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Hydrogen production from biomass using dark fermentation

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ABSTRACT

Hydrogen applicability in the power, chemical and petrochemical industries is constantly growing. Efficient methods of hydrogen generation from renewable sources, including waste products, are currently being developed, even though hydrogen is mainly produced through steam reforming or thermal cracking of natural gas or petroleum fractions. In paper alternative methods of hydrogen production with a particular emphasis on dark fermentation are discussed. The review compiles essential information on strains of bacteria used in the production of hydrogen from waste products in the agroindustry and from lignocellulosic biomass. The effect of such parameters as kind of raw material, method of processing, temperature, pH, substrate concentration, partial pressure of hydrogen, hydraulic retention time, method of inoculum preparation and the type and operating parameters of a reactor on the yield of dark fermentation is discussed. The review aims at presentation of current state of knowledge on the dark fermentation process utilizing waste materials as substrates. The results of investigations with emphasis on the most important issues regarding operating parameters of dark fermentation are also included.

1. Introduction

Depletion of fossil fuels, being at present the main energy sources, as well as a negative impact of their combustion products on the environment, have resulted in an increased interest in hydrogen as one of the most promising energy sources in the future. Hydrogen, called the fuel of the future can be converted into energy not only in internal combustion or jet engines, gas power turbines but also in fuel cells. The advantage of hydrogen as a fuel is attributed to its high net calorific value compared with other fuels (Table 1) [1,2]. One kilogram of hydrogen is equivalent to 2.75 kg of gasoline and 6 kg of methanol with respect to its net calorific value [3]. Hydrogen, due to its high energy efficiency, is also competitive with other alternative energy sources such as wind, solar, tidal and geothermal energy [2]. In the age of deterioration of the environment, the fact that hydrogen is an ecologically clean energy source is highly important. Combustion of hydrogen does not yield carbon dioxide, one of the greenhouse gases affecting the climate. A serious limiting factor in the use of hydrogen as an energy source is its explosivity in a mixture with oxygen. In addition, storage of hydrogen fuel is more difficult when compared to other fuels. Due to its low boiling point, hydrogen has to be stored in specially insulated pressure vessels. In spite of this, hydrogen storage is easier than energy storage [3].

Although hydrogen is being used as a fuel or energy source, at present its main applications are as a starting material in the chemical, refinery and pharmaceutical industries. It is used in the synthesis of ammonia and methanol and for hydrogenation of liquid oils [3]. Among other processes making use of hydrogen, one should mention the synthesis of aniline from nitrobenzene, the synthesis of hexamethylenediamine and the removal of trace amounts of oxygen in corrosion protection [3]. In refinery processes, such as hydrocracking or hydro refining, hydrogen is used to remove sulfur and nitrogen compounds.

Hydrogen does not occur in nature in its elemental form but only in chemical compounds. Thus, despite its abundance on Earth, in order to produce hydrogen it is necessary to convert compounds in which it occurs. At present, the most common sources of hydrogen are nonrenewable fossil fuels, such as crude oil (*ca.* 30%), natural gas (*ca.* 48%), coal (*ca.* 18%), and electrolysis of water (*ca.* 4%) [4]. The leading technologies of hydrogen production using conventional energy sources include steam reforming of natural gas and petroleum, catalytic decomposition of natural gas, partial oxidation of heavy hydrocarbons fraction of petroleum and gasification of coal or coke. These methods are very energy-intensive and require high temperatures (> 700 °C). Furthermore, all the processes mentioned above pollute the

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Table 1
Comparison of properties of synthetic fuels [2].

Fuel	Relative amount of fuel needed to match weight composition of H_2 [Heat of combustion / Heat of combustion of H_2]	Hydrogen density in fuel [g/dm^3]	Net calorific value [kJ/g]	Storage
Hydrogen	1	70.5	120.0	Very difficult
Methane	2.4	104.1	50.0	Difficult
Methanol	6.0	113.7	20.1	Easy
Ethanol	4.4	104.1	26.8	Easy
Gasoline	2.7	112.1	46.7	Easy

environment emitting large amounts of oxides of carbon, sulfur and nitrogen as well as ashes containing radioactive substances and heavy metals to the atmosphere [5,6]. Another important process generating hydrogen is electrolysis of water; however, it requires electrical energy coming from coal- or natural gas-fired power plants or from nuclear power plants. The advantage of electrolysis results from lack of emission of carbon dioxide to the atmosphere [4,7].

Novel methods of hydrogen production, such as photocatalytic, plasmochemical, magnetolytic or radiolytic splitting of water as well as high-temperature plasma gasification of hydrocarbons are being developed [8–11]. Decomposition of water yielding hydrogen and oxygen can also take place through mechano-catalytic splitting [12].

The share of individual raw materials in the production of hydrogen is shown in Fig. 1. At present 96% of produced hydrogen comes from fossil fuels; therefore, hydrogen cannot be treated as a product of green chemistry and an ecological energy source.

The objectives of the review are to:

- Describe the perspectives on hydrogen production concerning factors affecting dark fermentation that acquire basic understanding and experience about renewable resources for hydrogen generation and associated problems.
- Explain the technological possibilities for hydrogen production and scale-up.
- Identify the areas of additional research and practices to improve the efficiency and the gain of energy associated to the renewable resources management.

1.1. Perspectives on hydrogen production

Despite the broad industrial applications of hydrogen, it is highly probable that hydrogen will soon become a main fuel for transportation services. This is caused by crude oil depletion as well as ecological aspects related to gasoline and diesel fuel usage. The awareness of people and politicians is increasing, regarding the effects of conventional transportation services on environmental pollution. Exhaust fumes emissions *i.e.* nitrogen and carbon oxides, particulate matter or hydrocarbons, especially affect citizens of large urban locations. Beside novel methods of exhaust fumes reduction corresponding to increasingly restrictive regulations, new technological solutions for road transportation are investigated and implemented. Among these technologies, electrical cars gain importance, mainly due to zero local emissions. However, high price, little range, relatively long recharging time and the recycling problem of used batteries limit the popularity of electric cars. Driving electric cars with hydrogen fuel cells seems to be a convenient alternative, mainly due to efficient generation of electric energy [13]. Current technologies enable to offer a similar comfort of usage, comparing to conventional cars with internal combustion engines. Taking into account that there are 1,1 billion of cars globally, road transportation seems to be an important area of future application of hydrogen as a fuel. However, this scenario may be realized providing that the technologies for safe hydrogen storage and usage as well as hydrogen distribution network are further developed. Globally, an increasing number of countries invests in programs devoted to the development of hydrogen-driven transportation [14]. Moreover, application of hydrogen fuel cells favors the decentralization of electric energy generation for industry, rural and urban areas [15] because the fuel may be used at its generation place. Furthermore, the global increase of hydrogen fuel cells popularity results in an increasing significance of renewable energy sources from biomass of various origin. Hydrogen production from biomass results in a decrease of energetic dependence of countries having limited access to fossil fuels. Biomass to hydrogen conversion may be realized *via* several processes *i.e.* gasification, pyrolysis, steam catalytic reforming, photofermentation and biophotolysis. Above mentioned methods of biomass to hydrogen conversion are discussed in chapter two and are currently widely investigated [16,17]. It is worth notifying that besides fuel generation, biomass may be simultaneously converted to various useful chemical compounds. This concept is realized by so called biorefineries [18–22]. Our paper reviews the current state of hydrogen generation *via* dark fermentation. The authors are aware of vast applications of dark fermentation process, thus the paper does not cover all the available data. The authors believe that the paper contains valuable set of information as well as it is an updated supplement to previous review papers devoted to hydrogen dark fermentation [23–31].

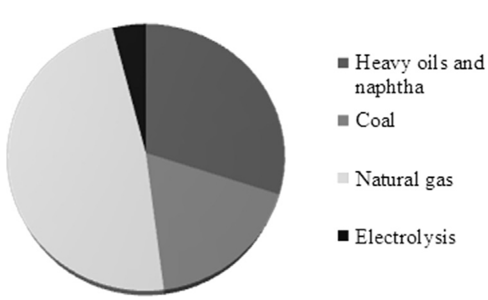

Fig. 1.

2. Hydrogen production methods

Production of hydrogen from renewable energy sources, including biomass, is an alternative to traditional methods of hydrogen generation. Wastes from agri-food industry rich in starch and cellulose (straw, manure, whey, distillery wastewater, molasses), pulp and paper industry wastes, wastes from the production of biofuels (technical grade glycerin) and sewage sludge can all be used in hydrogen production through metabolic processes of microorganisms [32,33]. Crops of rapidly growing plants (energy willow and poplar, silvergrass, switchgrass, grasses) are also used in the production of biomass. Carbon dioxide, being a byproduct in the process of hydrogen generation, can be completely absorbed through photosynthesis on such plantations.

An increasing interest has been put in thermochemical methods of hydrogen production. Biomass gasification is one of above mentioned group of methods. The process is realized in high temperature (600–1000 °C) with limited access to oxygen, air and steam so as incomplete combustion takes place. The resulting products are high volumes of gases and little amount of carbon. The process occurs analogously to gasification of coal, resulting in the formation of synthesis gas, containing combustible products, mostly hydrogen, carbon monoxide and methane and other hydrocarbons as acetylene, ethylene as well as noncombustible components: ammonia, carbon dioxide and water vapor [17,34–36] The advantage of gasification is the possibility of its application to various types of biomass. However, the biomass composition affects the composition of final products. A substrate pretreatment is of crucial importance for the gasification [37]. Following parameters are investigated: particle size, temperature, gasifying agent, the catalyst type and concentration and gasification time [38–42]. The