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СЕРИЯ ХИМИИ И ТЕХНОЛОГИИ

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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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HYDROGEN ENERGETICS CURRENT STATE AND HYDROGEN PRODUCTION METHODS

Abstract. Review about hydrogen energetics current state and obtaining hydrogen methods are given with using literature sources from near and far abroad. It is shown that hydrogen energy is an alternative to traditional energy based on natural resources and describes the technical aspects of hydrogen production methods. We described industrial methods three categories for producing hydrogen - an environmentally friendly energy carrier. It is shown that the first category includes hydrogen production thermochemical methods, one of which is natural gas steam reforming. Along with this, methods for methane partial oxidation, autothermal reforming, and steam and gas coal conversion are considered.

The second group of methods for the hydrogen production is represented by electrolytic methods. Among them, a noteworthy method is the electrolysis of water. At present, the promising hydrogen production technology is standard electrolysis, decomposing water into its components - hydrogen and oxygen with the passage of electric current.

In recent years, other methods of producing hydrogen have been developed and are being developed. Biomass gasification and biomass pyrolysis methods are described, it is shown how these methods differ.It is shown that all the methods considered have their own advantages and disadvantages.

Keywords: hydrogen, energy, energy carrier, reforming, electrolysis, biomass.

One of the modern scientific and technical research topical issues is the development of affordable, environmentally friendly, cheap types of energy. The search for clean fuels is crucial and vital for survival since in subsequent years (the next 40-50 years) there will be big environmental problems associated with climate change, depletion of the ozone layer and other adverse consequences for the planet. The results of mandatory monitoring indicate an annual increase in emissions of carbon dioxide and carbon monoxide into the atmosphere. The amount of carbon dioxide emissions in the biosphere is about 30 billion tons per year. This gas is a major component of greenhouse gases and has a significant adverse impact on the environment [1].

There is a hypothesis that if the change in the concentration of carbon dioxide when using natural resources increases the temperature by 0.60°C for 100 years, then until 2075 this change will be equal to 5.40°C [2-3].

In addressing these issues, it is clear that alternative energy sources should be used in place of traditional energy sources. And it is unlikely that hydrogen energy will be equivalent to alternative sources of energy. Ecologically pure hydrogen fuel, its inexhaustibility (water), but also a lot of opportunities for using hydrogen - all this shows the advantages of using hydrogen as a fuel. Compared with organic fuel, hydrogen has a very large amount of energy, and the amount of heat released when burning 1 ton of hydrogen is equal to the amount of heat burned for 3.5 tons of organic fuel.

The ability of hydrogen to catalytically oxidize at low temperatures, in this case, the direct oxidation of chemical energy to electrical energy opens the way for the use of hydrogen in power engineering. Devices that make it possible to realize such functions are fuel cells or electrochemical energy generators characterized by a very high efficiency factor (70 to 80%), which is 2.0-2.5 times higher than the thermal coefficient of efficiency of the engine.

Nevertheless, the current state of hydrogen technology does not completely replace traditional energetic. The reason for this is that there is no free hydrogen in the earth, and its production requires chemical raw materials and energy sources. In short, hydrogen is an energy carrier, not fuel.

Hydrogen is the most common chemical element in the universe (93% atomic percent and one of the most common elements on Earth is 15.52% atomic percent).The main sources of hydrogen on Earth are water and organic compounds: oil, natural gas, and biomass.Hydrogen has unique properties, and its properties can be used in many different areas [4-7].

Let's take a closer look at the basic methods of obtaining hydrogen. At present, $368 \cdot 10^{12}$ m^3 of hydrogen is produced worldwide [8].

Depending on the technological characteristics of the recovery and extraction of hydrogen from its compounds, we decided to divide it into three categories [9-11].

Let us first consider the thermochemical methods of producing hydrogen.One of them is steam reforming of natural gas. This method involves the conversion of natural gas under the action of various oxidants (CO_2, H_2O, O_2, air and their mixtures). As a result, the product contains a large amount of H_2 and CO [12-18]. This method is highly productive and cheap, so the amount of hydrogen produced by this method is 85% of the hydrogen produced in the world, and in the United States - even 95%.

The production of hydrogen in the steam reforming of natural gas is carried out in three stages. First of all, methane is reformed at 500-950°C and 3 MPa pressure in the presence of a catalyst (usually Ni), in this case, a synthesis gas (CO + $3H_2$ mixture) is formed:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 + 206 \text{ kJ / mol (for 1 mole of } CH_4) \quad (1)$$

The reforming reaction is usually endothermic and requires the supply of heat from outside, which in turn is generated by the combustion of a portion of natural gas (about 25%) or separated from exhaust gases (for example, gas from a hydrogen purification system). Then the resulting synthesis gas reacts with an excess of water vapor, and at this time an additional amount of hydrogen is formed by the following reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 - 42 \text{ kJ / mol CO} \quad (2)$$

This reaction takes place at temperatures below the reforming reaction (usually below 600°C). The reaction proceeds in several stages, each of which occurs at a temperature below its previous stage. At high temperatures (350-475°C), the degree of conversion of CO to hydrogen is also high; at this stage, an iron-based catalyst can be used. In the following steps, a copper-based catalyst is used at a lower temperature (200-250°C); and the CO concentration in the synthesis gas is significantly reduced. The gas produced during steam reforming mainly comprises (H_2) is hydrogen (70-80%) and a small amount of CH_4 (2-6%), CO (7-10%) and CO_2 (6-14%) [16,18].

The final stage of the process is devoted to the purification of hydrogen, purification degree depends on the volume of application of hydrogen. For the purification of hydrogen, pressure-reducing adsorption systems or Pd-membranes are used to remove water vapor, CH_4, CO_2, N_2 and CO. The purity of hydrogen obtained by such purification reaches 99.999% [16]. In this case, an oxidation system is mainly used, introducing air into the produced gas through the catalyst bed. The oxidation of hydrogen also requires the following reaction at a certain temperature:

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \quad (3)$$

Then the amount of CO decreases to the required level [16]. In some cases, the use of calcium oxide as a sorbent will reduce the amount of CO_2 and CO and increase the hydrogen content. The gas content is 90% H_2, 10% CH_4 and 0.5% CO_2.

Main drawbacks of hydrogen obtaining method from natural gas are:

- a large amount of air emissions, higher costs of hydrogen and required CO_2-gas formation. All this increases the valueof hydrogen;
- low installations productivity, the complexity of obtaining hydrogen peroxide by this method;
- The presence of CO in hydrogen composition, which means the need for additional purification for use in fuel cells production.

Another type of thermochemical methods of hydrogen extraction is methane incomplete oxidation. Methane or other hydrocarbons (for example, oil) are oxidized in this process, as a consequence of the following reaction, CO and H_2 are formed:

$$CH_4 + 1/2O_2 \rightarrow CO + H_2 + 36\ MJ/kmol\ CH_4 \quad (4)$$

The reaction does not require exothermic or external heat, so there is no need to use heat exchangers. Since the temperature is very high, the catalyst is also not needed.But you can use a catalyst to increase the flow of hydrogen (based on 1 mole of methane) or improve useful factor of the system. Unlike the steam reformer, the reactor designed for oxidation is more compact and its useful coefficient is higher (70-80%).Although the reactor itself is cheaper than a reformer, a working reactor and hydrogen purification systems are expensive. Taking into account these factors, it is necessary to invent cheaper hydrogen purification technologies [16,17,19].

Another type of reforming is autothermal. The outlet temperature of the reactor is 950-100 °C, and the gas pressure reaches 100 MPa [19]. Unlike steam reforming, there is no need to import external heat for autothermal reforming, since the reaction is exothermic and, accordingly, autoreformers are more affordable and cheaper. However, due to the need to purify exhaust gases, hydrogen production will be more expensive, and the beneficial effect will be reduced (65-75%) [18]. From these questions follows, from the ecological point of view, hydrogen production from natural hydrocarbon raw materials seems to be the same as from fossil fuels. This is due to the fact that in the latter case, harmful emissions into the atmosphere are formed when fuel is used, and in the first case these emissions are formed, but they are formed during the evaporation of hydrogen. Summarizing these reasons, basic scientific and technical research in the field of hydrogen extraction from natural resources should be aimed at improving the processes of capturing or disinfecting gases, especially carbon dioxide, in the production of new technologies.

Based on these views, it can be concluded that the method of obtaining hydrogen from coal by conversion of water and gas is significantly more promising.

Now let's move on to this method. Hydrogen can be obtained by various methods of coal gasification (for example, gasification in a fixed, liquid layer or a stream). In practice, high-temperature gasification is more effective because at that time the level of carbon dioxide is high, and the formation of high-flammable waste and phenol in large quantities is prevented [19].Typically, the gasification of carbon occurs when the temperature is 1200-1350°C and is carried out in accordance with the following equation [9, 10, 16, 17, 19, 20]:

$$C\ (solid) + H_2O + heat \rightarrow CO + H_2. \quad (5)$$

The reaction requires endothermic and external heating; this situation was also observed during natural gas reforming. The formed CO can then be used as an additional element for the production of hydrogen by interaction with water vapor:

$$CO + H_2O \rightarrow H_2 + CO_2. \quad (6)$$

At present, much attention is paid to improving methods of extracting hydrogen from solid fuels, since coal reserves still remain in sufficient quantities(According to British Petroleum Corp., coal reserves in 2008 amounted to 826 billion tons) [21].

In the United States, there is a national program called "Hydrogen production from coal," which reads as follows:introduction of hydrogen energy technologies into the industry will reduce the amount of greenhouse gases released into the environment and improve the ecological purity and productionenergy efficiency [22].

Carbon gas processing plants are currently environmentally friendly, and the coefficient of useful use (39-44%) is higher than solid waste for processing solid fuel. A significant disadvantage of this method is the low hydrogen content in the synthesis gas (usually 40% (volume) percent) [21].

The second group of methods for obtaining hydrogen are electrolytic methods. Requiring attention - electrolysis of water.

A promising technology of hydrogen production in the modern world is the standard electrolysis, which breaks down the water into components - hydrogen and oxygen under the influence of electric current:

$$2H_2O + \text{electric current} \rightarrow O_2 + 2H_2. \quad (7)$$

The doubtless advantages of this method are:
- an inexhaustible resource of raw materials (water);
- clean from an environmental point of view;
- possibility of having a wide range of productivity structures;
- ease of use and work;
- very high degree of hydrogen produced purity, as well as pure distribution and valuable gaseous products - gas oxygen.

At present, there are three technologies of hydrogen electrolytic reduction [13, 23-25] and their differences in the following: types of electrolyte (alkaline-aqueous solutions, protonionic membranes, with solid polymer electrolytes); solid oxide electrolyte - ceramics Zr-Y (with the conductivity of oxygen ions). Electrolytes filled with various electrolytes dissolve in different ways.

Electrolysis with an alkaline electrolyte is accompanied by the following chemical reactions [23]:

$$\text{Cathode reaction: } 2H_2O + 2e \rightarrow H_2 + 2OH^-$$
$$\text{Anode reaction: } 2OH^- \rightarrow 1/2O_2 + 2e$$
$$\text{Total reaction: } H_2O + \text{electric current} \rightarrow H_2 + 1/2O_2. \quad (10)$$

And if a polymer proton membrane is present in the cell, the water decay occurs as a result of the following reactions [23, 26]:

$$\text{Anode reaction: } H_2O \rightarrow 1/2O_2 + 2H^+ + 2e \quad (11)$$
$$\text{Cathode reaction: } 2H^+ + 2e \rightarrow H_2 \quad (12)$$
$$\text{Total reaction: } H_2O + \text{electric current} \rightarrow H_2 + ½\, O_2. \quad (13)$$

Solid oxide ceramic materials are used in solid oxide electrolysers as electrolytes (usually stabilized with yttrium oxide).In such cells, cathodic water absorbs electrons from the outer layer and forms hydrogen, as well as negative oxygen ions, which in turn transfer electrons to the outer chains in the anode and become oxygen in the gas [26]. The problem is that cells with a solid oxide ceramic electrolyte function operate at high temperatures (about 800-1000°C), and electrolysers equipped with protonionic membranes function at 80-200°C, an electrolyser filled with an alkaline electrolyte at 50-200°C. These differences are associated with the use of heat obtained at high temperatures from other sources in the activity of these cells (including nuclear energy), thereby reducing energy costs for electrolysis.

In some works [27] new types of electrolyzer are proposed. In this type, the anode and cathode chambers are placed separately; they have a cathode and an anode, whereas the second pair of electrodes is usually made of a ruthenium oxide material that does not interact with short-circuited oxygen.

The cost of hydrogen hydrolysis will affect the cost of electricity [13,23].Therefore, modern research of wastewater technology should be focused on the search for new electrode materials and electrolytes, which save energy and increase the efficiency of the process.

To reduce energy costs and associated financial costs, it is necessary to use methods that generate electricity without reducing costs. The value of hydrogen obtained at that time is also small. Such technologies are primarily associated with the production of energy from alternative sources - the Sun, Wind, Hydrothermal. The use of solar energy is a promising method. In this case, both hydrogen and electrical energy must be taken from renewable sources - water and the Sun. For example, consider the production of hydrogen by photolitical methods.In the case of electrochemical water splitting, the anode generally is a compound having a semiconductor effect, and electrolyte and electron-hole pairs are formed at the anode boundary under the influence of light, these pairs contribute to the oxidation and reduction reactions of water, and as a result, hydrogen and oxygen form from the water. Fusikima and Honda in 1972 for the first time described the device built into the H_2SO_4 solution, first combining the TiO_2-photoanode and the Pt-cathode. This information is then presented in this paper [28].As a result of the use of semiconductor photovoltaics, various studies have been carried out to increase the efficiency of hydrogen evolution from water.

It is not necessary to completely decompose water during photoelectrolysis to produce hydrogen.It is sufficient to conduct a cathodic reaction in which only hydrogen is formed:

$$2H_2O + 2e^- \rightarrow 2OH- + H_2\uparrow \quad (14)$$

The free electrons that are necessary for this reaction can be obtained from other reactions, and not only from anodic oxidation, for example, from the oxidation of sulfide ions or other compounds [29]. In this regard, as a photoanode, as a rule, a compound that absorbs light well but with a smaller forbidden band (for example, AIIBVI, AIIIBV, SnS, etc.) is used, rather than semiconductor metal oxides with a band gap in the range 2.7 to 3.2 eV. From a theoretical point of view, this method contributes to the efficiency of the process of converting solar energy into hydrogen energy [28].

The creation of photovoltaic systems, which can be used for semiconductor anodes sensitive to the visible spectrum of solar radiation and effective absorption of hydrogen cathodes, is a new direction in the creation of a solar irradiation and accumulation system [28].

One of the most important ways of obtaining hydrogen is the decomposition of water at high temperatures. Thermolysis of water by the direct method:

$$H_2O \rightarrow H_2 + 1/2O_2 \quad (15)$$

To conduct this reaction, the temperature must be above 2500°C, and hydrogen and oxygen must be separated by efficient methods [30, 16]. The problem of separation of hydrogen and oxygen from each other is realized by using thermochemical cycles at extremely low temperatures [19, 16, 18] or thermochemical hybrid processes of thermal decomposition of water [16,30], in this case we use nuclear reactors heat and other solar collectors heat sources [31].

In the production of hydrogen, the cycles of reactions of chemically active compounds arising at high temperatures in a thermochemical process, such as iodine and sulfur, are used. More than 100 chemical cycles are recommended for this process. The most effective and promising method for these cycles is the use of iodine and sulfur reactions. This method was proposed by General Atomics in mid-1970. In this system, water reacts with SO_2 and iodine (I_2), which leads to the formation of sulfuric acid and iodide (HI):

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \quad (16)$$

At a temperature of 800-1000°C in a thermal nuclear reactor, sulfuric acid decomposes in water into sulfur dioxide (SO_2) and oxygen, and HI decomposes into hydrogen and iodine:

$$H_2SO_4 + \text{heat} \rightarrow H_2O + SO_2 + 1/2O_2 \quad (17)$$

$$2HI + \text{heat} \rightarrow H_2 + I_2. \quad (18)$$

$$\text{Total reaction: } H_2O + \text{heat} \rightarrow H_2 + 1/2O_2 \quad (19)$$

Iodine and SO_2 react with water again, and oxygen is removed from the system or collected for use in production. In the modern world in reactor designs, the maximum operating temperature is about ≈ 827°C [12].

The thermochemical hybrid process is a combined cycle process that combines the thermochemical and electrolytic reactions of water decomposition and allows the electrons to react at low temperatures [12]. Modern nuclear reactors or solar energy concentrators can serve as a source of energy necessary for the reaction. It was suggested that the main contribution to the development of hydrogen energy will take place if an industrial hybrid thermochemical process is established [32].

Technology based on thermal ionization of water vapor also requires attention.This method is the basis for the thermal decomposition of the leading and conventional water, as well as the basis of technology aimed at burning highly heated water vapor [33]. The main stages of this technology include special preparation and activation of water, heat treatment of high heated steam, its thermonuclear activation, subsequent dissociation (using this catalyst this pair of H_2 and O_2) and burning on a special catalyst surface.

The most important sources of energy production when extracting hydrogen from biomass are wood and wood waste, agricultural crops,and waste generated during processing, solid waste in the city, food industry waste, algae, etc. Biomass is of great interest for hydrogen production. First, biomass is considered one of the many uses of renewable resources. According to The International Institute for Applied Systems Analysis, the biomass potential in the world is about 250 billion GJ. It is expected that this potential by 2050will grow to 350 billion GJ [23].

Secondly, biomass is a substance consisting of organic components formed by the absorption of carbon dioxide from the atmosphere after photosynthesis. Since the first types of biomass are renewed, carbon dioxide and other types of carbon can be used in the atmosphere as energy or material. Since the CO_2 concentration in this cycle is theoretically stable, it can be expected that the future biomass will become the main source of renewable energy [34].

Thirdly, comparing some other methods of obtaining hydrogen and taking into account the geographical location, biomass is relatively common in the world.

Fourth, in addition to the heat released during the production of hydrogen, biomass can be valuable as auxiliary products: glues, black powder, activated carbon, polymers, fertilizers, ethanol, various acids, Fisher-Tropys diesel fuel, paraffin, and methanol. Energy and biomass products are likely to satisfy the demand for them in the future. Removal of hydrogen from biomass is divided into two groups, one of which is pyrolysis of biomass.

Pyrolysis is the heating of biomass at a pressure of 0.1-0.5 MPa at a temperature equal to 650-800 K. As a result, solid and liquid products are formed [35,36]. Depending on the nature of the pyrolysis biomass, H_2, CH_4, CO, CO_2 and other gases are present in the gas products.Liquid products contain resins and oils that store the liquid form at room temperature. Solid products consist mainly of flammable substances in the form of residues that are formedfrom the rectification of coal, as well as from some pure carbon and some other inert substances. Pyrolysis of biomass is mainly concentrated on biofuel, but also during high-temperature pyrolysis and when the volatile phase is stabilized, hydrogen is formed by the following reaction:

$$\text{biomass} + \text{heat} \rightarrow H_2 + CH_4 + CO + \text{other products} \quad (20)$$

Methane and a couple of other hydrocarbons can then be modified to produce hydrogen by steam:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (21)$$

and then the amount of hydrogen increases as a result of the interaction of CO_2 with water:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (22)$$

Liquid pyrolysis products can also be used to extract hydrogen. Depending on their solubility in water, they are divided into two fractions. The water-soluble fraction is used to extract hydrogen and the insoluble fraction is used to absorb the adhesives [37].

Hydrogen is also produced by gasification of biomass.Gasification is the thermal treatment of biomass by a large number of gaseous substances, and a small amount of resin and ash. This process is essentially similar to gasification of coal and is carried out at 950-1500 K [38, 39]. Unlike gas cleaning of biomass it is carried out in the presence of oxygen or air. This biomass conversion process is based on the following reaction:

$$\text{biomass} + \text{heat} + \text{vapor} \rightarrow H_2 + CH_4 + CO + CO_2 + \text{light and heavy hydrocarbons} + \text{carbon flammable waste generated during rectification} \quad (23)$$

The gasification process can be considered as one of the types of pyrolysis, but at very high temperatures, since it is necessary to optimize the formation of the gas phase, and pyrolysis is aimed at obtaining biomass. Gas products obtained during gasification are then converted to hydrogen under the influence of water vapor. Hydrogen can be produced biochemically. Biochemical production of hydrogen (biohydrogen) as a substance of the metabolism of microorganisms is a relatively new technology. This method allows extracting hydrogen from renewable sources. This, in turn, contributes to the development of hydrogen energy in the future [36]. The production of biohydrogen can be divided into several groups:1) direct biophotolysis; 2) indirect biophotolysis; 3) biological shift of the gas-water reaction 4) fermentation [40].

The hydrogen production by direct bio-photolysis is a biological process using photosynthetic microalgae, which is aimed at converting solar energy into hydrogen in the form of chemical energy [41].

$$2H_2O + \text{solar energy} \rightarrow 2H_2 + O_2. \quad (24)$$

Two photosynthetic systems are necessary for photosynthesis:1) I photosystem (PSI), which actually produces a CO_2 gas reducer and II photosystem (PSII) - system of water decomposition and oxygen separation. In a biophytolytic process, two water protons with PSI recovers CO_2 gas or releases hydrogen in the presence of hydrogenase.Since green plants do not contain hydrogenase, only the CO_2 reduction reaction takes place. In contrast, green and cyanobacterial (blue-green) microbes contain hydrogenases that are capable of producing hydrogen.In this process, the electrons formed as a result of the absorption of the light energy of the PSII system are converted to ferredoxin (Fd). This replacement occurs for the production of hydrogen as a result of the use of solar energy absorbed by the PSI system.

Since the hydrogenase is sensitive to oxygen, it is necessary to maintain the oxygen content at low levels (<0.1%) in order to prolong hydrogen production [42].

Indirect biophytolysis consists of the following four stages:1) biomass production by photosynthesis; 2) biomass concentration; 3) deep fermentation of anaerobic, resulting in the formation of algae cells 4 moles of H2, which is calculated for 1 mole of glucose and 2 moles of acetate; 4) conversion of two moles of acetate to hydrogen.

Usually in indirect biophotosynthesis cyanobacteria are used, in this case, hydrogen is obtained by the following reactions [40]:

$$12H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2 \quad (25)$$

$$C_6H_{12}O_6 + 12H_2O \rightarrow 12H_2 + 6CO_2 \quad (26)$$

The production rate of hydrogen produced by indirect bio-photolysis can be compared with the production of hydrogen on the basis of hydrogenase with the help of green algae [42].

Hydrogen-rich carbohydrate compounds (eg, glucose, starch, etc.) can be obtained at temperatures of 30 to 80 °C and at atmospheric pressure, especially in the dark, by fermentation [36, 43].

In contrast to the usual process of bio-photolysis, in which only hydrogen is released, the difference in this method lies mainly in the fact that the fermentation products are hydrogen and CO_2.

However, the formation of other gases (CH_4, H_2S) takes place depending on the materials used and the reactions occurring in the process. The amount of hydrogen released affects the direction of fermentation and the resulting liquid products. For example, when glucose is used, and acetic acid is the final product of fermentation:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2 \quad (27)$$

(In this reaction, from 1 mole of glucose, 4 moles of H2).

And if fatty acids are formed as the final product:

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_2CH_2CH_2OOH + 2H_2 + CO_2 (28)$$

(from 1 mole of glucose, 2 moles of H_2).

But usually, in fact, 1 mole of glucose does not form 4 moles of hydrogen, because the fermentation product contains acetic acid and fatty acid ester [44].

In the dark, the amount of hydrogen produced by the fermentation method depends on the average pH, the time of hydraulic confinement and the partial gas pressure. For optimum hydrogen production conditions, it is necessary to keep the pH at 5-6 [36].

Alanaerobiumhydrogeniformanshaloalkaliphilic bacteria can produce 5- and 6-carbon sugars from hydrogen-containing hemicellulose and cellulose [45].

In addition to pure sugars and industrial raw materials, raw materials for the production of fermented hydrogen are considered (for example, agricultural and food waste and solid organic waste, including urban and agricultural waste and sewage sludge).However, the production of hydrogen from these raw materials has a number of disadvantages, one of which is the low yield of hydrogen. This method is currently realized by simple fermentation of sugar [46].

By combining photo fermentation in the dark, you can double the yield of hydrogen in a two-stage hybrid system. In the first stage anaerobic bacteria decompose glucose or starch acetate with enzymatic metabolism, and the resulting acetate is subjected to hydrogen direct photosynthetic bacterial changes in the second stage [47].

Conclusion

In industry today, only natural gas conversion, coal gasification and water electrolysis are used. Steam conversion of natural gas is one of the cheapest ways to use natural fuels, and CO_2 emissions in this method are extremely low. Water electrolysis is more expensive and is used only to produce hydrogen peroxide. If natural gas cost increasingis predicted, coal gasification method can be an alternative method of producing hydrogen starting around 2030. Biomass gasification and its pyrolysis for hydrogen production are at the research stage, but in the coming decades these methods are likely to become alternative methods of hydrogen production.

Biomass gasification and its pyrolysis for hydrogen production are at the research stage, but in the coming decades these methods are likely to become alternative methods of hydrogen production. According to the long-term International Energy Agency forecast, hydrogen, obtained by biomass gasification, will compete at a price with fully restored hydrogen, and its price will be the lowest among the extracted raw materials.

Biomass gasification is the simplest and most economical way of producing renewable hydrogen. This technology is likely to be the most advanced technology in the future. Hydrogen production from renewable sources (wind energy, solar energy, hydrothermal energy, etc.) will be economically advantageous for countries with a large number of renewable energy sources, for remote areas without natural resources and for less populated areas (for example, peninsula and islands) or for the accumulation of a huge amount energy from renewable energy sources.

In the long term, it will be necessary to produce hydrogen by a method without separating CO_2 or by separating a very small amount of.Electrolysis using renewable hydrogen electricity, using the sun, wind, hydrothermal energy, is maximum possible option, but these methods are not suitable for using hydrogen as an energy carrier. Before achieving this goal, the extraction of hydrogen from natural resources is very important, but the conservation and fixing of CO_2 gases are mandatory, especially in terms of environmental safety.

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СУТЕКТІК ЭНЕРГЕТИКАНЫҢ ҚАЗІРГІ ЗАМАНДАҒЫ ЖАҒДАЙЫ ЖӘНЕ СУТЕКТІ АЛУ ӘДІСТЕРІ

Аннотация. Бірқатар алыс және жақын шетелдік әдебиет көздеріне сүйене отырып, сутектік энергетика-ның қазіргі замандағы жағдайы туралы және сутекті алу әдістері жайында шолу жасалған. Сутектік энергетиканың табиғи қазба байлықтарға негізделген дәстүрлі энергетиканың баламалы түрі болып табылатыны көрсетілген және сутекті алу әдістерінің техникалық аспектері сипатталған. Экологиялық тұрғыдан таза болып табылатын энергия тасымалдаушы – сутектің өндірістік алыну әдістерінің үш категориясы сипатталған. Бірінші категорияға сутекті өндірудің термохимиялық жолдары қарайтыны, оның бірі – табиғи газдың булы риформингі екені көрсетілген. Бұл әдіс табиғи газды әртүрлі тотықтырғыштармен әсер ету арқылы конверсиялауды көздейді. Сонымен қатар метанды толық емес түрде тотықтыру, автотермалды риформинг, көмірді сулы-газды конверсиялау әдістері қарастырылған.

Сутекті өндіру әдістерінің екінші тобын электролиттік әдістер құрайды. Оны ішінде көңіл бөлуді талап ететіні – су электролизі. Қазіргі заманда сутекті алудың келешегі бар технологиясы – суды электр тогының әсерімен құрамдас бөліктеріне - сутекке және оттекке ыдырататын стандартты электролиз.

Кейінгі жылдары сутекті алудың басқа да әдістері жасалып, дамып келеді. Олардың ішінде биомассаны газдандыру және оның пиролизін жүргізу, олардың бір-бірінен айырмашылығы қарастырылған. Барлық әдістердің өзіндік артықшылықтары мен кемшіліктерінің бар екені көрсетілген.

Түйін сөздер: сутек, энергетика, энергия тасымалдаушы, риформинг, электролиз, биомасса

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СОВРЕМЕННОЕ СОСТОЯНИЕ ВОДОРОДНОЙ ЭНЕРГЕТИКИ И СПОСОБЫ ПОЛУЧЕНИЯ ВОДОРОДА

Аннотация. Проведен обзор о современном состоянии водородной энергетики и способах получения водорода с использованием литературных источников ближнего и дальнего зарубежья. Показано, что водородная энергетика является альтернативой традиционной энергетике, основанной на природных ископаемых и описаны технические аспекты способов получения водорода. Приведено описание трех категории промышленных методов получения водорода – экологически чистого энергоносителя. Показано, что к первой категории относятся термохимические способы получения водорода, одним из которых является паровой риформинг природного газа. Наряду с этим рассмотрены способы частичного окисления метана, автотермальный риформинг, парогазовая конверсия угля.

Вторую группу способов получения водорода представляют электролитические методы. Среди них заслуживающий внимания способ – электролиз воды. В настоящее время перспективная технология получения водорода – стандартный электролиз, разлагающий воду на ее составляющие – водород и кислород при пропускании электрического тока.

В последние годы разрабатываются и развиваются другие способы получения водорода. Описаны способы газификации биомассы и пиролиз биомассы, рассмотрены их различияя. Показано, что все рассмотренные методы имеют свои как преимущества, так и недостатки.

Ключевые слова: водород, энергетика, энергоноситель,, риформинг, электролиз, биомасса.

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