IRSTI 61.13.21

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https://doi.org/10.55956/XUEK6603

METHODS FOR PRODUCING HYDROGEN: A BRIEF OVERVIEW

Abstract. The ever-increasing energy consumption and dwindling fossil resource reserves, progressive global warming and the resulting deterioration of the environment have led to intensive development of research in the field of more advanced alternative energy sources. One of the directions in which the energy sector is moving towards a "green" economy is the transition to new energy sources, primarily hydrogen. The vision of hydrogen as a essential clean fuel of the future as part of the global energy transition aimed at decarbonization and climate neutrality has led to the adoption of hydrogen strategies for the coming decades in two dozen countries. The main problem of hydrogen energy is the search for accessible, inexpensive and environmentally friendly sources of hydrogen. The article provides a review of existing methods for producing hydrogen.

Keywords: hydrogen, synthesis gas, energy, conversion.

Sadykov V.A., Simonov M.N., Hassan A. Methods for producing hydrogen: a brief overview // Mechanics and Technology / Scientific journal. – 2024. – No.2(84). – P.284-288. https://doi.org/10.55956/XUEK6603

Introduction. Today, greenhouse gas emissions are the main cause of global warming. The main problem of anthropogenic emissions is the fossil fuel energy sector. Therefore, the Paris Agreement (2016) called on a change of the world energy structure to combat global warming. One of the directions of the energy movement to the "green" economy is the transition to new energy sources, primarily related to the use of hydrogen [1].

Currently, hydrogen is the most discussed alternative to traditional energy carriers. Its main advantages in this role are energy and environmental safety (water is formed during the combustion process) and high efficiency of hydrogen fuel cells. The value of this gas in the processes of processing all types of hydrocarbons and decarbonization of existing industries is increasing [2].

According to the data of 2022, hydrogen is obtained mainly (96%) in the process of conversion of fossil fuels: naphtha reforming (30%), steam reforming of natural gas (48%) and coal gasification (18%) [3]. The remaining 4% of H_2 comes from a combination of methods that include biomass conversion and production using alternative energy sources (solar, wind) for water electrolysis [4]. Due to the increase in demand (from 255.3 billion cubic meters in 2013 to about 324.8 billion cubic meters in 2020 [3]) and the tightening of requirements for its production, it is necessary to develop the above-mentioned methods that contribute to the reduction of the carbon footprint in the H_2 extraction process.

Currently, the most common industrial process producing 95% of syngas is steam reforming of methane [3], which together with steam conversion reaction can be an efficient source of hydrogen. This highly endothermic process, which produces a hydrogen-rich synthesis gas with a ratio of $H_2/CO = 3$, has been widely used on an industrial scale since the 1960s, when natural gas began to be used as a raw material instead of coal. This process is also the most popular and cheapest way to produce hydrogen. Compared to the electrolysis of water, much more H_2 is formed per unit of consumed energy.

Main section. There are three methods of oxidizing methane to synthesis gas:
– steam reforming:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

$$\Delta H^0_{298} = +206 \text{ kJ/mole} \quad (1)$$

– partial oxidation by oxygen:

$$CH_4 + 1/2O_2 \leftrightarrow CO + 2H_2$$

$$\Delta H^0_{298} = -35.6 \text{ kJ/mole} \quad (2)$$

– dry reforming:

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$$

$$\Delta H^0_{298} = +247 \text{ kJ/mole} \quad (3)$$

Carbon dioxide reforming of methane to $CO + H_2$ synthesis gas is one of the most important chemical reactions suitable for industrial production of hydrogen and synthesis of hydrocarbons (liquid fuels) and other technically valuable products. In this case, the purity of the obtained hydrogen is 95-98, 5%, with 1-5% methane and traces of CO and CO_2 gases as impurities. Hydrogen production from biofuels can solve the problem of greenhouse emissions, and also allows the use of renewable energy sources.

At the same time, during the last twenty years, many works on hydrogen production by steam reforming of ethanol in traditional reactors with a fixed bed of catalyst have appeared [5-7] and various reaction mechanisms have been proposed. There are several reactions of ethanol reforming for hydrogen production: steam reforming (4), partial oxidation (5); oxy-steam reforming (6), dry reforming (7):

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \qquad \Delta H^0_{298} = +374 \text{ kJ/mole} \quad (4)$$

$$C_2H_5OH + 1.5O_2 \rightarrow 2CO_2 + 3H_2 \quad (5)$$

$$C_2H_5OH + (3- 2x)H_2O + xO_2 \rightarrow 2CO_2 + (6-2x) H_2 \quad (6)$$

$$C_2H_5OH + CO_2 \rightarrow 3CO + 3H_2 \quad (7)$$

From equation (4), taking into account its endothermic nature, the highest values of ethanol conversion can be obtained at high temperatures and low pressures.

To obtain pure hydrogen from syngas, the most efficient are membrane technologies using different types of membrane materials based on Pd alloys or nanocomposites comprised of metal alloy nanoparticles and protonic conductors [4]. The most efficient, inexpensive and robust are asymmetric supported membranes where thin dense layers of nanocomposites are loaded on foam metal substrates stable to thermal stresses and corrosion.

Currently, there are three methods of implementing electrolysis technology for hydrogen production, which differ in the type of electrolyte used and electrolysis conditions. Alkaline electrolyser is a device that uses the process of passing an electric current through an electrolyte solution (20-30% KOH or NaOH solution) from the anode to the cathode, as a result of which hydrogen and oxygen gases are formed (8):

$$H_2O \rightarrow H_2 + 0.5O_2 \tag{8}$$

at the cathode: $2OH^- \rightarrow 0.5O_2 + H_2O + 2e^-$

anode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

The method of hydrogen production in electrolyzer with solid polymer electrolyte (SPE) [8] is historically associated with the design of the perfluorinated ion exchange membrane "Nafion" by DuPont. The first electrolyzers of this type were created in 1966, the membrane of such electrolytes is a perfluorinated carbon-based gas-tight polymer with mechanical strength, chemical stability and high electrical conductivity. The general chemical formula of the processes taking place at the electrodes:

at the cathode: $4H^+ + 4e^- \rightarrow 2H_2$

anode: $2H_2O - 4\,e^- \rightarrow O_2 + 4H^+$

The advantages of this method over that with alkaline electrolyte are a high efficiency of the process, wide range and speed of performance adjustment, short start-up and stop time, high purity and ability to obtain hydrogen under pressure, convenient operation, absence of toxic alkali in the device.

Solid polymer electrolyte electrolyzers are several times more expensive than aqueous-alkaline electrolyzers with a similar performance, but at the same time they are environmentally friendly and consume less energy, they have significantly lower mass characteristics, a higher safety level, the ability to work in non-stationary modes, simple maintenance. An important feature of water electrolysis systems using solid polymer electrolyte electrolyzers is that the purity of the produced hydrogen corresponds to the quality of gases required for use in SPE fuel cells. At the same time, the electrolysis systems based on solid polymer electrolyte electrolyzers set stricter requirements for the purity of the supplied water.

Estimates based on a lifetime (about 5 years) show that the cost of hydrogen produced by SPE electrolysis is lower than that of hydrogen produced by alkaline electrolysis, especially when considering the cost of buildings, auxiliary equipment, hydrogen treatment and disposal of alkaline solution.

High-temperature electrolysis of water vapor is carried out in zirconium-based solid electrolyte cells modified with heterovalent oxide mixtures of some rare earth elements to increase its electrical conductivity. A similar electrolyte has anionic conductivity – the current is carried through it by oxygen ions formed as a result of the dissociation of water and the release of hydrogen at the cathode:

at the cathode: H_2O (vapour) + 2e- $\rightarrow O^{2-} + H_2$

at the anode: $O^{2-} \rightarrow 0.5O_2 + 2e^-$

Hydrogen is removed from the cathode space together with undecomposed steam. The process of electrolysis of water vapor takes place at a significantly lower voltage compared to the electrolysis of water solutions. However, the harsh operating conditions make it difficult to choose materials that are sufficiently resistant under anodic polarization conditions for the anode and to create a reliable anode-electrolyte-cathode cell that can withstand temperature changes from room temperature to operating electrolysis.

During the implementation of this process, there is an opportunity to dramatically reduce the consumption of electricity for the production of electrolytic hydrogen - not all energy should be provided in the form of electricity, part of the energy can be provided in the form of heat, and the higher the operating temperature of the cycle, the greater the share of heat energy in it can be obtained from an external source, for example, utilizing the energy of a nuclear reactor or from renewable sources through combustion.

Conclusion. The parallel reactions that occur during the indicated methods can be the main reason for the formation of by-products such as CO, CH_4, acetaldehyde, ethylene, ethane and others along with hydrogen and CO_2. The relative importance of each of these reaction pathways depends on the chosen reaction conditions (e.g., reaction temperature, feedstock composition, and exposure time) and catalyst selection. Existing technologies of hydrogen production are reviewed and problems requiring solution for their efficient and broad application are considered.

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This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project FWUR-2024-0033).

Material received on 16.05.24.

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СУТЕК АЛУ ӘДІСТЕРІ: ҚЫСҚА ШОЛУ

Аңдатпа. Энергияны тұтынудың үздіксіз артуы және қазба ресурстарының азаюы, жаһандық жылынудың артуы және соның салдарынан қоршаған ортаның нашарлауы анағұрлым жетілдірілген баламалы энергия көздерін зерттеудің артуына әкелді. Энергетика саласының «жасыл» экономикаға бет бұратын бағыттарының бірі жаңа энергия көздеріне, ең алдымен сутегіне көшу болып табылады. Декарбонизацияға және климаттың бейтараптығына бағытталған жаһандық энергетикалық ауысудың бөлігі ретінде болашақтың маңызды таза отыны ретінде сутегінің көрінісі жиырмадан астам елде алдағы онжылдықтарға арналған сутегі стратегиясын қабылдауға әкелді. Сутегі энергетикасының негізгі мәселесі сутегінің қолжетімді, арзан және экологиялық таза көздерін іздеу болып табылады. Мақалада сутегін алудың қолданыстағы әдістеріне шолу жасалады.

Тірек сөздер: сутегі, синтез газы, энергия, конверсия.

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СПОСОБЫ ПОЛУЧЕНИЯ ВОДОРОДА: КРАТКИЙ ОБЗОР

Аннотация. Непрекращающийся рост энергопотребления и снижение ископаемых ресурсов, рост глобального потепления и как следствие ухудшение состояния окружающей среды привело к росту исследований более совершенных альтернативных источников энергии. Одним из направлений движения энергетики к «зеленой» экономике является переход на новые источники энергии, в первую очередь к ним относится водород. Рассмотрение водорода как важнейшего экологически чистого топлива будущего в рамках мирового энергетического перехода, направленного на декарбонизацию и достижение климатической нейтральности, привело к принятию водородных стратегий на ближайшие десятилетия в двух десятках стран. Основной проблемой водородной энергетики является поиск доступных, недорогих и экологически безопасных источников водорода. В статье проведен обзор существующих методов производства водорода.

Ключевые слова: водород, синтез-газ, энергетика, конверсия.