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## Biohydrogen Production - Sources and Methods: A Review

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### Abstract

This article is a review of available methods of biohydrogen production. In the introduction, properties of different fuels and yields of hydrogen are discussed. The actual and potential sources of hydrogen are reviewed. The suitable substrates for hydrogen production have been assigned with respect to different production method. Recent hydrogen-production techniques are classified using different criteria: substrates, production simplicity and stability. The most stable method according to various variables was determined, i.e. dark fermentation.

**Keywords:** Hydrogen Production; Dark Fermentation; Primeval Biomass; Photo Fermentation

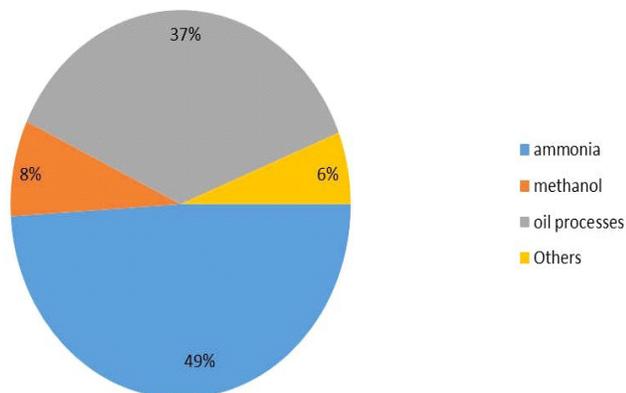
### Introduction

The traditional and main way of obtaining various chemical raw materials and energy carriers are based on fossil fuels. Fossil fuels such as: gas, oil, and carbon are very useful raw materials; however, their use carries a cost for the environment. Moreover, fossil fuels coming from 'primeval biomass' are limited and in view of a growing human population will soon be exhausted. Therefore, there are various attempts undertaken to obtain energy carriers and primary substrates to supply the chemical industry from renewable sources. Hydrogen due to the high heating value (~120 kJ/g) and low density is a competitive energy carrier when compared to other sources like solar, wind, tidal or geothermal energies [1]. Besides, hydrogen fuel generates the least pollution compared to other fuels. A comparison of a few chosen fuels is shown in (Table 1), Michel et al. [2].

Fuel	Heat of combustion low heating value, KJ/g	Relative amount of fuel per unit volume required to equal H <sub>2</sub> heat *content by weight	Boiling point, °C	Storage
Hydrogen H <sub>2</sub>	119.66	1	-253	Very difficult
Methane	50.208	2.4	-162	Difficult
Methanol	20.08	6	65	Medium
Ethanol	26.78	4.4	78	Easy
Gasoline	44.35	2.7	125	Easy

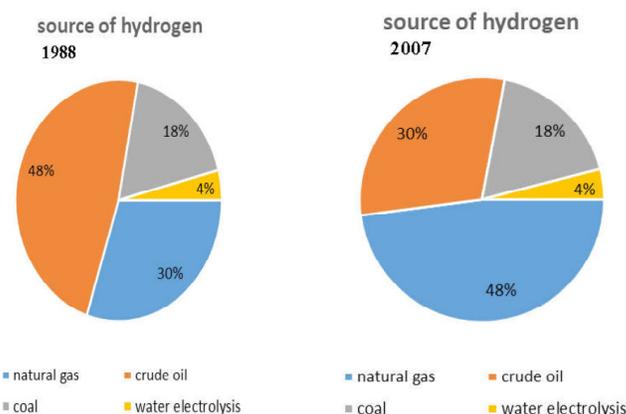
**Table 1:** A comparison of a few chosen fuels.

Besides being a promising carrier of energy, hydrogen is one of the basic raw materials for technological processes like: synthesis of aniline from nitrobenzene, hexamethylene diamine synthesis, hydro cracking, synthetic gas generation (ICI process, Lurgi, gasification of coal), hydrogenation of hard coal, ammonia synthesis, methanol synthesis, hydrogenation of fats, oxo- processes, Fischer-Tropsch or 1,4-butanediol synthesis. 49% of manufactured hydrogen is used for ammonia synthesis.



**Figure 1:** World consumption of hydrogen in chemical and other processes [3].

Hydrogen stores three times more energy (in terms of volume) than gasoline and seven times more than coal. However, storage of hydrogen is troublesome when comparing to other fuels due to low boiling point and low energy density [4], although it is still easier than storing electric energy [5]. Hydrogen, due to its low boiling point needs to be stored in super insulated vessels. Lack of feasible storage and no efficient way of producing it in a renewable way are the main difficulties of hydrogen. Besides, the special properties of hydrogen lead to its occurrence in elemental form, usually bound in compounds and rarely in a pure molecular form of H<sub>2</sub>. Therefore, to obtain hydrogen it is often necessary to break down compounds that contain hydrogen. The selection of hydrogen production-process and hydrogen-containing substrate is based on cost analyses of processes, the abundance of substrate and the number of expected moles of hydrogen obtained from a mole of substrate. Recently hydrogen for an industrial scale application is produced from petrochemical cracking (crude oil or natural gas cracking), coal-based processes or water electrolysis. Petrochemical and coal-based processes are related to steam reforming of hydrocarbons (mainly methane) [6]. Rapid changes in substrates for hydrogen production were observed between 1988 and 2007 presented by Weismerssel and Arpe [6] in (Figure 2).



**Figure 2:** Substrates for global hydrogen production in 1988 [4-6] and 2007 [7].

According to Hussein et al. [3] the share of natural gas in hydrogen production today is more than 50%. Besides, hydrogen is still produced in more than 96% from (fossil fuels - Figure 2). Furthermore, taking into account that water electrolysis is usually performed using electrical energy from fossil fuels, then the actual share of fossil fuels in hydrogen production is 98% or more. Therefore, hydrogen cannot be considered today as a carrier of green energy and raw material for green chemistry. Hydrogen is produced mainly from natural gas in a two-stage process called steam methane reforming. This process is limited in that it cannot be used for hydrocarbons heavier than naphtha [6]. There are several other processes to obtain hydrogen: water splitting, decomposition of biomass or ammonia. Water splitting is the decomposition of water into hydrogen and oxygen during electrolysis [8], applying heat from other chemical reactions (thermo chemical splitting [9]), using biological processes or solar energy (biophotolysis[10]), applying anode working-potential produced by microbial cells (microbial or biocatalytic electrolysis [11]), applying friction of water molecules by mechanocatalysts and magnetic stirrer [12], in electrical discharges (Plasmolysis [13]), applying magnetic induction (Magnetolysis)[14] or irradiation by radioactive materials (radiolysis)[15]. Hydrogen can be obtained by decomposition of biomass in several thermo chemical (gasification, pyrolysis) and biological (biophotolysis, fermentation, and biological gas shift) processes. Thermo chemical methods produce hydrogen by thermal decomposition of various compounds. Biomass Pyrolysis involves heating of substrate under oxygen less (anaerobic) conditions. Biomass gasification is a hydrogen generation by decomposition of biomass under the limited presence of an oxidizer (air, steam, CO<sub>2</sub>, etc.). Biomass fermentation is a decomposition of organic

matter by applying proper microbes under anaerobic conditions. Fermentation with hydrogen generation may be classified as either photo fermentation (fermentation under influence of light with wavelength in UV-VIS spectral range) or dark fermentation (first stages of anaerobic fermentation when hydrogen, carbon dioxide and lower organic acids are formed) [16]. During photo fermentation of carbohydrates, organic compounds are decomposed by green algae and anaerobic bacteria. Recently, alternative methods of obtaining hydrogen in a renewable way, especially by microbial or vegetal conversion of biomass into hydrogen (called biohydrogen) have been developed [17-24]. Other potential methods of hydrogen production are: decomposition of hydrogen sulfide or ammonium as well as ammonium production in indirect biophotolysis [25]. In this paper potential sources of hydrogen and methods of the hydrogen production are reviewed. The review brings ideas which combination can provide fully renewable and sustainable procedure of hydrogen production. The hydrogen production methods are developed very rapidly and improved during last 20 years [26-34]. There are several reviews of hydrogen production technologies [3,35-38], including more recent methods [39-49]. This work contains a broad description and comparison of alternative methods of hydrogen production with conventional ones. The article includes also examination of various raw materials for being suitable substrates. A wide review of methods is provided, with stress on biological methods (biohydrogen production).

## Raw Materials

### Substrates Suitable for Hydrogen Production

The substrates suitable for hydrogen production can be divided according to their complexity, kind of material, methods required for their pretreatment, energy demand for hydrogen production or production costs. Traditional methods use substrates related to fossil fuels i.e. primeval biomass. The alternative source of hydrogen is contemporary biomass and simple inorganic compounds containing from 1 to 3, usually 2 hydrogen atoms per molecule (e.g. H<sub>2</sub>O, NH<sub>3</sub>, H<sub>2</sub>S, HCl). The selection method of hydrogen source is presented using

the example of dark fermentation. Since alternative ways of hydrogen production are limited to laboratory scale the most suitable raw materials are still sought. The selection of hydrogen containing compounds based on ‘golden mean’ by abundance, production conditions and efficiency [36, 37,50-55]. Suitable raw materials for dark fermentation include wastes containing a high fraction of carbohydrates, such as: lignocelluloses, sugar-containing and starch containing crops, chitin, starch, hemicelluloses starch in wastewater, cellulose, glucose, sucrose, organic municipal wastes, waste from dairy products, manures, compost, and waste water from food industries [44]. The substrate availability is limited by possible competing uses such as nourishment and fodder.

According to Bartacek et al. [56] And Hawkes et al. [57-59] the raw materials to be suitable for commercial hydrogen production using the dark fermentation method should possess high content of carbohydrates, no or low need for pre-treatment and minimum costs. Other relevant factors are: sufficient fermentative conversion degree and process energy recovery. Kargi et al. [60] considered that the optimal raw material should be composed of high content of carbohydrates, proteins and fats, e.g. Cheese whey contains carbohydrates (from 5% to 6% of lactose), proteins (from 0.8% to 1%) and fats (0.06%) and there is still needing to increase content of carbohydrates [12]. Some materials like glucose or sucrose were used for dark fermentation under experimental conditions. Examples of sugar-containing crops are sugar-beet or sweet sorghum, while starch-containing are corn and wheat. Other quite efficient raw materials for hydrogen production seem to be those related to livestock waste [61-64]. The substrates can be classified as direct or indirect hydrogen sources. In direct processes hydrogen is produced at one-stage of the process (in Tables 2a-d, Table 3 marked as D). If hydrogen is produced as the result of two or more stages (and only finally hydrogen is produced) the process is considered as indirect (in Tables 2 a-d, Table 3 marked as ID). In the indirect process of hydrogen generation in the last stage there is usually a mixture of simple compounds that in pure form can be sources of D process. In (Tables 2-5) several raw materials and methods of hydrogen production are presented.

Raw Material	Chem. Form.	Method	Type	Remarks	Ref.	Year
Ammonium	NH <sub>3</sub>	Catalytic Ammonia Decomposition	D	Conversion 99% at T=650°C	[53]	2001,2016
Ammonium	NH <sub>3</sub>	Electrolysis	D	Potential required 0.06 V, i.e. 1.17 V less than for water	[65,66]	2015, 2016
Methane (Natural Gas)	CH <sub>4</sub>	Steam Methane Reforming (SMR)	D	Conversion 65% - 85%	[6]	1997
Methane (Natural Gas)	CH <sub>4</sub>	Pyrolysis	D	More energy efficient than SMR	[67]	2005

Water	H <sub>2</sub> O	Electrolysis	D	Potential required 1.23 V	[5]	2008
Water	H <sub>2</sub> O	Microbial Electrolysis Cell	D	Potential up to 0.3 V To cover it extra power is needed	[68-70]	2015, 2016
Water	H <sub>2</sub> O	Direct Term chemical Water Splitting	D	High energy requirements	[37]	2015
Water	H <sub>2</sub> O	Sulfur Iodine Term chemical Water Splitting	ID	Thermal hydrogen iodide formation and decomposition.	[9]	2015
Water	H <sub>2</sub> O	UT-3 method	ID	High costs of substrates	[71]	2015
Water	H <sub>2</sub> O	Copper-Chlorine Cycle	ID	Thermal hydrogen chloride formation and decomposition	[72]	2015
Water	H <sub>2</sub> O	Magnetolysis	D	No published research since 1985	[14]	1985

**Table 2:** Substrates for various hydrogen generation methods from ammonia, water and methane.

Material	Chem.Form.	Method	Type	Remark	Ref	Year
Methanol	CH <sub>4</sub> O	Plasmolysis	D	High conversion 87.1% for 5% solution of CH <sub>4</sub> O in argon	[71]	2011
Hydrogen Sulfide	H <sub>2</sub> S	Thermal Dissociation	D	Method designed for sulfur production	[72]	2015
		Plasmolysis	D	conversion 87.1% for 5% H <sub>2</sub> S in nitrogen	[73]	2011
Hydrogen Chloride	HCl	Copper-Chlorine Cycle	D	High costs of substrate	[54]	2013
Hydrogen Iodide	HI	Sulfur-Iodine Hydrogen Production Cycle (Sulfur Iodine Thermochem. Water Splitting)	D	It uses sulphur dioxide as substrate, can be used to prevent its emission	[9]	2008
Acetic Acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Photo fermentation	D	Hydrogen yield 69 ml of H <sub>2</sub> per g of C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> ( <i>R. spareoides</i> RV)	[74,75]	2006, 2015
Ethanol	C <sub>2</sub> H <sub>6</sub> O	Plasmolysis	D	Hydrogen Yield 17.2% for 0.08% C <sub>2</sub> H <sub>6</sub> O in CO <sub>2</sub>	[76]	2016
Propionic Acid	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Photo fermentation	D	Hydrogen yield 60 ml of H <sub>2</sub> per g of propionic acid ( <i>R. palustris</i> A7)	[77]	2015
Lactic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	Photo fermentation.	D	Hydrogen yield 138 ml of H <sub>2</sub> per g of butyric acid ( <i>R.monas</i> )	[78]	2005
Isopropanol	C <sub>3</sub> H <sub>8</sub> O	Plasmolysis	D	Hydrogen Yield 23.5% for 0.11% C <sub>3</sub> H <sub>8</sub> O in CO <sub>2</sub>	[76]	2016

**Table 3:** Substrates for various hydrogen generation methods.

Raw Material	Chem. Form.	Method	Type	Remarks	Ref.	Year
Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	Dark Fermentation	D	Hydrogen yield 172.87ml of H <sub>2</sub> per g of glycerol [ <i>E.aerogenes</i> ]	[79]	2014
		Photolysis	D	Hydrogen yield is 0.086 ml of H <sub>2</sub> per g of glycerol	[80]	2016
Butyric Acid	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Photo fermentation	D	Hydrogen yield 209 ml of H <sub>2</sub> per g of butyric acid [ <i>R. spareoides</i> RV]	[81]	2016
Malefic acid	C <sub>4</sub> H <sub>8</sub> O <sub>5</sub>	Photo fermentation	D	Hydrogen yield 100 ml of H <sub>2</sub> per g of maleic acid [ <i>R. spareoides</i> RV]	[82]	2008
Succinic Acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	Photo fermentation	D	Additive fermentation to low organic acids and sugars	[83]	2015

**Table 4:** Substrates for various hydrogen generation methods from glycerol and low organic acids.

Raw Materials	Chem. Form.	Method	Type	Remarks	Ref.	Year
Xylose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	Dark Fermentation	ID	Hydrogen yield 117.97 ml of H <sub>2</sub> per g of glucose ( <i>E. aerogenes</i> strain HO-39)	[84]	2012
Arabinose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	Dark Fermentation	ID	Hydrogen yield 120.96 ml of H <sub>2</sub> per g of arabinose ( <i>E. aerogenes</i> strain HO-39)	[85]	2009
Hexane	C <sub>6</sub> H <sub>14</sub>	Plasmolysis	D	Conversion 95% in 5% water solution	[73]	2011
Rhamnose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	Dark Fermentation	ID	Hydrogen n yield 69.69 ml of H <sub>2</sub> per g of rhamnose ( <i>E. aerogenes</i> strain HO-39)	[86]	2009
Galactose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	Dark Fermentation	ID	Hydrogen yield 118.218 ml of H <sub>2</sub> per g of galactose ( <i>En. aerogenes</i> strain HO-39)	[86]	2009
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	Dark Fermentation	D	Hydrogen yield 124.45 ml of H <sub>2</sub> per g of glucose ( <i>E. aerogenes</i> strain HO-39)	[87]	2002
		Photo fermentation	D	Hydrogen yield 33 ml of H <sub>2</sub> per g of glucose ( <i>R. palustris</i> ATCC RV)	[74]	2015
		Plasmolysis	D	Conversion 95% in 5% water solution	[88]	2015
		Photolysis	D	Hydrogen yield was 7% with lantan perovskite catalyst and 1.84% with home- made titanium oxide	[89,90]	2016
Fructose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	Dark Fermentation	D	Hydrogen yield 121.952 ml of H <sub>2</sub> per g of fructose [ <i>E. aerogenes</i> strain HO-39]	[91]	2004
Mannose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	Dark Fermentation	D	Hydrogen yield 121.96 ml of H <sub>2</sub> per g of mannose [ <i>E. aerogenes</i> strain HO-39]	[86]	2009
Mannitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	Dark Fermentation	D	Hydrogen yield 206.76 ml of H <sub>2</sub> per g of mannitol [ <i>E. aerogenes</i> strain HO-39]	[86]	2009

**Table 5:** Substrates for various hydrogen generation methods from 5 and 6-membered carbohydrates.

Raw Materials	Chemical Formula	Lists of methods	Type	Remarks	Ref.	Year
Citric Acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	Photo fermentation	D	Hydrogen yield 36 ml of H <sub>2</sub> per g of citric acid ( <i>R. palustris</i> AT7)	[76]	2015
Isooctane	C <sub>8</sub> H <sub>18</sub>	Plasmolysis	D	Process occurs in 5-15% solution in water	[75]	2011
Sucrose	C <sub>12</sub> H <sub>24</sub> O <sub>11</sub>	Dark Fermentation	D	Hydrogen yield 109.40 ml of H <sub>2</sub> per g of sucrose ( <i>E. aerogenes</i> strain HO-39)	[94]	2009
Sucrose	C <sub>12</sub> H <sub>24</sub> O <sub>11</sub>	Photo fermentation	D	Hydrogen yield 33 ml of H <sub>2</sub> per g of sucrose ( <i>R. palustris</i> AT7)	[76]	2015
Maltose	C <sub>12</sub> H <sub>24</sub> O <sub>11</sub>	Dark Fermentation	D	Hydrogen yield 140.65 ml of H <sub>2</sub> per g of maltose ( <i>E. aerogenes</i> strain HO-39)	[95]	1995
Lactose	C <sub>12</sub> H <sub>24</sub> O <sub>11</sub>	Dark Fermentation	D	Hydrogen yield 37.767 ml of H <sub>2</sub> per g of lactose ( <i>E.aerogenes</i> strainHO-39)	[88]	2009
Starch	(C <sub>6</sub> H <sub>12</sub> O <sub>5</sub> ) <sub>n</sub>	Dark Fermentation	ID	Common food waste component	[96]	2015
Cellulose	(C <sub>6</sub> H <sub>12</sub> O <sub>5</sub> ) <sub>n</sub>	Dark Fermentation	ID	Promising material due to its abundance	[79]	2015
		Pyrolysis	ID	Dehydration is quite expensive	[40]	2016

**Table 6:** Substrates for various hydrogen generation methods for some carbohydrates, isooctane and citric acid.

Analyzing (Tables 2-6) it can be discerned that the majority of alternative methods use substrates in water solution. In (Tables 2-6) there are more substrates with even numbers of hydrogen atoms than with odd numbers (odd number of hydrogen atoms occur in hydrogen iodide, hydrogen chloride, ammonium and glutamic acid). This results from process kinetics and requirement of even number moles of hydrogen per stage [66]. The ratio of oxygen to carbon O: C in short- chained organic compound (C≤6) (being hydrogen source, especially for dark fermentation process) is 1. Exceptions are butyric, propionic, lactic, maleic and glutamic acids, raw materials for photo fermentation and alcohols for plasmolysis [95]. For larger organic compounds the ratio of O:C lowers. The ratio is 0.92 in the case of sucrose, maltose and lactose. In the case of starch and cellulose ratio O:C in molecule is 0.83. In table 7 there is a comparison of complex raw materials that are used or are potential hydrogen sources.

Raw material	Method	Type	Remarks	Ref.	Year
Livestock: Bovine manure	Dark Fermentation	ID	Hydrogen yield- 58.48 ml of H <sub>2</sub> /g of manure;	[62,96]	2009, 2010
Swine manure			209 ml of H <sub>2</sub> /g of manure		
Sewage Sewage	Dark Fermentation	ID	Pretreatment needed to prevent inhibitors passing to digester	[97]	2015

	Biomass gasification	ID	Low temperature process but costs of drying still high	[98]	2016
Wood	Biomass gasification	ID	High temperature is required	[51,99,100]	2013,2014
Coal	Coal gasification	ID	Highly polluting, catalysts can easily be poisoned	[101]	2008
Oil	Pyrolysis	ID	Highly polluting, catalysts can easily be poisoned	[101]	2008
Kerosene	Plasmolysis	ID	Hydrogen yield is 11.7% for 0.06% kerosene in CO <sub>2</sub>	[76]	2016

**Table 7:** Complex substrates for various hydrogen generation methods.

As it can easily be discerned from (Table 7), complex raw materials are biomasses of different ages. The traditional complex raw materials for hydrogen production like coal and oil can be replaced by recently formed indirect sources of hydrogen [e.g. animal manure] via dark fermentation, gasification or pyrolysis. Lignocelluloses crops (miscasts, fodder grass) and industrial solid waste are cheap and commonly available for the dark fermentation. However, it may be troublesome due to presence of lignin. Recently, in the case of bean and rice bran residues, proteins (in high content) are considered also to be hardly digestible. Lignocelluloses is composed mainly of biopolymers: cellulose (25 -50%wt), hemicelluloses [15-40%wt] and lignin [10 -40%wt] [96,102]. Cellulose is a polymer in some parts amorphous in another crystalline in character. Cellulose is in a form of D-glucose subunits compiled in chains called fibrils [40]. Hemi cellulose is a complex structure composed of pentose (xylose, arabinose) and hexoses (glucose, mannose, and galactose) units. The main hemicelluloses compound in straw and grasses is xylan. Hemi cellulose in seed producing plants like conifers or *Ginko biloba* is built from glucomannan [95]. Due to the specific extraction conditions for glucomannan there is little interest in researching dark fermentation of seed-producing plants [95,103]. The methods of alternating hydrogen production started to be developed in 1980s. Among method of hydrogen production appeared to become some of few years' scientific interest like Magnetolysis (one article) or mechanocatalytical [5 years by one group]. In case of biophotolysis the method is known from 1942 but their potential of hydrogen production is investigated from 1990s. The dark fermentation is also being more widely investigated from the time. From 2013 there are appear also ideas of microbial electrolysis [69,106] that is developed by Logan group after finishing investigation of dark fermentation process [107]. Recently in the United States dark fermentation most significant works are being investigated and published by Blake group [108] with cooperation with Mexico group of Perez-Pimienta [109]. In 1990 s there can be observed the highest interest of the developing of hydrogen methods in Japan and Canada and Turkey [110-112]. From 2000s there most active countries of the world are Japan, India China and Holland in developing method of biohydrogen production like dark fermentation, photo fermentation and biophotolysis [35,113-123]. The methods of biohydrogen production have not been extended from lab scale into industrial one. Therefore, the published materials consider both on prime products and more complex.

## Methods of Hydrogen Production

The methods of hydrogen production presented in (Tables 2-7) are shown in (Figure 3). The biomass is assumed to be pretreated appropriate to the method applied. The relevant factors are: size, shape and form of substrate entering the final stage of the hydrogen production process.

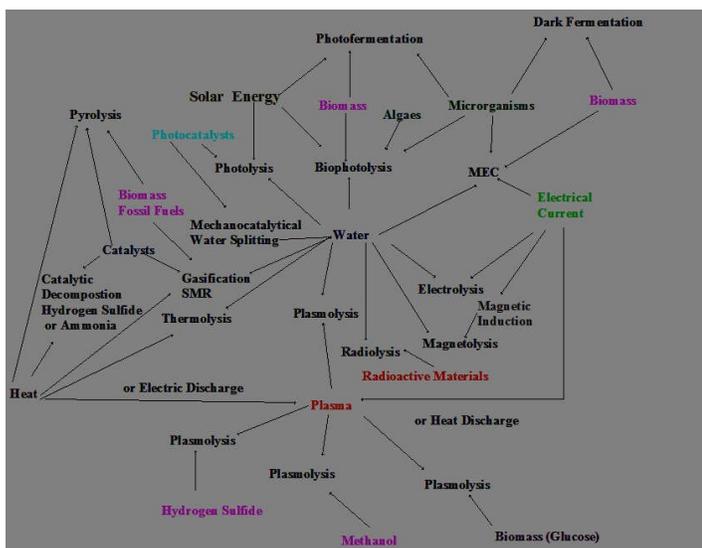


Figure 3: Methods of hydrogen production and relations.

The methods marked in black (Figure 3) are connected to factors considered to be the most relevant for efficient hydrogen production. The biological decomposition methods depend on microorganisms. In certain conditions, microorganisms digesting biomass lead to potential generation in a system allowing for water splitting or to hydrogen production as one of the metabolites. In certain conditions microorganisms can activate the work of enzymes responsible for hydrogen or potential generation. The microorganisms can provide hydrogen production if:

- In **dark fermentation** anaerobic bacteria owing hydrogenases are properly pretreated and cultivated under suitable conditions (temperature, pressure, pH, nutrients, etc.) and biomass is pretreated in the water solution of a suitable (depending on bacteria) concentration of pentoses, hexoses or glycerol or be a solution of one of these compounds (glucose solutions are usually used [104-107]),
- In **photo fermentation**: The system for hydrogen production is in the region of irradiation of visible light, anaerobic bacteria possessing hydrogenases and nitrogenases are bred under suitable conditions (temperature, pressure, pH, nutrients, etc.) and biomass is pretreated in the water solution of a suitable (depending on bacteria) concentration of low organic acids, or sugars [77,108] (see Tables 2-5),
- In **MEC (Microbial Electronic Cells)**: Bacteria are properly pretreated and cultivated in the anode; biomass is prepared to be water solution of simple carbohydrates of suitable concentration in contact with water of suitable flow and purity. Recent research indicated the need for additional supply of electric current for splitting of water,
- In **biophotolysis**: the system for hydrogen production is

irradiated by visible light; cyanobacteria or algae are bred under suitable conditions (temperature, pressure, pH, nutrients, etc.) and biomass is prepared as a water solution of simple carbohydrates of suitable concentration are in contact with water of suitable flow and purity. The water (Figure 3) is a relevant factor for the majority of hydrogen production biomethod. Water independent methods are: Pyrolysis, some cases of Plasmolysis (generation of hydrogen from methanol and hydrogen sulfide), thermal decomposition of hydrogen sulfide, and catalytic decomposition of ammonia. No biological and waterless hydrogen generation can occur:

- In **Plasmolysis** raw material under proper solution in solvent (inner gas) is placed in the reactor with discharge (electric or heat);
- During **Pyrolysis of hydrocarbons**, catalytic decomposition of ammonia or hydrogen sulfide, when the substrate is in system under proper pressure, amount of heat, and in contact with suitable catalysts,
- In **Pyrolysis of biomass**, raw materials are dry enough, pretreated to receive suitable size and shape, placed in system under the appropriate pressure and amount of heat, in contact with suitable catalysts. The hydrogen can be produced by the gasification method of sufficiently dry biomaterial, and pretreated to achieve suitable size and shape, is placed in the system under proper value of pressure, heat and in contact with the suitable catalysts. The hydrogen can also be obtained in Plasmolysis from glucose, in certain solution in water, placed in the reactor where discharge (electric or heat) can operate.
- There are several nonbiological ways of hydrogen production by water-splitting. nonbiological water-splitting can occur:
- In electrolysis in a solution of water, for example alkaline (KOH) between anode and cathode appear proper potential produced by electrical energy,
- In Magnetolysis in water solution between anode and cathode appeared potential produced by magnetic induction,
- In direct thermolysis when substrate is properly heated,
- In indirect thermolysis when proper water solution of iodine and sulfuric dioxide or, solution of water and chloride or water, calcium bromide bromine and magnetite is properly heated;
- In mechano-catalytical process in the presence of water of certain purity and flow, mechanical catalysts and magnetic stirrer,
- during radiolysis in the presence of water and radioactive elements,
- In photolysis: the system is irradiated in the range of

absorbance of applied water solution and photo catalysts (usually of UV or UV-VIS region).

Nonbiological and nonsolar method of hydrogen generation is easier to stabilize due to the smaller amount of factors influencing the process; one needs only the proper amount of energy (radiational, thermal, and electrical) and raw material. In these methods amounts of energy are higher or produce much more pollutants than biological methods and some require special catalysts. The solar-based methods allow periodic production of hydrogen. During these periods irradiation value depends on location, the seasons and diffuse radiation value [79,80,109]. Furthermore, the parameterization of irradiations very complex [110]. Therefore, stable, only solar system of hydrogen production can still hardly be designed. The biological and nonsolar method (like dark fermentation) to obtain stable production needs 'just' a map of bacteria with proper preparation of feed and of proper conditions for breeding and pretreatment of bacteria. In other biological and nonsolar methods (MEC) need to map also water properties and additional current supply. In photo fermentation - solar-based and biological method it is necessary to coincide stabilization of variables of dark fermentation with stabilization of sun - irradiation variables.

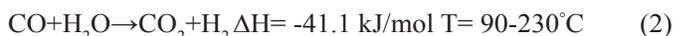
In case of biophotolysis, it is necessary to map appropriate conditions of breeding of organisms and selecting with proper substrate preparation, water purity and flow, with setting system for suitable sun irradiation. Therefore, dark fermentation is the most competitive among the currently available methods due to its simplicity, low operating cost and stability. Although, the MEC method of Microbial Reverse-Electro Dialysis Cells can also solve some problems such as too low potential produced by bacteria in other MEC [93]. In relation to substrates, the sustainability and biomass availability is likely to be limited by global population growth. One study suggests that when there will be more than 13 billion people, then biomass potential will not fulfill human demand according to ref. [111].

### Heat Dependent Methods of Hydrogen Production

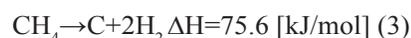
Heat dependent method does not include biological processes but the source of hydrogen for the method can be biomass thus can be classified as biohydrogen source. However, besides biomass pyrolysis and gasification there are source of biohydrogen there are described for better comparison between hydrogen and biohydrogen source.

### Steam methane reforming and pyrolysis

Steam methane reforming (SMR), it is a process requiring high temperature and pressure. During the process hydrogen is generated in reactions (1) and (2) with methane/CO and water participation under pressure from  $P= 1.5 - 3\text{MPa}$



Chemical equipment at steam methane reforming needs to be built from material resistant to the temperature shift between first and second stage. The process requires catalysts from nickel or nickel alloy. The gas needs to be desulfurized to prevent catalyst poisoning. The conversion efficiency of fuel to hydrogen is 65 - 85% [5]. The gas flow rate of hydrogen produced by the SMR process is higher than in the case of biological method. The method produces carbon dioxide as a byproduct which is a greenhouse gas. Pyrolysis is the thermal decomposition of methane, reaction (3), at a temperature in the range  $T=700 - 1100^\circ\text{C}$  and pressure  $P=0.5 - 2 \text{MPa}$ .

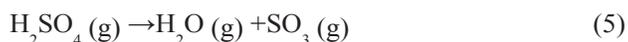
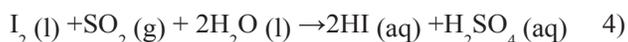


The process produces less hydrogen than in steam reforming because the process includes only one source of hydrogen but requires less heat energy; 37.8 kJ/mol of 63 kJ/mol [67] with SMR. Both methods require large amounts of heat, and catalysts that can be easily poisoned by sulfurous pollution. However, both methods are much more efficient than green methods. However, due to higher energy requirements and increasing consumption of the fossil fuels the methods should preferably be replaced by the more renewable ones.

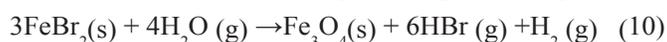
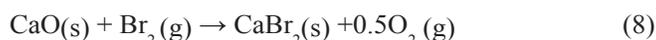
### Thermochemical water splitting

The thermochemical water-splitting method may proceed as one step direct, two steps indirect, and multistage thermolysis. In direct thermolysis water is directly split by high temperature. Water decomposition by temperature can occur at a pressure of 1 bar in temperature above  $1627^\circ\text{C}$  but practically occurs at temperatures higher than  $4023^\circ\text{C}$  [112]. The water splitting method applies the solid nonporous membrane from palladium or palladium-silver alloys. The hydrogen produced is separated by a porous membrane from zirconium. High temperature can be supplied by means of solar energy concentrators. In the two-step thermolysis, the first step proceeds as reduction of metal oxide using high temperature. The second step of water-splitting is performed in the reaction of water with reduced in the first step metal catalyst. Temperature range of the process is from  $1427 - 2727^\circ\text{C}$  under pressure 0.1 MPa.

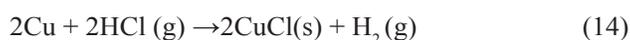
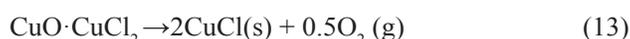
The multistage water thermolysis is performed in: sulfur - iodide cycles, UT-3 or copper- chlorine cycles. In the sulfur-iodine cycle hydrogen is obtained in a three-stage process: Bunsen reaction of iodine with water and sulfur dioxide (4), sulfuric acid decomposition (5) and thermal decomposition of hydrogen iodide at  $T = 650^\circ\text{C}$  (7). Conditions of earlier reactions are: Bunsen reaction at  $120^\circ\text{C}$  and decomposition of sulfuric acid at  $T = 950^\circ\text{C}$  under pressure 0.5 MPa [9]. The method could be considered as hydrogen iodide decomposition because strictly this compound is the hydrogen source:



UT-3 thermolysis is a four-step process -reactions (7) - (10). The first two-steps include hydrogen bromide and calcium bromide formation. They are followed by reduction of magnetite by hydrogen bromine and reverse reaction of iron bromide with steam to obtain magnetite and hydrogen [69]. The temperature of steps is between 220 and 960°C at a pressure of 0.1MPa.



Copper - chlorine cycle is set of four reactions including thermolysis of copper chloride and reaction with water to obtain copper chlorine (II) and hydrogen, reactions (11) - (14) [70]. The processes involve temperatures from 100 - 550°C. The last stage reaction of copper with hydrogen chloride form copper chloride and hydrogen at temperature 837°C and then reverse synthesis of sulfuric acid with obtaining hydrogen [5].



The thermo chemical method of hydrogen generation is expensive and mostly cannot be used in large-scale because of the high temperature requirement. Therefore, it cannot compete commercially with the dark fermentation method.

### Water, hydrogen sulfide and some organic compound decomposition using plasma system

Plasmolysis occurs when water or its vapour is sprayed into or passed through plasma formed in the reactor and hydrogen collected in the output. Plasmolysis, also called plasma reforming, takes place in special PACT (Plasma and Catalyst integrate Technology) reactors [113]. Tubular PACT reactor comprises a quartz tube with two electrodes: inner from catalytic metal (Ru, Au, Pd, Ni, Rh) inside the tube and outer aluminum electrode. Plasma is formed in a quartz tube by electric field of a low frequency (8.1 kHz). The feed contains a solution of water in argon or other gas. Hydrogen can be generated from water by plasma using a plasma jet under temperature 3127 - 3227°C and pressure of 0.1 MPa [13]. At a voltage of 2.5 kV and concentration of water in argon 14.2%, water was converted to 0.32 mole% of hydrogen [114]. In plasma with

water in argon solution lower than 1.6%, conversion of water to hydrogen was 60%. Lozano-Pareda et al. [13] designed kinetic models for nonthermal plasmolysis. In this case the optimal concentration of water in nitrogen was 72%. According to Rehman et al. [115] generation of ozone improves conversion of hydrogen from water to 99%. Plasma systems can also be used for hydrogen production via methanol decomposition. The process occurs under gas temperature from 727 - 9727°C [71]. A high conversion (up to 87.1% of methanol) was achieved when the concentration of methanol in nitrogen was 5% and gas temperature was varied between 27 - 277°C [71].

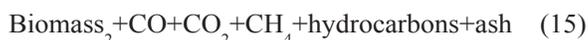
Wang et al [116] used microwave discharge at frequency of 2.45 GHz for a solution of 8% methanol in water resulting in 64% conversion to hydrogen. The hydrogen sulfide decomposition by nonthermal plasma occurs in temperature from 20-152°C [73]. The conversion 20% was at a frequency of 150 MHz for concentration of 5% H<sub>2</sub>S in argon. Another relevant factor is band gap. The conversion of 42% was obtained for band gap 3.5 mm at flow rate 50 ml/min. The concentration range of H<sub>2</sub>S diluted with argon was from 5%-25% [73].

Glucose can also be decomposed into hydrogen by plasma discharge. For decomposition of glucose Syahiralet al. [88] used radio frequency of 27.12 MHz. The highest hydrogen yields 72% was obtained in initial 1% concentration of glucose in water. Besides hydrogen and oxygen, methane, ethylene, acetylene, carbon monoxide, and carbon dioxide were also detected. Paulmieri et al. [39] reported Plasmolysis of hexane and isooctane in temperatures from 900-1100°C. Czykowski et al. [76] used dry reforming Plasmolysis for decomposition of organic compounds like ethanol, Isopropanol and kerosene in solutions with carbon dioxide. The decomposition undergoes under frequency of 915 MHz for concentration of: Isopropanol 0.0011%, ethanol 0.0008% and kerosene 0.0006% in carbon dioxide. The highest yield is obtained from Isopropanol 23.5%, the lowest kerosene 11.7%.

Wang et al. [116] achieved conversion of 8% ethanol in water solution at yield 64.56% in the microwave discharge of 2.45 GHz. Jimenez et al. [117] obtained similar yield 64.5% of 0.4% ethanol concentration in argon in microwave plasma frequency 2.45 GHz. The disadvantages of plasmolysis are necessity of pure raw materials and high amount of energy for the process, much higher than in the case of biological methods. Another disadvantage is the low concentration of substrate to be diluted in inert gas for obtaining high efficiency. This seems to be a far more expensive method than dark fermentation, due to cost of plasma production and purification of substrates.

### Biomass pyrolysis

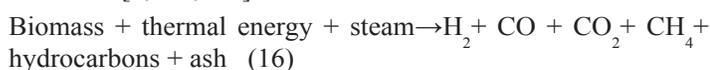
Pyrolysis of biomass, reaction (15) is a thermal decomposition that depends on catalysts (gasifying agents), biomass property and temperature [37,118].



Pyrolysis of biomass is achieved by rapid heating of organic wastes to high temperatures 400-600°C and pressure 0.1 - 0.5 MPa. The products of the process are: hydrogen, carbon monoxide, methane, tar and oils. Optimally hemicelluloses are degraded at temperatures T= 250- 350°C, cellulose at temperature 325 - 400°C and lignin from 300 - 550°C. Biomass for the process should be fragmented and dried. The methane and hydrocarbons produced can be used for further generation of hydrogen [67,119]. Pyrolysis of biomass requires less heat than in case of steam reforming, but far more than dark fermentation. Pyrolysis produces pollutants such as carbon dioxide and other gases [5,120].

### Biomass gasification

Biomass gasification is a decomposition of biomass using heat and gasifying agents like steam. The waste biomass useful for the process (16) should have dry matter content higher than 65% [5,121,122].



The catalysts proposed to be used are e.g. dolomites, alkali catalysts and noble metals. Temperature of process depends from raw materials, for sewage sludge from 180 - 250°C and pressure 1.5 MPa, for wood temperature range is between 950 - 1500°C [123], for lignocelluloses with copper-zinc catalyst from 700 - 800°C [124], for rapeseed the optimum temperature was found to be 750°C [125]. The methane produced in the process can be further used for synthesis of hydrogen in methane forming processes. According to Moreno and Dufour [99] the process is suitable for utilization of residues from woodland or orchards (eucalyptus, almond, vine pruning). Wood residue gasification requires a high energy temperature around 1000°C. From 1.32 kg of pine wood and 1.01 kg of vine, 0.26 m<sup>3</sup> of hydrogen are generated while from 1.44 kg of almond pruning 0.31 m<sup>3</sup> of hydrogen. Moreno and Dufour [99] designed hybrid system for biomass gasification, with the syngas gasification plant where previously mentioned kinds of biomass were processed by reforming and process swing adsorption. The methane produced in biomass gasification can be used further for production of hydrogen by gasification or SMR. In the case of sewage sludge or manure the dehydrating pretreatment is sufficient [98]. Also, this process depends on catalysts (gasifying agents), biomass property and temperature. Biomass gasification in comparison to dark fermentation produces more pollutants and requires more energy to generate 1 m<sup>3</sup> of hydrogen.

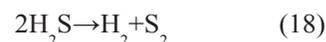
### Catalytic decomposition of ammonia and hydrogen sulfide

Generation of hydrogen from ammonia is an endothermic process, reaction (17) with enthalpy  $\Delta H = 2.63 \text{ kJ/mole}$ .



Temperature of decomposition depends upon the catalysts used and varies from 500- 700°C. The catalysts used are from nickel, iridium or ruthenium supported on silica, or both silica and aluminum [53]. The conversion degree of ammonia to hydrogen increases with temperature and the highest were obtained for ruthenium catalyst. At temperature T = 650°C ammonia is converted in 99% and 30.9 mol of hydrogen per minute per gram of catalyst was obtained. Other catalytic method of hydrogen production is hydrogen sulfide decomposition, reaction (18) - Startsev et al. [72,126]. The process occurs in quartz ampoules in the presence of 0.5% Pt/SiO<sub>2</sub> catalyst with stainless steel chips supported on aluminum oxides or special material SIBUNIT.

The enthalpy of the decomposition was  $\Delta H = 84.726 \text{ kJ/mole}$ .

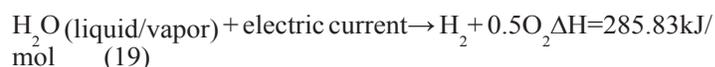


According to Startsev et al. [72] the process is designed for sulfur production, but in the process hydrogen is also produced. Heat decomposition of hydrogen sulfide occurs at 1000°C, and consumes more energy than catalytic decomposition [127]. It can be applied for decomposition of the hydrogen sulfides - co-product of Pyrolysis or gasification. In comparison biological conversion the process requires more energy.

### Water Splitting Methods

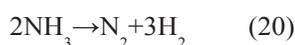
#### Electrolysis of Water and Ammonia

During water and ammonia electrolysis, hydrogen is collected at cathode and oxygen at anode region. The process proceeds under conditions T=25°C, P=1.5 - 3 MPa and is based on reaction (19):



The voltage required to split water at standard condition is 1.229 V [5]. There are several types of reactors (electrolyzers) which use different electrolyte: alkaline, solid polymer electrolyzers (SPE) or solid oxide electrolyzer (SOE). The alkaline electrolyzers apply sodium or potassium hydroxide electrolyte. Electrolyzer comprises anode, cathode, cell frame and separator. The cell frame is built from steel. The hydrogen is collected at the cathode (built from nickel, cobalt or steel) and oxygen at the anode (built from elements of 8<sup>th</sup> and of 10<sup>th</sup> group or their alloys). The separator from asbestos or polytetrafluoroethylene divides the electrolyzer into anode and cathode section. Hydrogen production rates range from 0.01 to 10 m<sup>3</sup>·h<sup>-1</sup> in small scale and from 10 to 100 m<sup>3</sup>·h<sup>-1</sup> in industrial scale. The important part of SPE is a Proton Exchange Membrane built from perfluorinated polymers membrane e.g. perfluorinated sulfonic acid, that due to side chain serves as

electrolyte and separator [8]. The membrane is coated with catalysts: Pt or noble metals alloys, serving as cathode. Anode is built from Ir, Rh, Pt or their alloys. There were attempts to introduce renewable energy sources like windmills or solar cell to feed the system although both sources are unstable [128,129]. Another option is geothermal energy that can be used in this case [129]. The SOE cells use solid ceramic electrolytes (yttrium stabilized zirconium). There are two compartments: cathode from Ni-ZrO<sub>2</sub> and Pt-ZrO<sub>2</sub> and anode from LaNiO<sub>3</sub>, LaMnO<sub>3</sub> or LaCoO<sub>3</sub> through which gaseous feed is passed. The operated temperature of SOE is around 1000°C. According to Estejab et al. [65,130] there is a possibility of ammonia splitting that needs much lower potential than water-splitting - see reaction (20).



The voltage required to split ammonia at standard conditions 0.06 V [130]. Therefore, ammonia electrolysis is much cheaper to run and can be more likely used than water electrolysis. The difficulties of electrolysis are high costs and materials as well as higher energy consumption than during dark fermentation.

### Hydrogen production by water splitting due to photo catalysts: photolysis and mechano-catalysis

Photolysis or photo electrolysis of water occurs in the presence of solar energy absorbed by semiconductors (photo catalysts) with covalent bond more negative than the H<sup>+</sup>/H<sub>2</sub> [131]. Photo catalysts suitable for photolysis are metal oxide like SrTiO<sub>3</sub> with band gap E<sub>g</sub> lower than 3.2eV, although optimal band gap for water-splitting semiconductor should be near 2eV [132]. The water for photolysis does not need, indeed should not be distilled [4]. The most commonly used photo catalyst is titanium oxide TiO<sub>2</sub> (anatase E<sub>g</sub>=3.1 eV). As per Augustyński et al. [132,133] and Ni et al. [134] the most suitable materials for photoanodes seems to be: tungsten oxide WO<sub>3</sub> (E<sub>g</sub>=2.5 eV), α - Fe<sub>2</sub>O<sub>3</sub> hematite (E<sub>g</sub>=2.0-2.2 eV), BiVO<sub>4</sub> (E<sub>g</sub>=2.4 eV), SiC (E<sub>g</sub>=3.2 eV), CdS (E<sub>g</sub>=2.4 eV) and TiSi<sub>2</sub> (E<sub>g</sub> differs from 1.5 to 3.4 eV). Sadandam et al. [80] used silver-load nano TiO<sub>2</sub>/graphene for decomposition of 5% glycerol. Iervolino et al. [89] recommended photo catalysts of rare earth elements like lanthanum perovskite nanoparticle (band gap E<sub>g</sub>=2.09) better stability and low toxicity (in the case of decomposition of glucose registered hydrogen yield was 7%). Parida et al. [135] in the case of water decomposition using lanthanum perovskite photo catalyst achieve an efficiency of 24.07%. Li et al. [136] designed 8 porous conjugated polymers for photo catalysis and obtained efficiency up to 1.2%. As the photolysis is a light dependent method it seems to be harder to stabilize than the process of dark fermentation or pyrolysis. The energy comes from a fully renewable source. However, the most efficient catalysts are based on expensive rare-earth elements, which will probably limit their use at an industrial scale. Mechanocatalytical water splitting (mechano-catalysis) is an

experimental method hydrogen generation that was discovered accidentally in 1998 by Ikeda et al. [137]. Published researches on the subject continued for about 5 years. Since 2004 and in reply to a comment [138] of Ross [139] there has not been any paper published on the subject. As mechano catalysts a group of metal oxide semiconductors with excess of p-type oxygen have been recorded [140]. They include binary oxides like NiO, Cu<sub>2</sub>O, Co<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, RuO<sub>2</sub>, IrO<sub>2</sub>, and some ternary oxides of Cu<sub>2</sub>, Co, Ni like Cu<sub>3</sub>AlO<sub>4</sub> or CuFe<sub>2</sub>O<sub>4</sub> [141]. The water-splitting occurs when catalysts in powder form were spilled into a vessel with distilled water and magnetic stirrer. Then, during stirring and due to friction, hydrogen and oxygen is generated [142]. The volume of generated hydrogen and oxygen from 200 ml after 20 hours was about 700 ml [137]. Temperature, shape of stirrer and material of the vessel influence the efficiency of the process. The vessels from quartz and Pyrex glass give the best results [141]. Light increased production rate up to 3 times in the case of Cu<sub>2</sub>O [142]. The highest efficiency 4.3% was obtained for the NiO catalyst [141]. Mechano-catalysis is a very complex process, scarcely known and possibly no further development can be expected due to low hydrogen yield in comparison to other methods [5].

### Magnetolysis

Magnetolysis is a special type of electrolysis where the electrolyzer uses magnetic induction to split water. The electrolyzer comprised a stainless-steel disk connected to a bearing with isolated shaft vertically in an electrolytical cell with 35% KOH. For production of 1 m<sup>3</sup> h<sup>-1</sup> of hydrogen magnetic field of 0.86 T, and frequency 2100 rpm, potential difference of 2 V is required [3,5]. The method is too expensive for the commercial generation of hydrogen and it has not been subject of published research since 1985 [14]. The method seems to be much more expensive than biological methods or photo catalysis.

### Radiolysis

Radiolysis is a water-splitting process by radiation from radioactive materials. Radiolysis can appear nuclear plants where water is used as a coolant. In nuclear plants the appearance of hydrogen with hydrogen peroxide and oxygen increases the risk of reactor-core corrosion. In the case of γ-radiation from <sup>60</sup>Co and deposited energy 100 eV, 1.5 mole of hydrogen was generated in the presence of zeolites. In the case of α-radiation for <sup>244</sup>Cm and deposited energy 100 eV, 8 mole of hydrogen were produced [5]. Frances et al. [15] developed a method of hydrogen releasing in the presence of γ-radiation from <sup>137</sup>Cs in the presence of zeolites 4A. Maximum hydrogen radiolysis yield was 4%. Development of this method into a commercial scale is troublesome due to higher risk of gas stream contamination with radioactive materials. This risk usually does not appear in the case of other methods like dark fermentation or photolysis.

## Hydrogen Production by Biological Methods

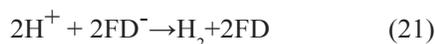
### Biophotolysis

Biophotolysis is a process of water decomposition by photoautotrophic organisms, like cyanobacteria and algae (like *Scenedesmus* [143]). Abilities to split water to hydrogen have been known from 1896 in the case of cyanobacteria and from 1942 in the case of algae [144]. More commercial researches of hydrogen generation by photoautotrophic organisms have been started from 1970s after the energy crisis [144]. Biophotolysis includes: direct, indirect and two -stage indirect processes. The efficiency of water splitting using biophotolysis is below 1.5%, however, it can be increased to the range from 3%-10% after oxygen removal (for process with cyanobacteria) [5]. In biophotolysis, organisms absorb light of the wavelength in the range of visible light between 380 and 750 nm. The photo heterotrophic organisms produce two enzymes; hydrogenase and nitrogenase (cyanobacteria), or only hydrogenase (algae) [5,145]. In biophotolysis, the enzymes are activated by ferredoxin [146]. Hydrogenase is enzymes active in the hydrogen production process. Hydrogenase can be of two kinds: reversible (classical) and membrane uptake. In the reversible type hydrogenase ferredoxin is oxidized in a reversible reaction. In membrane uptake, hydrogenase is used in organism to derive hydrogen as reductant (in small immeasurable portion). Hydrogenases are produced by bacteria active in both: the biophotolysis and dark fermentation (anaerobic) processes. Hydrogenase in algae can be classified by the metal composition of active part of enzyme: Fe- hydrogenase, Ni-Fe-hydrogenase, Fe-S-hydrogenase (in cyanobacteria). Fe-hydrogenase is a very active enzyme, allowing the production simultaneously of O<sub>2</sub> and H<sub>2</sub> in the ratio 1:2 [147]. Green algae convert 12%-15% of water to hydrogen [146]. Thus, from the volume of 10 l of green algae, 1-2 l of hydrogen per day can be obtained [148].

Ni-Fe-hydrogenase seems to be active during uptake hydrogenase but in the case of cyanobacteria this enzyme recovers also hydrogen from nitrogenase [148]. Ni- Fe-hydrogenase is usually undesirable and there are many efforts to inhibit its activity. Nitrogenase is used by cyanobacteria to convert nitrogen to ammonia; as a byproduct it produces also hydrogen [149]. The ratio of ammonia to hydrogen produced is 2:1 [145]. Nitrogenase contains two enzymes: dinitrogenase and nitrogenase reductant. The biophotolysis process takes place in thylakoid membrane in chloroplasts. Light is absorbed by two membranes-integrated protein complexes named also as photosystem I and II.

Hydrogen generation is sensitive to the presence of sulphur. Besides, in the case of cyanobacteria lower amounts of nitrogen allows for higher production of hydrogen [146]. Nitrogenase is divided into three types due to metal cofactor as Fe-nitrogenase, Mo-nitrogenase, and V- nitrogenase.

Androga et al. [150] and Tsygankov et al. [151] pointed out that influence of metal depends on the bacteria species and its location in active enzyme centers. Hallenbeck[30] has shown that in heterocystous cyanobacteria more hydrogen is generated by nitrogenase than by reversible hydrogenase. In the case of microalgae systems, the efficiency of biophotolysis improves depletion of sulphur. In direct biophotolysis there are no intermediates [5]. Photosystems absorb light; ejected electrons are transported linearly from water with potential 0.82 V to ferredoxin (FD) with potential (-0.44 V) - see reaction (21)



Reduced ferredoxin is the electron donor to hydrogenase that allows hydrogen to be generated [35,144,152]. According to Akkerman et al. [143] bioreactors with photoautotrophic organisms should operate under anaerobic and nitrogen-free conditions. Both enzymes hydrogenase and nitrogenase are sensitive to oxygen, but nitrogenase also to ammonia. Therefore, the first direct biophotolysis lasted only for 15 minutes [144]. Direct biophotolysis lasts much longer in anaerobic conditions, but a method of efficient removal of accumulated oxygen has not been yet found [144]. High sensitivity of the direct processes to oxygen makes the commercialization of the process difficult [153]. Other disadvantages of direct biophotolysis are large- impermeable photobioreactor and risk related to explosive oxygen/hydrogen mixtures [30]. Indirect biophotolysis, occurring in non-heterocystous cyanobacteria, is a process related to a series of reactions leading to water-splitting [154]. They could be stimulated by nitrogenase reversible hydrogenase, and uptake hydrogenase [5]. During the process a reduction of ATP to ADP reaction occurs -see eq. (22)



In the case of indirect biophotolysis, hydrogen generation processes do not occur simultaneously, and they are not sensitive to the presence of oxygen [143]. The general reaction (22) is the case where both enzymes take part - nitrogenase with Mo-Fe-hydrogenase [5,155]. According to Koku et al. [108,156] optimum temperature for *A. vinelandii* is 30°C in pH 7.1-7.3. One of the draw- backs to biophotolysis of cyanobacteria's nitrogenase is a possibility of activation of uptake hydrogenase enzymes [146]. Therefore, there are attempts to modify the recently considered most efficient cyanobacteria from filamentous heterocystous groups like mutants bred by Shestakov et al. [157]. In 1996 a pilot plant was built in Osaka that generated hydrogen based on microalgae and cyanobacteria producing 3.39 liters of hydrogen per day with a culture volume of 150 [158]. The efficiency of hydrogen generation in biophotolysis is high, but unstable due to dependence on the sun. It cannot be used for production of hydrogen 24 h/day. The other difficulty of green microalgae is that different organism types, including multicellular and cell organisms,

can have different ageing characteristics, causing unstable hydrogen production. The method is more unstable than photo fermentation, fermentation or photolysis.

### Photo fermentation

Photo fermentation is a special type of fermentation occurring in presence of visible light. The visible-light is 45%, quite a high proportion of all radiation emitted by the Sun. The photo heterotrophic bacteria used for the process are also called purple non-sulphur (PNS) bacteria like *Rhodospillum rubrum* that decompose organic acids into hydrogen [159]. Liu et al. [74] reported on photo fermentation of carbohydrates like sucrose or glucose by bacteria *Rhodospillum* and *Rhodobacter*. Photoheterotrophic organism's use as a source of energy light and organic carbon. Hydrogen is a byproduct of ATP generation with oxidation of carbon monoxide. Photo heterotrophic organisms like cyanobacteria generate hydrogen using both hydrogenizes and nitrogenase and the same reaction pathways as in cyanobacteria [145]. However, nitrogenase enzyme is decomposed by oxygen and inhibited in the case of ammonium (higher than 20 mmole/l), ammonium salts and nitrogen excess [74,160]. Therefore, in the case lactate/glutamate mixture as substrates, excess of ammonium can be avoided, when lactate is consumed after glutamate. For *Rhodobacter spareoides* nitrogenase can occur in the presence of Molybdenum while in case of *Rhodobacter (R.) capsulatus* absence of the metal is tolerated [159,161].

Nitrogenase of PNS differs from cyanobacteria. In some of PNS bacteria besides Mo-nitrogenase occur also V-nitrogenase and Fe-nitrogenase [146]. V-nitrogenase allows the production of 3 times more 598 hydrogens than Mo-nitrogenase, while Fe-nitrogenase generates 9 times more hydrogen than Mo-nitrogenase [148,162,163]. Hydrogen produced by nitrogenase is partially lost back to bacteria when uptake hup hydrogenase enzymes are activated [82]. To avoid the activation of uptake hydrogenase Kars et al. [82], Öztürk et al. [75], and Ooshima et al. [164] genetically modified *Rhodobacter* removing genes or operons responsible for producing hup- hydrogenase enzyme. Ooshima et al. [164] improved hydrogen yield from malate up to 43%, at temperature T=33°C, by modification of the *R. capsulatus* B100 to *R. capsulatus* ST410. Kars et al. [82] modified long hup gene of *Rhodobacter sphaeroides* O.U.001 improving the hydrogen yield from maleic and glutamic acids to 20%. Hydrogenase can be inhibited in *Rhodobacter rubrum* by the presence of carbon monoxide [16

Other inhibitors of hydrogenase are EDTA and oxygen [82]. Optimum conditions of hydrogenase depend also on the species: temperature T=55°C for *R. rubrum* or T=70°C for *R. sulfidophilus*, pH6.5 - 7.5. Optimum carbon source for photo fermentation depends upon bacteria species. Most of bacteria prefer lactate (*Rhodobacter* 8604, *Rhodobacter capsulatus*,

*R. spareoides*), butyrate (*R. spareoides* RV), pyruvate (*Rhodobacter capsulatus* Z1), malate (*R. sphaeroides* O.U. 001) and acetate (*Rhodobacter monas*) [82]. Conversion of substrate in the case of *R. spareoides* RV was up to 80% for lactate [168-170]. According to Montiel-Corona et al. [169,171,172] short-chained hydrogen is preferred in feed mixture, but this statement does not work under conditions of Thales et al. [81] experiments. The differences of these two experiments can be explained by substitution of lactose with glucose but also due to different illumination conditions.

The process can be improved by mixing photo heterotrophic with another bacteria group, for example acrogenic *Lactobacteria delbrueckii* [173] or with anaerobic fermentative bacteria like *Clostridium butyricum* [174,175], *Clostridium pasteurianum* [149,163] and *Enterobacter aerogenes* [175]. Yokoi et al. [87] improve yield of mixed *Rhodobacter sp.*M-19 (initially 3.6 moles of hydrogen) and *Clostridium butyricum* (initially 1.9 moles of hydrogen) to 6.6 mole of hydrogen from 1 mole of glucose. Yokoi et al. [175] have mixed cultures of *Clostridium butyricum*, *Enterobacter aerogenes*, *Rhodobacter sp.* M-19 and obtained yield 7.1 mole of hydrogen from 1mole of glucose. The photo fermentation is determined by the Sun's operation and light conversion; 1-5% is not very high. In the case of hybrid process: a continuous dark fermentation and repeated batch photo fermentation process, hydrogen yield was 7.2 mole of hydrogen per mole of glucose [87]. The optimum pH ~ 7.5 for photo fermentation is higher than for dark fermentation. Another disadvantage of photo fermentation is lower efficiency than for dark fermentation. However, Provost [176] reported theoretical yield for glycerol photo fermentation equal to 75%. There are attempts to build a hybrid system of biophotolysis, dark fermentation and photo fermentation or two of these processes. Such combination can lead to generation of 12 mole of hydrogen per mole of hexose [146]. Melis and Melnicki [149] proposed a hybrid composed of three- stages:

- Biophotolysis performed by green algae *Chlamydomonas reinhardtii*;
- Photo fermentation with *Rhodospirillum rubrum* application and
- Dark fermentation producing, besides hydrogen, lower organic acids for photo bacteria and carbon dioxide for green algae's [146,149].

### Biocatalyst electrolysis

Biocatalyst electrolysis, also called Microbial Electrolysis Cell (MEC) uses microorganisms to activate reactions on electrodes [177]. MEC system is often built from several polycarbonate plates [178]. Bacteria like *Geobacter*, *Shewanella* or *Pseudomonas* are growing on the surface of anode [178]. Bacteria decompose complex organic matter into carbon

dioxide, protons and electrons. Voltage needed to decompose water in MEC electrolysis is 1.2 V [179]. The hydrogen production rate was 0.2 - 3 m<sup>3</sup> of hydrogen per 1m<sup>3</sup> of water per day [178]. According to Hatzell et al. [180] the potential produced by bacteria is too low for water-splitting and needs to be reinforced by an external energy source to generate hydrogen. According to Logan et al. [181] potential 0.3 V produced by bacteria should be increased to 1.23 V for water-splitting. To solve this problem MREC (Microbial Reverse-Electro Dialysis Cells) system was designed.

### Dark fermentation

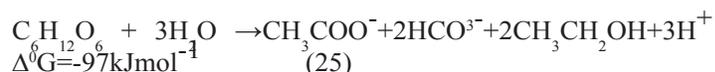
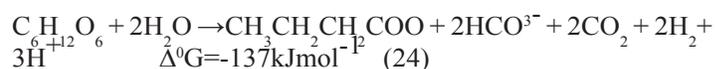
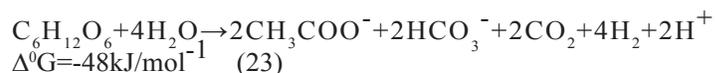
Dark fermentation is an anaerobic process, in which organic material; usually carbohydrates like glucose are decomposed by bacteria to carbon dioxide, hydrogen and low weight organic acid. Hexoses or pentoses originate usually from hydrolysis of higher carbohydrates like hemicelluloses, cellulose, starch or molasses [30].

The organic material is a potential source of hydrogen via dark fermentation if it can be transformed into pyruvate. According to Hallenbeck [4] and Gottshalk [182] dark fermentation can be a one-stage process if the substrates are simple carbohydrates or glycerol [183]. Hallenbeck [4] and Gomez et al. [177] state that the theoretical maximum yield of hydrogen from glucose (and other hexoses) in dark fermentation is 33%. Similar theoretical efficiency (32%) occurs in the case dark fermentation of pentoses [184]. In the case of glycerol, theoretical maximal hydrogen yield was 38% [176,185]. Efficiency of dark fermentation is influenced by such parameters as: temperature, partial pressure, metal ions or pH [186,187]. The importance of particular factors depends on the reactor type and feed. The general aim of optimization of dark fermentation is to obtain the highest efficiency of Fe-hydrogenase and usually inhibiting Ni Fe-hydrogenase as well as avoiding conditions suitable for methane production. Bacteria producing hydrogen are from a group of endospore-forming rods Bacillaceae (genuses *Clostridium*, *Bacillus*), Gram positive cocci (Micrococcaceae, Peptococcaceae), Gram positive asporogenous rod-shaped bacteria (Lactobacillae), Gram negative facultatively anaerobic rods (*Enterobacteria*, Vibrionaceae) and cocci (Veillonellaceae) [1]. Unfortunately, the majority of these bacteria produce hydrogen in amounts considered unsuitable for use in full-scale plants. Hydrogen is produced most efficiently by species of *Clostridium*, *Bacillus*, *Enterobacter* and some thermophilic bacteria like *Thermocellum* and *Thermatoga*. Clostridia belong to strict anaerobic bacteria, most important bacteria in mixtures producing hydrogen most efficiently. Despite the high yield of hydrogen production clostridium are very sensitive to oxygen and to improper form of substrate [56]. Some clostridium like *Clostridium* sp. strain No.2 is able to convert glucose and xylose with similar efficiencies [29]. There are attempts of reducing

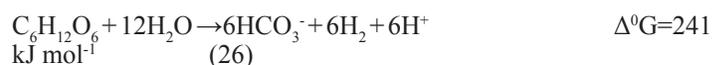
oxygen sensitivity by using in mixture with another less air sensitive group of bacteria called also facultative one such as *Enterobacter aerogenes*. Groups of bacteria can be classified taking into account the optimal temperature of culture growth such as: extrathermophilic, thermophilic, mesophilic and psychrophilic.

The thermophilic bacteria produce hydrogen in the range from 45 to 90°C with optimum 55 to 60°C. The mesophilic bacteria work in temperature from 25 to 45°C with optimum range 33 to 37°C. The psychrophilic bacteria sustain in low temperatures from 5 to 25°C with optimum between 20 and 25°C. Productivity of hydrogen by psychrophilic bacteria is much less than the others; therefore, dark fermentation using this type of bacteria is investigated quite seldom. The psychrophilic bacteria can lead to efficient hydrogen production only in high mountainous and high latitude regions [188]. The hydrogen production occurs when bacteria are stressed by the influence of heat (heat-shock, freezing, sterilization), electric shock, chemicals (acid/base, chemical agent like chloroform) and centrifuging [142,143]. The stress conditions cause spore-forming that is quite an 'expensive' process - consuming a lot of the organic matter. Therefore, when risk passes away the bacteria needs to regain organic matter to the cell.

Therefore, the bacteria decrease to the minimum removal of carbon and thus mainly hydrogen is removed from cells. The necessity of carbon saving causes blocking of hydrogenase uptake that allows for methane formation [189,190]. According to Bartacek et al. [56] and Woodward et al. [191] there are three thermodynamically possible dark fermentation pathways from hexose: acetate equation (23), butyrate equation (24) and acetate- ethanol equation (25). The acetate pathway is the one with the highest theoretical hydrogen yield of 4 hydrogen moles/mole of hexose - reaction (23):



Other possible theoretical method of obtaining from 1 mole of glucose 12 moles of hydrogen -see eq. (26), is impossible due to positive standard Gibbs free energy.



So, the most efficient is the acetate way (23) but the most often occurring is the butyrate fermentation (24). Preparation of suitable mixtures for hydrogen production including raw materials like lignocelluloses residues [192,193], cellulose

[194], livestock [96] and food wastes [94,195] is not always easy.

## Conclusions

Conventional raw materials for hydrogen production will be exhausted (oil before year 2090, gas 2120 and coal 2300). So, there is a need to replace them by renewable energy sources [196]. Existing and potential hydrogen sources preferably comprise an even number of hydrogen atoms. The feed compound being a direct source of hydrogen (short-chained organic compound  $C \leq 6$ ) has a ratio of oxygen to carbon: C equal 1. Indirect source of hydrogen should be pretreated to form one or a mixture of direct sources of hydrogen. There are several methods of hydrogen production; but further development of sustainable methods is required to replace conventional ones. The biomass gasification, biomass Pyrolysis, photo fermentation and dark fermentation can be applied for hydrogen production from various biomass sources. The most common direct hydrogen source is water but due to higher energy consumption its decomposition is usually more expensive than process of biomass decomposition using various biological methods. The ammonium electrolysis requires smaller voltage than water electrolysis and can be used also in water treatment system. The most stable and the simplest design for a biological method of hydrogen production due to numbers of variation is dark fermentation. The most stable and the simplest design for a biological method of hydrogen productions dark fermentation. The optimal system for hydrogen production will be a combination of several methods which enables the highest possible volume of hydrogen to be produced for a given unit of biomass. There are some combinations of biophotolysis, dark fermentation and photo fermentation already investigated and reported. The biomass conversion helps in the waste management process and provides hydrogen to industrial chain [197]. There is no industrial method of production of biohydrogen, due to lack of find of stabilized way of obtaining of the element.

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