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Review

Production of hydrogen from renewable resources and its effectiveness

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ABSTRACT

At present, hydrogen is used mainly in a chemical industry for production of ammonia and methanol. In the near future, hydrogen will become a significant fuel which can solve the local problems connected with an air quality. Because the hydrogen is most widespread component on the Earth, it can be obtained from a number of sources, both renewable and non-renewable, moreover, by various processes. Pure hydrogen can be acquired by the energy-demanding electrolysis of water. Global production has so far been dominated by hydrogen production from fossil fuels, with the most significant contemporary technologies being the reforming of hydrocarbons, pyrolysis and co-pyrolysis. In the near future, biological method can be used.

This work is aimed to an evaluation of possibilities of the hydrogen production from the renewable sources by biological methods and comparison of effectiveness with the conventional methods.

1. Introduction

Hydrogen is presently used predominantly for the production of methanol and ammonia and in the refining industry. Nevertheless, hydrogen production has become a subject of interest for many global companies for its broad application and ecological aspects, and in a number of countries an intensive R&D of the methods of obtaining hydrogen through affordable technologies is being conducted. The annual production of hydrogen is now ca 55 million tons, with its consumption increasing by approximately 6% p.a. Hydrogen can be produced in many ways from a broad spectrum of initial raw materials. Hydrogen is produced predominantly from fossil fuels; roughly 96% of hydrogen is produced by steam reforming of natural gas [1–3]. Perhaps 4% of hydrogen is produced by the electrolysis of water. Electrolytic and plasma processes demonstrate a high efficiency of hydrogen production but unfortunately consume the most energy [4–8]. It can be predicted that in the future, besides the steam reforming of natural gas and the gasification of coal, hydrogen production will be provided by the gasification of biomass and by enzymatic processes. It is therefore necessary to devote some attention to the biological methods, especially their efficiency.

The fundamental question lies in the discovery of alternatives to hydrogen production from fossil fuels with its utilization especially for means of transportation. This problem can be resolved by the utilization of alternative renewable resources and the related methods of production, e.g. the gasification or pyrolysis of biomass or photolytic

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cracking of water using solar energy and microorganisms as well as dark fermentation. It is not possible to consider only the ecological perspective, because e.g. photolytic cracking of water is very environmentally friendly, but its efficiency for industrial use is very low. It is clear that the processes must be taken into account not only in terms of ecology but at the same time also in terms of economics.

In the first place, it is possible to consider thermochemical processes. For instance, through two-step co-pyrolysis, a significant amount of hydrogen can be obtained from mixes of waste polymers or biomass with a marginal share of coal [9,10]. Though, very promising processes for hydrogen production are the biological processes of the treatment of biomass.

Biomass is one of the most prospective renewable resources, because its energetic usage, which includes also hydrogen production, has multifaceted importance. Currently, the share of biomass in the contemporary global energy supply is around 12%, but in many developing countries its share is 40–50% [11]. An advantage is that biomass and the derived phytofuel contains hardly any sulfur and the emissions of sulfur dioxide are thus negligible. The disadvantage of the energetic utilization of biomass is its as-yet insufficient competitiveness with fossil fuels. The yield of hydrogen that can be produced from biomass is relatively low, 16–18% based on dry biomass weight [12]. In terms of economics is likely that pyrolysis or co-pyrolysis of biomass, namely thanks to the valuable byproducts and low costs, represent the best possibilities. The oxidation of hydrocarbons or biomass for hydrogen production through the cracking of sugars in the vapor phase with catalysts (e.g. 150 °C, Pt/Al_2O_3; 225 °C, 22 bar, Ni, Pd, Pt, Ir, Ru and Rh/Al_2O_3) [13,14] is for the time being in the stage of development.

From the outline above, it is clear that the selection of the resources and methods of hydrogen production must be carefully evaluated, because besides the environmental viewpoint also the economic perspective is important, given other than by the availability of the resources mainly by the effectiveness of the process.

The aim of this work is to provide an overview of the promising and developing technologies of hydrogen production and determine the most promising methods for acquiring hydrogen in the future.

2. Biological processes of hydrogen production

Interest in research in the area of biohydrogen has increased in the last decades because of the rising amount of waste materials and the need for their minimization. Biological processes are in contrast with electrolysis and thermochemical processes catalyzed by microorganisms in an aqueous environment under atmospheric pressure and at an ambient temperature. These processes can be utilized in localities with a well-accessible source of biomass or another suitable waste material, which leads to a reduction of the energy costs and the costs for the transport of the initial raw material. The major criteria for the selection raw materials are cost, content of carbohydrate, biodegradability and availability. Biological processes usually work with various types of the anaerobic bacteria or algae. The effect of the microorganisms differs from one another by the type of substrate and the process conditions.

The objective of the development of the processes of biohydrogen production is the acquisition of a higher yield of the produced hydrogen through an economically acceptable method. Biological hydrogen production as a byproduct of the metabolism of the microorganisms includes newly developed technologies utilizing various renewable resources, which can be divided into five separate categories: direct biophotolysis, indirect biophotolysis, biological water–gas conversion, photofermentation and dark fermentation. All of these processes are controlled by enzymes producing hydrogen, particularly nitrogenase and hydrogenase, whose properties are shown in Table 1 [15].

The main components of nitrogenase are the molybdenum–iron protein and iron. The creation of hydrogen by nitrogenase can be described by the chemical reaction (Eq. (1))

$$4ATP + 2H^+ + 2e^- \rightarrow H_2 + 4ADP + 4Pi \quad (1)$$

where ATP is adenosintriphosphate, ADP is adenosindiphosphate and Pi is inorganic phosphate, respectively.

In the majority of photosynthetic microorganisms, hydrogenases exist as acceptor and reversible hydrogenases. The important components of acceptor hydrogenase are NiFe and NiFeS, which consume molecular hydrogen by the reaction (Eq. (2)) [15,16]

$$H_2 \rightarrow 2e^- + 2H^+ \quad (2)$$

Reversible hydrogenases have the ability to create molecular hydrogen as well as to consume it depending on the reaction conditions

$$H_2 \leftrightarrow 2e^- + 2H^+ \quad (3)$$

The initial material for the creation of hydrogen through a photolytic process is water, with a fermentation-process

Table 1 – The properties of nitrogenase and hydrogenase [15].

Property	Nitrogenase	Hydrogenase
Substrates	ATP, H^+or nitrogen, electrons	H^+, hydrogen
Products	H_2, NH_4^+	ATP, H^+, hydrogen, electrons
Number of proteins	2 (Mo–Fe and Fe)	1
Metal components or sulfur	Mo, Fe	Ni, Fe, S
Optimal temperature	30 °C (*A. vinelandii*)	55 °C (*R. rubrum*) 70 °C (*R. capsulatus*)
Optimal pH	7.1–7.3 (*A. vinelandii*)	6.5–7.5 (*R. sulfidophilus*)
Inhibitors	N_2, NH_4^+, O_2, high N:C ratio of H_2 production	CO, EDTA, O_2, some organic compounds
Stimulators	Light	Absence of organic compounds (*R. rubrum*, *R. capsulatus*)