology Center, owned by NREL. According to NREL calculations, in the near future the cost of producing hydrogen from wind energy will be $ 4.03 per kg of hydrogen. In the long term, the cost of hydrogen will decrease to $ 2.33 per kg of hydrogen. The United States will be able to annually produce 154 billion kg of hydrogen from wind energy of class 4 and higher [1].

Startups employ *solar concentrators* to achieve high radiation levels, splitting water into hydrogen and oxygen. *Wind turbines* also contribute to green hydrogen production via electrolysis. Further, industries are adopting renewable hydrogen to fuel transportation fleets and replace conventional energy sources in manufacturing, fostering a green economy [5].

US-based startup HiSeas Energy develops offshore wind turbines to power electrolyzers. The ***HiSeas Free-Floating Offshore Wind Turbine*****(*FFWOT*)** platform provides a low-cost, low-mass, and stable platform for turbines up to 40 MW. Energy delivery to shore is completed using liquid organic hydrogen carriers (LOHC), with green hydrogen supplied from the electrolysis of water. Each electrolysis/LOHC platform is attached to the startup's turbines via sea floor power cables [5].

In October 2006, the London Hydrogen Partnership published a study on the feasibility of producing ***hydrogen from municipal and commercial waste***. According to the study, 141 tons of hydrogen could be produced daily in London through both pyrolysis and anaerobic digestion of waste. 68 tonnes of hydrogen could be produced from municipal waste. 141 tonnes of hydrogen would be enough to power 13,750 hydrogen-powered buses. There are currently over 8,000 buses in use in London [1].

In the near term, ***biomass*** is anticipated to become the most likely renewable organic substitute to petroleum. Biomass is available from a wide range of sources, such as animal wastes, municipal solid wastes, crop residues, short rotation woody crops, agricultural wastes, sawdust, aquatic plants, short rotation herbaceous species (e.g., switch grass), waste paper, corn, and many others [7, 8].

Hydrogen is produced from biomass by thermochemical or biochemical methods. In the thermochemical method, biomass is heated without access to oxygen to a temperature of 500-800 ° C (for wood waste), which is much lower than the temperature of the coal gasification process. As a result of the process, H_2, CO and CH_4 are released. The cost of the process is $ 5-7 per kilogram of hydrogen. In the future, it is possible to reduce to $ 1.0-3.0. In the biochemical process, hydrogen is produced by various bacteria, for example, Rodobacter speriodes. It is possible to use various enzymes to accelerate the production of hydrogen from polysaccharides (starch, cellulose) contained in biomass. The process takes place at a temperature of 30 °C under normal pressure. The cost of hydrogen is about $2 per kg [1, 7, 8].

Microbial biomass conversion processes take advantage of the ability of microorganisms to consume and digest biomass and release hydrogen. Depending on the pathway, this research could result in commercial-scale systems in the mid- to long-term timeframe [2, 4]. The organic matter can be refined sugars, raw biomass sources such as corn stover, and even wastewater. Because no light is required, these methods are sometimes called "dark fermentation" methods [4].

Pyrolysis and Copyrolysis. Another currently promising method of hydrogen production is pyrolysis or copyrolysis. Raw organic material is heated and gasified at a pressure of 0.1–0.5 MPa in the 500–900◦ C range [9-12]. The process takes place in the absence of oxygen and air, and therefore the formation of dioxins can be almost ruled out. Since no water or air is present, no carbon oxides (e.g., CO or CO_2) are formed, eliminating the need for secondary reactors (WGS, PrOx, etc.). Consequently, this process offers significant emissions reduction. However, if air or water is present (the materials have not been dried), significant CO_x emissions will be produced. Among the advantages of this process are fuel flexibility, relative simplicity and compactness, clean carbon byproduct, and reduction in CO_x emissions [9–12].

Aqueous Phase Reforming. Aqueous phase reforming (APR) is a technology under development to process oxygenated hydrocarbons or carbohydrates of renewable biomass resources to produce hydrogen [13, 14].

A promising and prospective alternative to industrial processes for obtaining hydrogen ***is the decomposition of water using solar energy in the processes of photosynthesis and bioconversion***. During photosynthesis, green plants and seaweeds (microscopic single-celled plants) convert carbon dioxide, water and sunlight (green light with a wavelength of 500 nm) into carbohydrates, water and oxygen.

Hydrogen can be produced by a group of green algae, for example Chlamydomonas reinhardtii. Algae can produce hydrogen from seawater or sewage.

Research in the field of biological methods for obtaining hydrogen is still of an exploratory nature. In 1999, scientists from the University of California at Berkeley (UC Berkeley) discovered that if algae lack oxygen and sulfur, their photosynthesis processes sharply weaken and vigorous production of hydrogen begins.

Conclusions and recommendations. There are not less than 7 quite promising technologies to obtain the hydrogen. Unfortunately, the most of researchers consider that steam reforming of methane is the most economic near-term process among the conventional processes. Second prospective technology to produce the hydrogen by the year 2030 is catalyzed biomass gasification. In a relatively small extent both coal gasification and electrolysis will be used. The third promising technology is electrolysis. But it can be possible powerful hydrogen technology just if scientists can decrease the cost of electrolysis-based hydrogen. Probably, the role of solar energy will increase by 2050.

If we are talking about environmentally friendly technologies for producing hydrogen, then we should focus on obtaining hydrogen from renewable energy sources such as solar, wind and hydroelectric resources and their combination. The use of renewable energy sources for hydrogen production should be based on the prospects for using renewable energy sources in general for a particular region.

As a recommendation for further research, it is advisable to propose the development of a combined decentralized system including solar, wind and hydropower to supply electricity to hydrogen production based on electrolysis and/or pyrolysis. Using of several RES simultaneously can increase the effectiveness and decrease the cost of RES-based electricity and by this way to decrease the cost of produced hydrogen.

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