

THE RESOURCES AND METHODS OF HYDROGEN PRODUCTION

Olga BIČÁKOVÁ* and Pavel STRAKA

*Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, v.v.i.,
V Holešovičkách 41, 182 09 Prague, Czech Republic
Corresponding author's e-mail: bicakova@irms.cas.cz

(Received January 2010, accepted March 2010)

ABSTRACT

In the near future, hydrogen will become an important fuel which may be able to resolve local problems connected with air quality. Hydrogen-propelled transport means are being developed and are already used in the automobile industry. Since the combustion of hydrogen does not produce any emissions of carbon oxides but only water, hydrogen is considered as a key fuel of the future. Hydrogen is abundantly present all over space and can be obtained from a number of resources, be they renewable or non-renewable. 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. Plasma cracking is still in the developmental stage.

The preferred method of hydrogen production on an industrial scale is steam reforming of natural gas for its low operational and production costs. When the operational costs of steam reforming and partial oxidation are compared, partial oxidation seems to be a more acceptable process, but the subsequent shift makes this process more expensive.

Pyrolysis processes have acceptable investment costs and besides the production of hydrogen also satisfactory yields of oils. Two-stage co-pyrolysis is suitable considering its acquisition of a high amount of hydrogen from mixed charges. It is apparent that the co-pyrolysis of organic materials with coals is a process for hydrogen production capable of competing. It can therefore play a significant role in the future.

KEYWORDS: conventional methods, hydrogen, pyrolysis, co-pyrolysis, thermochemical cycles, electrolysis

1. INTRODUCTION

Hydrogen is currently used primarily in the production of ammonia and methanol as well as for the purposes of the refining industry. It is, however, utilized also in the metallurgical, electronic, pharmaceutical and food industries. Nevertheless, in the near future, hydrogen will become also an important fuel which may help resolve local problems with air quality. In the automobile industry, cars are already being developed using it as the carrier of the energy necessary for propulsion. The annual production of hydrogen is now approximately 55 million tons, whereas the usage increases by about 6 % every year, and its growth may be even 10 %. Global production is dominated by hydrogen production from fossil fuels, but methods of its production from renewable resources – from water and biomass – are being intensively studied. The production of hydrogen is a subject of the interest of many global industrial companies. More than thirty countries have already initiated the research and development of hydrogen technologies and a number of companies have established hydrogen divisions.

Hydrogen is even considered as a key fuel of the future, because its combustion does not produce any

emissions of carbon oxides but only water, with the reaction with oxygen being extremely fast. It is significant that hydrogen is widely spread and can be obtained from a number of diverse resources. It always appears, however, in combination with other elements, and therefore a viable way to its production is the cracking of raw materials. A common example of an element combination is water. Its electrolysis is a simple way to hydrogen production that is, however, very demanding in terms of energy, which leads to high production costs and a high price. A feasible production in this way is tied to the cheap production of electricity from solar, wind and water resources or from nuclear facilities. It is clear from this example that it is necessary to find promising technologies and resources and assess the effectiveness of the production methods along with their impact on the environment. For example, the photolytic process, in which sunlight and microorganisms are used to crack water, is very environmentally friendly, but it is not very effective and cannot continuously provide hydrogen for industrial use.

It may be practical to divide the effective technologies of hydrogen production into:

- contemporary, utilizing fossil fuels;

- promising in the near future, utilizing the joint thermal treatment of fossil fuels and selected waste organic mixtures such as waste rubber and polymers;
- promising in the long term, utilizing biomass and water.

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. In terms of energy, these productions proceed from the equivalent that one kilogram of hydrogen is the equivalent in terms of energy of 3.79 liters of gasoline (Holladay et al., 2009). The hydrogen from these processes serves as the carrier of energy, e.g. in fuel cells.

2. CONVENTIONAL METHODS OF HYDROGEN PRODUCTION

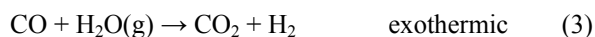
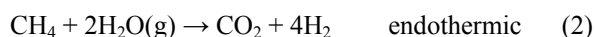
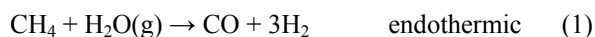
The technologies of the treatment of fuels transform raw materials like gasoline, hydrocarbons, ammonia, methanol or ethanol into gaseous substances rich in hydrogen. Most hydrocarbon fuels contain a certain amount of sulfur, whose removal is a significant task in the planning of the hydrogen economy. The thermochemical processes are important (www.hytep.cz, 2009). They are characterized by the fact that during them the temperature exceeds the limits of the stability of the given substance under the given conditions and is in the range of approximately 200 °C to 3000 °C. In terms of the character of the chemical reaction, the thermochemical processes can be divided into oxidation and reduction processes. In the oxidation processes, the amount of the oxidizer in the reaction zone is higher or equal to stoichiometric combustion, whereas in reduction processes the amount of oxidizer is substoichiometric or even zero (gasification, pyrolysis). Hydrogen can be produced only by processes of the second group.

Hydrogen can be acquired from hydrocarbon fuels through three basic techniques: steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR). These methods produce a great deal of carbon monoxide. The subsequent step therefore uses one or more reactors for the water-gas shift (WGS) reaction (see below).

Steam Reforming

Steam reforming is currently one of the most widespread and at the same time least expensive processes of hydrogen production, through which more than 90 % of the hydrogen used is produced (Palmová and Schöngut, 2004). Its advantage comes from the high efficiency of its operation and low operational and production costs. The most frequently used raw materials are natural gas and lighter hydrocarbons. The process requires an external source of heat, which is added into the process by the direct

combustion of part of the natural gas. The process has two stages. In the first stage, hydrocarbon raw material is fed into steam (500–900 °C, 0.3–2.5 MPa) in a tube reactor filled with a catalyst on the basis of nickel oxide (or Ni + MgO, Pt, Rh) (Wang et al., 2004; Song et al., 2007). The catalytic process requires a desulfurized initial raw material. During its reaction, syngas (H₂ + CO) is produced along with a lower proportion of CO₂ (reactions 1, 2). The reaction is endothermic. The necessary temperature is achieved by the addition of oxygen or air for the combustion of a part of the raw material (heating gas) inside the reactor. The reaction products are led through the boiler for the production of steam and through the condenser, where they are cooled to approximately 360 °C. In the second stage, the cooled gas is led into the converters, where carbon monoxide is converted by means of steam into carbon dioxide (3).



The nascent carbonic gas is removed by a reversible exothermic reaction (4) usually implemented in two stages. In the first, so-called high-temperature stage, the temperature of the products is raised to almost 500 °C, which has the result of lowering the balanced yield of CO₂ and H₂. The products are then cooled to approximately 360 °C and are led to the low-temperature converter filled with a highly active copper catalyst (the second stage), where the concentration of CO is lowered to 0.2–0.3 vol. % at low temperatures of 180–230 °C (Holladay et al., 2009). The gaseous products exiting the low-temperature converter are further cooled and led to the absorber with ethanalamines, in which the CO₂ is washed.

An important factor characterizing steam reforming is the H:C proportion in the initial raw material. The higher is this proportion, the lower the production of carbon dioxide emissions. Hydrogen is produced on an industrial scale by the steam reforming of methane, during which the heat efficiency of the process is around 85 % (Holladay et al., 2009). A number of other raw materials will be possible to process in this way in the near future: solid communal waste, wastes from the food industry, oils, purposefully cultivated or waste agricultural biomass and fuels of a fossil origin, e.g. coals. The disadvantage is the high production of CO₂, around 7.05 kg per 1 kg of hydrogen produced (www.svazarm.cz, 2009).

Table 1 The composition of the syngases by the method of the transformation of natural gas (%).

Element	Steam reforming* + autothermal cracking by		Autothermal cracking by steam and		Partial oxidation by steam and oxygen
	oxygen	air	oxygen	air	
H ₂	66–68	56–57	68	53	60
CO	22–24	10–15	20	15	35
CO ₂	8–9	7–12	10	10	3
N ₂	0.5–1	22–23	0.2	22	1.5
CH ₄	0.5	0.2–0.3	0.4	0.3	0.3

* a two-stage process

Partial Oxidation

Another relatively widespread process of the production of hydrogen and syngases is partial oxidation and the catalytic partial oxidation of hydrocarbons. The gasified raw materials can be methane, biogas but primarily heavy oil fractions (vacuum remnants, mazut), whose further treatment and utilization are difficult (Holmen, 2009). Partial oxidation is a non-catalytic process, in which the raw material is gasified in the presence of oxygen (5, 6) and possibly steam (7) (autothermal reforming) at temperatures of 1300–1500 °C and pressures of 3–8 MPa. In comparison with steam reforming (H₂:CO = 3:1), more CO (H₂:CO = 1:1, 2:1) is created. The process is therefore complemented by a steam conversion of the carbon monoxide into hydrogen and carbon dioxide. This reaction contributes to the maintenance of the equilibrium between the individual reaction products.



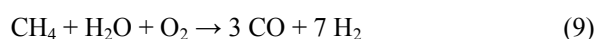
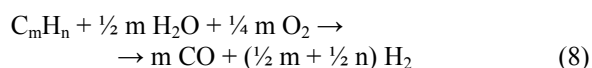
The gaseous mixture created through partial oxidation contains CO, CO₂, H₂O, H₂, CH₄ and hydrogen sulfide (H₂S) and carbon oxysulfide (COS). A part of the gas is burned to provide enough heat for the endothermic processes. The soot created by the decomposition of acetylene as a transitional product is an undesired product. Its amount depends on the proportion of H:C in the initial raw material. There has therefore been, like with steam reforming, an endeavor to shift to raw materials with a higher ratio of H:C, e.g. to natural gas. While the operation of the reactor is less expensive in comparison with steam reforming, the subsequent conversion makes this technology more expensive (Palmová and Schöngut, 2004). The efficiency of this process is 60–75 % (Holladay et al., 2009). Since the process does not require the use of a catalyst, it is not necessary to remove sulfurous elements from natural gas, which would lower the efficiency of the catalyst. The sulfurous compounds contained in the gasified raw

material are converted into hydrogen sulfide (ca 95 %) and carbon oxysulfide (ca 5 %).

However, partial oxidation conducted at lower working temperatures of 700–1000 °C and pressures in the range of 6–8 MPa works in the presence of catalysts. The typical catalysts for the partial oxidation of natural gas are catalysts based on nickel or rhodium.

Autothermal Reforming

As has already been mentioned, if steam is added to the gasified raw material and an oxidant (O₂), it is an autothermal reforming. Autothermal cracking utilizes mixtures of air or oxygen and steam in suitable proportion according to the further application of syngas, e.g. for Fischer-Tropsch synthesis. The heat necessary for the production of steam for the cracking reactions in the catalytic zone is supplied by partial oxidation, i.e. combustion of a part of natural gas or other raw material treated (Holladay et al., 2009). Nickel-based catalysts are used to lower the energy demands of the process. The heat from POX reduces the need for an external heat source, which simplifies the given system and shortens the heating rise time. The autothermal reforming of methane (8, 9) has a heating efficiency comparable to partial oxidation, i.e. 60–75 %, and slightly lower than steam reforming (Holladay et al., 2009).



It is evident from Table I how the selection of the way of transforming the natural gas can influence the composition of the syngas created (Beneš et al., 1997).

Water-Gas Shift

Syngas can be further modified according to other requirements, e.g. through the conversion of CO + H₂O to CO₂ and H₂ or through the addition of gas of another composition to increase the content of a desired gaseous component or through the complete removal of carbon monoxide.

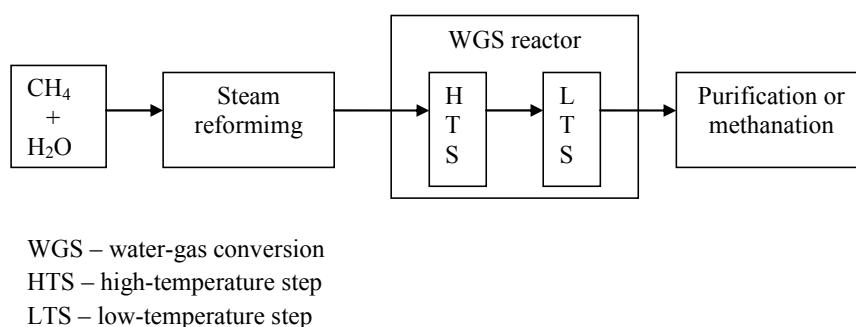
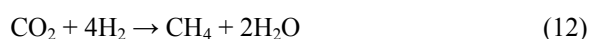


Fig. 1 A diagram of steam reforming with the subsequent conversion.

Water-gas shift serves for the transformation of carbon monoxide to carbon dioxide and hydrogen by means of a reaction with steam at temperatures of 400–500 °C in the presence of catalysts of chrome oxide and iron oxide (Cr_2O_3 , Fe_2O_3) (10). This leads to a drop in the concentration of CO down to 0.5–1 mol. %.



The reaction has an exothermic course, which means that the reaction equilibrium will be shifted to the right and will support the formation of hydrogen and carbon dioxide at lower temperatures. In terms of kinetics, a higher temperature is preferred. For this reason, it is common to use two successive steps, first a high-temperature and then a low-temperature step. The conversion in the high-temperature reactor takes place at temperatures of 350–370 °C and is limited by the balanced composition at those temperatures. Here an almost 90 % conversion of carbon monoxide occurs. A higher level of the conversion of carbon monoxide to hydrogen by steam is achieved when the gas exiting the high-temperature reactor is cooled to 200–220 °C and fed into the low-temperature reactor. The remaining amount of carbon monoxide can be removed in the third step, including catalytic methanation or purification. The methanation reactor transforms the residual carbon monoxide (11) or carbon dioxide (12) into methane, thus lowering its concentration down to the desired 10 ppm, but at the cost of higher hydrogen demand, which leads to a lower overall yield (Holladay et al., 2009).



On the other hand, at higher temperatures the equilibrium shifts to the left and is limited by the complete transformation of carbon monoxide to hydrogen (13).



The water–gas shift reaction is the basis of the global industrial production of hydrogen from natural

gas by steam reforming. In terms of technical issues, the process is operated similarly to the reforming of methane or biogas in three steps (Fig. 1) (Holladay et al., 2009; Amos, 2004). In the first step, methane is exposed to steam reforming at temperatures of 700–800 °C in the presence of a nickel catalyst into a gas mixture containing carbon oxides and hydrogen in the presence of steam (Holladay et al., 2009; Amos, 2004).

All three processes can take place simultaneously in one reactor and the final composition of the products depends on the type of catalyst used. The most common catalysts (www.svazarm.cz, 2009) for steam reforming are Co/ZnO, ZnO and Rh/Al₂O₃. The most utilized catalysts for WGS are copper-based catalysts (for a low-temperature reactor), although currently even molybdenum carbide (MoC_2) catalysts are used. For a high-temperature reactor (Holladay et al., 2009), they are catalysts based on Fe-Pd alloys. Other suitable catalysts for WGS are Ru/ZrO₂ and Pt/CeO₂ catalysts, or Cu/ZnO and Fe/Cr₂O₃ catalysts, more suitable in terms of price. Any catalytic process requires desulfurized raw material for its course. Considering the initial raw materials used and the character of the process, the most frequent polluting substances are CO, CO₂, N₂, NH₃, H₂S and COS. The main emphasis is placed on the removal of catalytic poisons, i.e. of carbon monoxide and sulfur compounds. Technologies dealing with their removal are quite widespread in the industry. At the same time, hydrogen is purified by also alternative approaches, namely pressure-swing adsorption, cryogenic distillation and membrane technologies, which can ensure the necessary purity of hydrogen, 98–99 %. The most advantageous gas-purification method is the pressure-swing adsorption for its high efficiency (> 99.99 %) and flexibility.

3. PYROLYSIS AND CO-PYROLYSIS

Another currently promising method of hydrogen production is pyrolysis, or co-pyrolysis. Raw (organic) material is heated and degasified *in vacuo* at a pressure of 0.1–0.5 MPa to a temperature

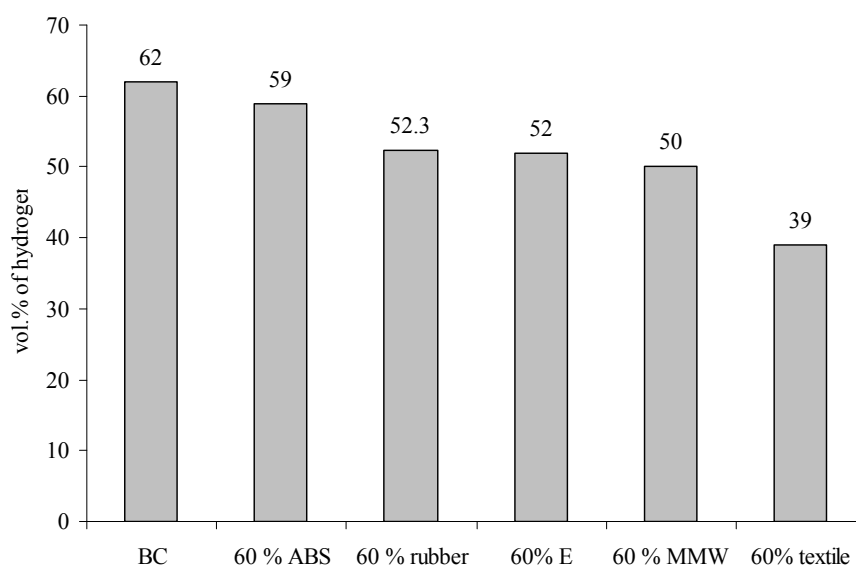
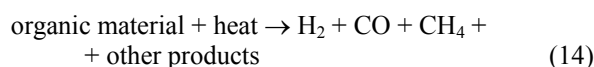


Fig. 2 The dependence of the hydrogen content on the type of additive in one-stage co-pyrolysis with bituminous coal; BC – bituminous coal, for other symbols see the text

of 500–900 °C (Ni *et al.*, 2006). The process takes place in the absence of oxygen as well as air, and therefore the formation of dioxins can be almost ruled out. Carbon oxides (CO, CO₂) are formed in a minority, which leads to the exclusion of the use of secondary reactors (WGS, POX etc.) (Holladay *et al.*, 2009). As a result, this process offers a significant lowering of emissions. The presence of air (for instance if the initial raw materials have not undergone preliminary drying) results in the creation of CO and CO₂ emissions. The advantages of this process lie in the adaptability of the fuel and its relative simplicity. The by-product is pure carbon. The reaction can be generally described by the following equation (14) (Ni *et al.*, 2006).



Based on the temperature range, we can divide the pyrolysis processes into low-temperature (up to 500 °C), medium-temperature (500–800 °C) and high-temperature (over 800 °C). Pyrolysis can be slow or fast, but slow pyrolysis is not intended for hydrogen production. Fast pyrolysis is one of the latest processes for the transformation of organic material into products with a higher energetic content. It is a high-temperature process in which the initial organic material is intensely heated to a temperature of 450–550 °C with a short dwell time in the reaction zone (max. of 2 s). The heating can be ensured in various ways, e.g. the recirculation of hot sand or gases, additional combustion or hot walls. The created gaseous and liquid products are cooled as quickly as possible. The products of fast pyrolysis appear in all

of the phases, i.e. solid, liquid and gaseous (Ni *et al.*, 2006):

- liquid products include tars and oils in liquid form at room temperature;
- solid products include coke, almost pure carbon and inert materials;
- gas products contain these elements: hydrogen, methane, carbon monoxide and carbon dioxide and other gas substances, which depend on the character of the organic material used.

The application of the co-pyrolysis of a mixture of coal with organic wastes has recently come to the fore of interest in industrially advanced countries, as it should limit and lighten the burden of wastes in waste disposal (Bičáková, 2001). The wastes include for instance plastics, rubber, cellulose, paper, textiles and wood. At the beginning of the development of the co-pyrolysis process, the aim of the addition of organic additives (tar, lignite pitch, petroleum distillation residues) was the improvement of thermochemical and thermomechanical properties of blast-furnace coke. With this in mind, organic wastes in pre-modified granulated form were added in the coking chambers for example in Poland (Žmuda and Minkina, 1999). Their co-pyrolysis with coal (coals/organic wastes) is a more effective way of using organic waste materials for products with higher utility value Straka *et al.*, 2004; Straka and Náhunková, 2004). The coal has a clear-cut function as a hydrogen donor, through which it becomes a relatively inexpensive hydrogenation reagent of waste materials.

The potential of high-temperature co-pyrolysis of waste materials (polymers – acrylonitril butadiene

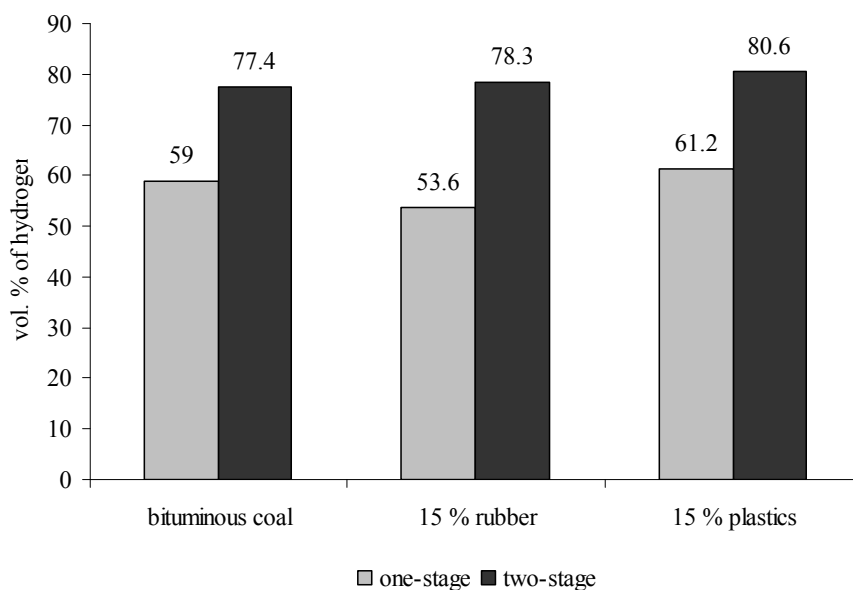


Fig. 3 The dependence of the hydrogen content on the type of the additive from one-stage and two-stage co-pyrolyses with bituminous coal.

styrene /ABS/, epoxide /E/, rubber, textile, sawdust, mixed municipal waste /MMW/, straw) with bituminous coal or lignite has been devoted extensive studies (Bičáková, 2001; Kříž and Brožová, 2007; Kříž et al., 2008; Kříž et al., 2008; Straka and Kříž, 2008; Kříž and Brožová, 2007). The experiments were conducted in the laboratory model pyrolysis unit HOR 2 with a stationary bed and in an inclined rotary kiln installed at the IRSM of the ASCR, v.v.i. The proportion of the additive in the charge of bituminous coal or lignite was 15, 30 and 60 wt. %. The charge was heated in the reactor to the temperature of 900 °C (5 °C/min., a dwell time of 30 min at 900 °C). A one-stage pyrolysis of pure coal without an additive yielded gas containing 57–62 vol. % and 50 vol. % of hydrogen from pyrolysis of bituminous coal or lignite. The increasing addition of additive (up to 60 wt. %) caused a decrease in the hydrogen content in the pyrolysis gas (Figure 2) (Bičáková, 2001; Kříž and Brožová, 2007; Kříž, 2007).

The degree of the decrease of hydrogen depends on the type of waste material used. It was determined that the amount of rubber and mixed plastics during co-pyrolysis with coal significantly redistributed hydrogen into liquid products, whereas during co-pyrolysis with a textile hydrogen was mainly distributed into the pyrogenic water (Bičáková, 2001; Kříž and Brožová, 2007).

The continuous pyrolysis of an admixture of lignite with 30 wt. % additive (rubber, ABS, cellulose) in a rotary kiln at 900 °C is a two-product technology. We obtain pyrolysis gas and a solid product (carbonaceous residue) (Kříž et al., 2008). The gas from pyrolysis of lignite alone contained 41.5 vol. % of hydrogen, whereas the addition of

30 wt. % of the additives caused a decrease in the hydrogen content to 34.5–38.9 vol. % depending on the additive used. Although the additives contain a significantly greater amount of hydrogen ($H^{\text{daf}} = 7.9$ and 8.0 % for ABS and rubber) than the coal combustible matter ($H^{\text{daf}} = 4.8$ %), the hydrogen content was reduced in the pyrolysis gas as a result of its redistribution into methane. This was caused by the temperature being too low (900 °C) for all the hydrocarbons present in the steam–gas mixture to be perfectly decomposed into hydrogen and pyrolytic carbon. The higher amount of methane however has a positive influence on the gross calorific value of the gas (ca 17 MJ/m³), through which we obtain energetically well-utilizable gas (Kříž et al., 2008).

Besides the classic one-stage co-pyrolysis, the two-stage co-pyrolysis of coal with organic materials was examined for the purpose of acquiring gas with high hydrogen content. The pyrolysis unit was expanded by a degradation module (Kříž and Brožová, 2007; Kříž et al., 2008; Straka and Kříž, 2008) of liquid and gaseous products coming from the stationary reactor, which runs at 1200 °C. The liquid products from the first stage are quantitatively cracked in the degradation module and transformed into gaseous components. It was determined that raising the temperature in the degradation module from 1000 °C to 1200 °C increased the concentration of hydrogen in the gas from 59.3 vol. % (one-stage pyrolysis of bituminous coal) to 64–77.4 vol. % of hydrogen (Kříž et al., 2008). A further step lies in the use of organic materials, e.g. rubber and mixed plastics, by means of the two-stage co-pyrolysis (Fig. 3; Kříž et al., 2008; Straka and Kříž, 2008; Kříž and Brožová, 2007; Kříž, 2007).

Table 2 The effectiveness of plasma technologies.

Technology	Fuel	Conditions		Products (vol.%, dry)				Temperature	η^*
		Chem. reaction	Proportion of air	H ₂	CO	CO ₂	CH ₄	K	%
Non-thermal GAP	naphtha	ATR	0.4	23	17	6.2	1.2	1000–1300	85
Dielectric discharge	isooctane	ATR	0.28	46	16	16	-	900–1100	55
Thermal GAP	isooctane	POX	0.25	22	15	2	3	1200	9
Thermal GAP	naphtha	POX	0.25	23.5	23	0.1	0.03	1200	9
Microwaves	hexane	SR	-	66	25	-	-	?	?

* - efficiency

An increase in the yields of gaseous products in hydrogen production is reached at high temperatures with high heating speeds and longer dwell times at the volatile phase (Holladay et al., 2009). These parameters can be influenced by a suitable selection of reactor type and regime of temperature transfer. Some inorganic salts like chlorides, carbonates and chromates have a favorable influence on the speed of the pyrolysis reaction (Holladay et al., 2009). The influence was tested of also other types of catalysts: Ni-based catalysts, zeolites, K₂CO₃, Na₂CO₃ and CaCO₃ as well as various metal oxides (Al₂O₃, SiO₂, ZrO₂, TiO₂ and Cr₂O₃) (Ni et al., 2006). The most efficient of the carbonate-based catalysts is Na₂CO₃. Catalysts of the rare metals ruthenium and rhodium are much more efficient than nickel-based ones and are less sensitive to the formation of carbon. However, they are not commonly used because of their high prices.

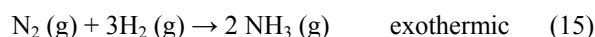
For the production of hydrogen by means of pyrolysis, a wide range of waste substances was tested: agricultural residue, peanut shells, consumer wastes like plastics, lubricants, mixed biomass, waste synthetic polymers, rape-seed etc. (Ni et al., 2006).

4. THE PRODUCTION OF HYDROGEN ON A SMALL SCALE

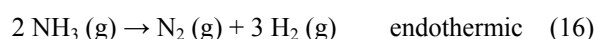
Besides the classic and most used conventional methods of acquiring hydrogen, research has proceeded also along other paths by which hydrogen can be produced on a small scale. They include for example plasma cracking, where the reactions are the same as with conventional cracking, but the energy and free radicals are provided by plasma formed by electricity or heat (Hammer et al., 2004; Paulmier and Fulcheri, 2005; Matsui et al., 2005). When feeding water or steam along with fuel, also electrons are formed besides the radicals of H, OH and O, which creates the conditions for both reduction and oxidation reactions (Holladay et al., 2009). This method may be applied also within the pyrolysis process and in processes facilitating steam reforming, autothermal cracking or partial oxidation. A significant problem however is lowering the energy consumption.

There are two categories of plasma cracking: thermal and non-thermal (Holladay et al., 2009). In non-thermal plasma, the temperature rises to markedly high values (> 5000 °C) (Hammer et al., 2004; Paulmier and Fulcheri, 2005; Matsui et al., 2005). Since the electrons are immediately excited, wattage of only a few hundred watts is needed (Paulmier and Fulcheri, 2005). Non-thermal plasma cracking can be divided into gliding arc plasma (GAP), dielectric barrier discharge (DBD), microwave plasma and corona discharge (Hammer et al., 2004; Paulmier and Fulcheri, 2005; Matsui et al., 2005). The first three use dynamic discharge for the formation of plasma, whereas corona discharge is created by a static discharge (Paulmier and Fulcheri, 2005). The efficiency of the plasma technologies differs markedly. The most effective seems to be non-thermal cracking in gliding arc plasma, which reaches an efficiency of as much as 85 %. A promising method of obtaining hydrogen is also dielectric discharge with an efficiency of 55 %. The problem in the use of this process is predominantly in the energy demand for reaching a plasma state. A comparison of the efficiency of the plasma technologies is provided in Table 2 (Paulmier and Fulcheri, 2005).

Hydrogen production on a small scale also includes the decomposition of methanol or ammonia. Cracking of ammonia was designed in the first place for use in fuel cells (Holladay et al., 2009). Ammonia is an inexpensive fuel. On an industrial scale, the synthesis of ammonia is conducted at 500 °C and a pressure of 25 MPa. Its synthesis is described by the following reaction (15).

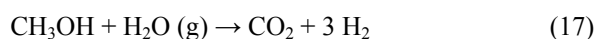


The cracking of ammonia leading to the production of hydrogen is on the other hand an endothermic reaction (16).



Catalysts such as iron, molybdenum, ruthenium and nickel oxides are used both for the synthesis of

ammonia and for its cracking. The decomposition of ammonia takes place at temperatures of 800–900 °C and, unlike the syntheses of ammonia, occurs under reduced pressure (Holladay et al., 2009). The temperature necessary for the course of cracking can be reached either by the combustion of part of the hydrogen produced by the decomposition of ammonia or the combustion of additional fuel (propane or butane). Besides the cracking of ammonia, hydrogen can be acquired on a small scale by cracking methanol with steam. The reaction takes place at temperatures of 300–400 °C, with a pressure of 3 MPa and in the presence of catalysts of zinc oxide and chromium oxide (reaction 17) (www.hytep.cz, 2009).



The efficiency of the cracking is as high as 90 %, whereas the performance can be changed within the range of 20–100 %. In the case of the above-mentioned hydrogen production, it is necessary to bear in mind also the energy demand and complexity of the production of ammonia as well as methanol, which should be subsequently cracked into hydrogen again.

5. ALTERNATIVE RESOURCES AND SOME RESOURCES AND SOME PROMISING METHODS OF HYDROGEN PRODUCTION FOR THE FUTURE

A promising method for the acquisition of hydrogen in the future could be water electrolysis. Currently, approximately 4% of hydrogen worldwide is produced in this way (Holladay et al., 2009; www.hytep.cz, 2009). The electrolysis of water, or its cracking into hydrogen and oxygen, is a well-known method which began to be used commercially already in 1890 (Holladay et al., 2009). The cracking of water can be divided into three categories: electrolysis, thermolysis and photoelectrolysis.

Electrolysis is a process in which a direct current passing through two electrodes in a water solution results in the cracking of the chemical bond of water into hydrogen and oxygen (18).



The hydrogen cation H^+ reacts at the cathode, resulting in the creation of hydrogen, which is collected and later stored. At the negative electrode (anode), oxygen is created. The space between the electrodes is separated by a membrane to avoid a blending of the gases. The process is ecologically clear, because no greenhouse gases are created and the oxygen produced has further industrial application. However, in comparison with the foregoing methods, it is a highly energy-demanding technology. The electrolysis processes take place at room temperatures and for their course it is necessary to supply only electrical energy.

A commonly used electrolyte in water electrolysis is sulfuric acid and the electrodes are of

platinum, which does not react with sulfuric acid. The disassociation molecules of sulfuric acid produce H^+ cations and SO_4^{2-} anions in the solution. Hydrogen cations move towards the negative electrode, from which they adopt the electron and merge into a hydrogen molecule. Sulfate anions move towards the positive electrode, to which they pass redundant electrons, and the electrically neutral SO_4 molecule immediately reacts with the water, through which a new molecule of sulfuric acid forms again. At the same time, oxygen molecules are released in this reaction. The same number of molecules of sulfuric acid remains in the electrolyte, with the number of water molecules dwindling and the concentration of the solution rising. The energetic efficiency of the electrolysis of water (chemical energy acquired/electrical energy supplied) in practice reaches 60–70 % (Holladay et al., 2009).

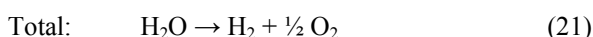
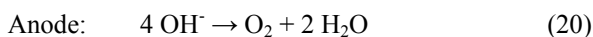
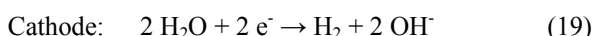
The most common electrolysis technologies are based on the electrolysis of alkaline solutions. The addition of an electrolyte (salt) increases the conductivity of water, and hydrogen is a by-product e.g. in the production of chlorine or sodium hydroxide. On the other hand, a more effective technology in which more protons are exchanged utilizes proton-exchange membrane (PEM) electrolyzers and the electrolysis units of solid oxide electrolysis cells (SOEC) (Holladay et al., 2009). While the solid oxide electrolyzers are more efficient in terms of electricity, this technology has problems with corrosion, thermal circulation and chromium migration. PEM electrolyzers are more efficient than alkaline ones, are corrosion resistant unlike SOEC, but their price is higher than that of a classic alkaline system. Alkaline systems are hence the most advanced and their market price is the lowest. The efficiency is low 50–60 %, depending on the calorific value of hydrogen, and the price of the electricity supplied is the highest of all the systems.

5.1. ALKALINE ELECTROLYZER

Alkaline electrolyzers are composed of electrodes, a microporous separator and an alkaline solution of ca 30 wt. % of potassium hydroxide or sodium hydroxide (Holladay et al., 2009; Turner et al., 2008). The most commonly used cathode material in alkaline electrolyzers is nickel with a catalytic layer of platinum. The anode is comprised of nickel or copper covered by oxides of metals (of mangan, wolfram, ruthenium). The electrolyte is not expended in the reaction but must be continuously complemented because of the loss of other systems like the regeneration of hydrogen.

In the alkaline electrolyzer, water is fed into the cathode, where it is disassociated into hydrogen and hydroxyl ions (OH^-), which pass through electrolytic material to the anode, where oxygen is, formed (19–21). Hydrogen leaves an alkaline solution and is separated from water in a gas–liquid separation unit outside of the electrolyzer (Holladay et al., 2009). The

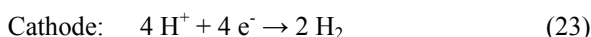
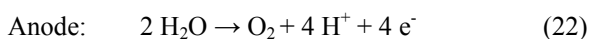
typical current density is 100–300 mA/cm². The efficiency of alkaline electrolyzers reaches ca 50–60 % according to the calorific value of hydrogen.



A certain amount of hydrogen can be created also in other processes such as the electrochemical production of chlorates or perchlorates.

5.2. PROTON EXCHANGE IN A POLYMER ELECTROLYTE MEMBRANE ELECTROLYZER

A proton-exchange membrane electrolyzer works with the technology of a fuel cell with a polymer electrolyte membrane (PEM). The base of the typical PEM electrolyzers is the use of black platinum, iridium, ruthenium and rhodium for electrode catalysts and the thin Nafion polymer membranes, which serve as a gas separator (Holladay et al., 2009; Turner et al., 2008). Water in the PEM electrolyzer is fed to the anode, where it is split into a hydrogen cation and oxygen. The hydrogen cations pass through the polymer membrane to the cathode. At the cathode, the hydrogen cations merge with the electrons flowing from the outer circuit, which results in the creation of gas hydrogen (22–24). The efficiency of a PEM electrolyzer is around 55–70 % (Turner et al., 2008).



The total is the same as for the alkaline electrolyzer:



The overall efficiency of the electrolytic production of hydrogen can be attributed mainly to the efficiency of the electrical energy production (30–40 % for conventional resources). The overall efficiency of electrolysis is thus roughly in the range of 25–35 %. An advantage is the simultaneous production of oxygen for its wide application.

5.3. SOLID OXIDE ELECTROLYSIS CELLS

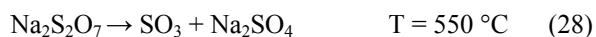
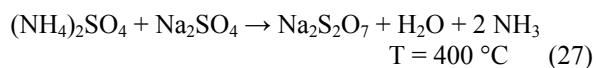
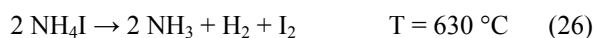
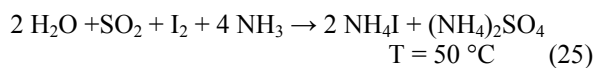
Solid oxide electrolysis cells (SOEC) are essentially the solid oxides of fuel cells which use a solid material as an electrolyte (Holladay et al., 2009). The electrolyte selectively transfers oxygen anions at increased temperature. SOEC work like the alkaline system, because the oxygen ion passes through the electrolyte while leaving hydrogen in a non-reactive flow of steam. The reactions have been listed in Chapter 5.1. At the cathode, water bonds with the electrons from the outer circuit to form hydrogen gas and negatively charged oxygen ions. The oxygen

ions pass through the membrane and react at the anode to form oxygen gas and leave electrons in the outer circuit. The solid oxide electrolysis cells work at high temperatures of 500–800 °C in comparison with PEM electrolyzers, which work at temperatures of 80–100 °C, and alkaline electrolyzers, which work in the temperature range of 100–150 °C. The solid oxide electrolyzers can effectively utilize the heat available at these higher temperatures (from various sources, including nuclear energy) to reduce the amount of electrical energy necessary for the production of hydrogen from water. These systems compensate for a part of the electrical energy necessary for cracking water with thermal energy. Higher temperatures increase the efficiency of the electrolyzer at decreasing anode and cathode overvoltage, which causes a drop in performance during electrolysis. For instance, an increase of temperature from 100 °C to 770 °C lowers the combining of thermal and electrical energy of the apparatuses nearly to 35 %. The materials used for SOEC are similar to the materials developed for solid oxide fuel cells (SOFC) such as the Y₂O₃ in ZrO₂. The material for the anode is Co-ZrO₂ or Ni-ZrO₂, whereas LaMnO₃ doped with strontium is used for the cathode (Holladay et al., 2009; www.hytep.cz, 2009). The efficiency of high-temperature electrolysis depends on the temperature and the thermal source and can reach values of 85–90 %.

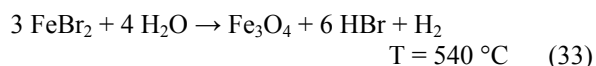
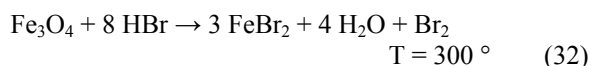
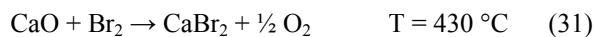
5.4. THERMOCHEMICAL CRACKING OF WATER

Thermochemical cycles have been developed already since the 1970s and 1980s, when they were to contribute to the search for new sources of the production of alternative fuels during a petroleum crisis. The thermochemical cracking of water, also labeled as thermolysis, is the decomposition of water into hydrogen and oxygen by means of a series of subsequent chemical reactions, which are initiated by heat or electrical energy if they are hybrid cycles. The total attainable efficiency of the closed cycles of these processes is around 50 % (Funk, 2001). Water breaks down at extremely high temperatures over 2500 °C, for which we do not yet have suitable construction materials and thermal resources. Chemical reagents should therefore be designed for lower temperatures. So far, more than 300 various cracking cycles of water have been described. All of the processes markedly lowered the working temperature from 2500 °C, at the price of higher pressure. The cycles mentioned below are closed, which means that the chemical substances used are recycled during the process and re-enter the process (Holladay et al., 2009; www.hytep.cz, 2009; Funk, 2001; Andress et al., 2009; T-Raissi, 2003). Only the initial raw material, i.e. water, is complemented, with the resultant products being hydrogen and oxygen. An example of a cycle is presented below (25–29).

Kapra Mark-10 (Holladay et al., 2009):



The UT-3 thermochemical cycle is developed to be connected with nuclear energetic reactors (T-Raissi, 2003; Brown et al., 2002). The efficiency of the UT-3 cycle is in the range of 40–50 % and includes these reactions (30–34).

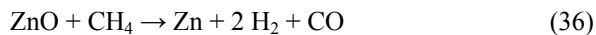


In terms of kinetics, the first reaction is the slowest of the above-mentioned reactions and limits the speed of the whole cycle. Since it is indispensable that all of the reactions take place at a certain speed for the continuity of the cycle, the efficiency of the process is adversely affected by the lower speed of the hydrolysis of calcium bromide. For the process to be run in a fixed-bed reactor the gases have to flow alternately in the opposite direction, i.e. during endothermic reactions the gas in the reactor is run in one direction for ca 2 hours and then during exothermic reactions the gas is run in the opposite direction for another 2 hours etc.

Another thermochemical cycle lies in the passing of zinc oxide through the reactor heated to 1800 °C. At this temperature, zinc oxide breaks down and the cooled zinc reacts with water to form hydrogen gas and solid zinc oxide, which is recycled back into the process (34,35) (Holladay et al., 2009).

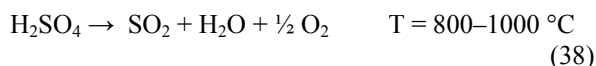
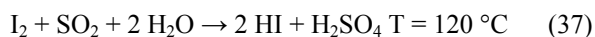


The process called SynMet lies in the combination of the reduction of zinc oxide and methane cracking inside of a solar reactor (36), comprised of the vertical flow of solid particles and gas captured in the solar accumulator, which is exposed to intensive solar radiation.



The process transforms methane in the absence of a catalyst and optimizes the production of syngas suitable for the synthesis of methanol and joint production of zinc and syngas devoid of CO emissions through the traditional ZnO reduction.

In the middle of the 1970s, sulfur-iodine thermochemical cycle was developed in General Atomics (San Diego, USA), which allowed inexpensive and at the same time effective hydrogen production by means of atomic energy (Holladay et al., 2009; T-Raissi, 2003; Brown et al., 2002). The initial raw material is water in a liquid state and high-potential heat. Iodine and sulfur dioxide are in a liquid state as well and are recycled during the process and reused. The resulting raw materials are hydrogen, oxygen and low-potential heat (37–39):



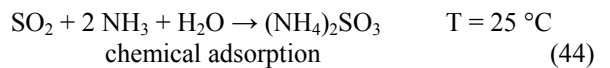
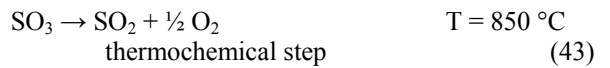
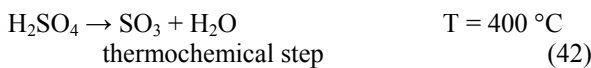
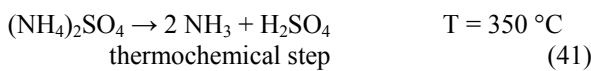
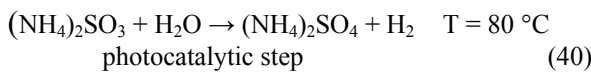
The first step is an exothermic Bunsen reaction, during which sulfuric acid and hydroiodic acid are created. The subsequent thermal decomposition is endothermic and needs heat to be supplied for the decomposition of sulfuric acid and then hydroiodic acid. The efficiency of the whole hydrogen production cycle is 40–52 % (ca 50 % at 950°C). With rising temperature, the efficiency of the cycle will increase. In comparison with electrolysis, the efficiency is higher, because losses do not occur in the production of electrical energy. The disadvantage of this cycle lies in the requirement of high temperatures and in the high aggressiveness of both of the produced acids. This places high demands on the chemical resistance of the materials used.

A variation of the sulfur-iodine cycle is the Bowman-Westinghouse cycle, which includes reactions with bromine instead of iodine and the electrolysis of hydrobromic acid rather than the thermal decomposition of hydroiodic acid (Holladay et al., 2009; T-Raissi, 2003). The main disadvantage of this cycle lies in the maintenance of a low concentration of sulfuric acid, leading to a higher energetic consumption of concentrated acid and to a separation process. A new thermochemical sulfur-ammonia cycle has therefore been designed for the decomposition of water into hydrogen and oxygen (T-Raissi, 2003). The cycle includes three steps (40–44): 1) a photocatalytic oxidation of ammonium sulfite to ammonium sulfate, whereas water is reduced to hydrogen utilizing both the thermal and UV portion of the solar spectrum; 2) the decomposition of ammonium sulfate into ammonia and sulfuric acid with the use of a reductive process like in the

Table 3 The identified of Fe-Cl thermochemical cycles and their edic.

Cycle	Temperature (°C)	Efficiency (%)
6 H ₂ O + 10 FeO → 2 Fe ₃ O ₄ + 2 H ₂ + 4 Fe(OH) ₂	127	42.5
2 Fe ₃ O ₄ + 3 Fe(OH) ₂ → 3 H ₂ O + O ₂ + 9 FeO	850	
Fe(OH) ₂ → H ₂ O + FeO	850	
8 H ₂ O + 4 Fe → 4 H ₂ + 4 Fe(OH) ₂	127	44.1
4 H ₂ + 4 Fe(OH) ₂ → 6 H ₂ O + O ₂ + 4 Fe	850	
8 H ₂ O + 4 Fe → 5 H ₂ + 2 FeO + 2 Fe(OH) ₃	127	48.8
H ₂ + 2 Fe(OH) ₃ → 4 H ₂ O + O ₂ + 2 Fe	850	
H ₂ O + 2 FeO → H ₂ + Fe ₂ O ₃	127	
3 H ₂ + Fe ₂ O ₃ → 3 H ₂ O + 2 Fe	850	
2 H ₂ O + Fe → H ₂ + Fe(OH) ₂	127	Excessive
Fe + 3 Fe(OH) ₂ → 3 H ₂ + O ₂ + 4 FeO	850	
3 H ₂ O + 5 FeO → H ₂ + 2 Fe(OH) ₂ + Fe ₃ O ₄	127	
Fe ₃ O ₄ + 3 H ₂ → 3 H ₂ O + 2 Fe + FeO	> 850	
3 H ₂ O + 5 FeO → H ₂ + 2 Fe(OH) ₂ + Fe ₃ O ₄	127	
2 H ₂ + 4 Fe(OH) ₂ → 6 H ₂ O + O ₂ + 4 Fe	850	35.0
5 H ₂ O + 3 Fe → 3 H ₂ + 2 Fe(OH) ₂ + FeO	127	
Fe ₃ O ₄ + Fe → 4 FeO	850	
9 H ₂ O + 4 Fe → 6 H ₂ + 2 Fe(OH) ₃ + Fe ₂ O ₃	127	
Fe ₃ O ₄ + 3 H ₂ → 3 H ₂ O + 2 Fe + FeO	850	Excessive
FeO + Fe ₂ O ₃ → Fe ₃ O ₄	127	
H ₂ + 2 Fe(OH) ₃ → O ₂ + 2 Fe + 4 H ₂ O	> 850	
6 H ₂ O + 10 FeO → 2 Fe ₃ O ₄ + 2 H ₂ + 4 Fe(OH) ₂	127	
2 Fe ₂ O ₃ + 3 Fe(OH) ₂ → 3 H ₂ O + O ₂ + 7 FeO	850	43.0
Fe ₃ O ₄ + Fe(OH) ₂ → H ₂ + 2 Fe ₂ O ₃	850	
Fe ₃ O ₄ + H ₂ → 3 FeO + H ₂ O	850	
6 H ₂ O + 10 FeO → 2 Fe ₃ O ₄ + 2 H ₂ + 4 Fe(OH) ₂	127	
2 Fe ₃ O ₄ + 3 Fe(OH) ₂ → 3 H ₂ O + O ₂ + 9 FeO	850	41.7
FeO + Fe(OH) ₂ → H ₂ + Fe ₂ O ₃	850	
H ₂ + Fe ₂ O ₃ → 2 FeO + H ₂ O	850	
5 H ₂ O + 9 FeO → 2 Fe ₃ O ₄ + 2 H ₂ + 3 Fe(OH) ₂	127	
Fe + 3 Fe(OH) ₂ → 3 H ₂ + O ₂ + 4 FeO	> 850	Excessive
Fe ₃ O ₄ + H ₂ → 3 FeO + H ₂ O	850	
Fe ₃ O ₄ + 2 H ₂ → 2 FeO + 2 H ₂ O + Fe	850	
8 H ₂ O + 4 Fe → 4 H ₂ + 4 Fe(OH) ₂	127	Excessive
4 Fe(OH) ₂ → 4 H ₂ + O ₂ + 2 Fe ₂ O ₃	127	
6 H ₂ + 2 Fe ₂ O ₃ → 6 H ₂ O + 4 Fe	> 850	

Westinghouse-Bowman sulfuric cycle; and 3) a joint chemical adsorption of ammonia and sulfur dioxide to produce ammonium sulfite, which is recycled for the production of hydrogen and ammonium sulfate. The cycle has the potential of attaining high total efficiency by the use of commonly available and inexpensive chemicals. The source of heat is solar energy and a part of the UV radiation is used for the photocatalytic redox reaction.



In terms of environmental protection and the economic issues, the Fe-Cl cycle (Andress et al., 2009) seems to be ideal, because it is a reaction of ideal elements (Fe, Cl, H and O). Ten different cycles have been identified in the wide temperature range of 100–900 °C (Table 3).

There are five criteria for selecting the suitable cycle, which can occur simultaneously (Holladay et al., 2009):

1. Within the temperatures considered, the ΔG of the individual reactions must approach zero;
2. The number of steps should be minimal;

3. Each individual step must have both stages with a quick reaction and proportions which are similar to the other steps in the sequence;
4. The reaction products cannot result in chemical-by-products and any separation of the reaction products must be minimal in terms of cost and energy consumption;
5. The intermediates must be easy to control.

There are currently several processes which meet these five criteria such as the Ispra-Mark 10, 11, 13, 15, UT-13 processes and the decomposition of sulfuric acid (Westinghouse Process). These processes are however not able to compete with the other technologies of hydrogen production in terms of their costs and efficiency (Holladay et al., 2009; Funk, 2001). The combination of high temperatures, high pressures and corrosion result in a need for new, more resistant materials.

5.5. PHOTOELECTROLYSIS

Photoelectrolysis is one of the renewable ways of hydrogen production, exhibiting promising efficiency and costs, although it is still in the phase of experimental development (Holladay et al., 2009; Turner et al., 2008; Turner et al., 2007; Huang, 2002). Currently, it is the least expensive and most effective method of hydrogen production from renewable resources. The photoelectrode is a semiconducting device absorbing solar energy and simultaneously creating the necessary voltage for the direct decomposition of the water molecule into oxygen and hydrogen.

Photoelectrolysis is a complex of the solar energy collection and water electrolysis into simple semiconducting photoelectrodes. This apparatus removes the need for an independent generator and electrolyzer feeding, which leads to a reduction of the overall costs and increase of the efficiency of the process.

Photoelectrolysis utilizes a photoelectrochemical (PEC) light collection system for the driving of the electrolysis of water. If the semiconductor photoelectrode is submerged in an aqueous electrolyte exposed to solar radiation, it will generate enough electrical energy to support the generated reactions of hydrogen and oxygen. When generating hydrogen, electrons are released into the electrolyte, whereas the generation of oxygen requires free electrons. The reaction depends on the type of semiconductor material and on the solar intensity, which produces a current density of 10–30 mA/cm². At these current densities, the voltage necessary for electrolysis is approximately 1.35 V.

The photoelectrode is comprised of photovoltaic (semiconductor), catalytic and protective layers, which can be modeled as independent components (Holladay et al., 2009; Huang, 2002). Each layer influences the overall efficiency of the photoelectrochemical system. The photovoltaic layer

is produced from light absorbing semiconductor materials. Testing has been conducted on various materials, e.g. TiO₂, Fe₂O₃, WO₃, n-GaAs, n-GaN for a photoanode, and e.g. CIGS/Pt (Cu-In-Ga-diselenid), p-InP/Pt and p-SiC/Pt for a photocathode (Holladay et al., 2009; Turner et al., 2008; Huang, 2002). The light absorption of the semiconductor material is directly proportional to the performance of the photoelectrode. Semiconductors with wide bands provide the necessary potential for cracking water. An increase in light absorption can be supported by modifying the semiconductor material or adding a photosensibilizer like e.g. dyes absorbing the greater part of the solar spectrum. The most promising dyes are the color N3 and the color black (Holladay et al., 2009). The color N3 is cis-RuL₂(NCS)₂ with the L position for 2,2'-bipyridyl-4,4'-dicarboxylic acid. The color black is (tri)ciano-2,2'-bipyridyl-4,4'-tricarboxylate ruthenium (II). The advantages of these systems include the use of inexpensive materials and their capacity for higher efficiency.

The catalytic layers of the photoelectrochemical cell also influence the performance of the electrolysis and require suitable catalysts for water cracking. The encased layer is another important component of the photoelectrode, which prevents the semiconductor from corroding inside the aqueous electrolyte. This layer must be highly transparent to be able to provide the maximum solar energy so that it could reach the photovoltaic semiconducting layer. Other than the semiconductor devices for photoelectrolysis, it is suitable to use metal complexes suspended in solution as photochemical catalysts. The typically used materials (Holladay et al., 2009; Huang, 2002) could be ZnO, Nb₂O₅ and TiO₂ nanoparticles.

6. CONCLUSION

In the near future, hydrogen will become an important fuel which may be able to resolve local problems connected with air quality. Hydrogen-propelled transport means are being developed and are already used in the automobile industry. Since the combustion of hydrogen does not produce any emissions of carbon oxides but only water, hydrogen is considered as a key fuel of the future. Hydrogen is abundantly present all over space and can be obtained from a number of resources, be they renewable or non-renewable. Numerous processes have a minimal impact on the environment. The development of these technologies should lower the dependence primarily on fossil fuels. 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. Plasma cracking is still in the developmental stage.

The preferred method of hydrogen production on an industrial scale is steam reforming of natural gas for its low operational and production costs. When the

operational costs of steam reforming and partial oxidation are compared, partial oxidation seems to be the more acceptable process, but the subsequent shift makes this process more expensive.

Pyrolysis processes have acceptable investment costs and besides the production of hydrogen also satisfactory yields of oils. Two-stage co-pyrolysis is suitable considering its acquisition of a high amount of hydrogen from mixed charges. It is apparent that the co-pyrolysis of organic materials with coals is a process for hydrogen production capable of competing. It can therefore play a significant role in the future.

With its conditions, electrolysis connected with renewable energy approaches low-emission technologies. However, for its energetic consumption, it is among the expensive technologies. In recent years, significant progress has been made in the development of systems of alternative hydrogen production including the thermochemical cracking of water and photoelectrolysis. While photoelectrolysis is currently the least expensive and most effective method of hydrogen production, thermal processes from non-renewable resources remain a less expensive method of hydrogen production.

ACKNOWLEDGEMENT

This work was supported by the project of the Czech Science Foundation No. 105/07/1407 and conducted within Research Plan AVOZ30460519.

REFERENCES

- Amos, W.A.: 2004, Biological water-gas shift conversion of carbon monoxide to hydrogen; Milestone Completion Report, National Renewable Energy Laboratory, Research Report, NREL/MP-560-35592, Golden Colorado, 1–21.
- Andress, R.J., Huang, X., Bequette, B.W. and Martin, L.L.: 2009, A systematic methodology for the evaluation of alternative thermochemical cycles for hydrogen production, *International Journal of Hydrogen Energy* (34), 4146–4154.
- Beneš, M. et al.: 1997, Gas industry 1847-1997, Malínský J. (ed.), ATYPO, Praha, (in Czech).
- Bičáková O.: 2001, Co-pyrolysis of coal/organic wastes mixtures. Dissertation, Department of gas, coke and air protection, Faculty of Environmental Technology, Institute of Chemical Technology, Prague.
- Brown, L.C., Besenbruch, G.E., Schultz, K.R., Showalter, S.K., Marshall, A.C., Pickard, P.S. and Funk, J.F.: 2002, High efficiency generation of hydrogen fuels using thermochemical cycles and nuclear power, U. S. Department of Energy under Nuclear Energy Research Initiative (NERI) Grant Nos. DE-FG03-99SF21888 and DE-FG03-99SF02398, General Atomics Project 30047, <http://npre498.ne.uiuc.edu/NPRE%20498%2005%20LECT%209B.pdf>, 1–31.
- Funk, J.E.: 2001, [Thermochemical hydrogen production: past and present](#), *International Journal of Hydrogen Energy* (26), 185–190.
- Hamer, T., Kappes, T. and Baldauf, M.: 2004, [Plasma catalytic hybrid processes: gas discharge initiation and plasma activation of catalytic processes](#), *Catalysis Today* (89), 5–14.
- Holladay, J.D., Hu, J., King, D.L. and Wang, Y.: 2009, An overview of hydrogen production technologies, *Catalysis Today* (139), 244–260.
- Holmen, A.: 2009, Direct conversion of methane to fuels and chemicals, *Catalysis Today* (142), 2–8. <http://www.hytep.cz/> downloaded on March 2, 2009. <http://www.svazarm.cz/cz/zivotni-prostredi/> downloaded on April 14, 2009.
- Huang, R.: 2009, Hydrogen production by photoelectrolysis, <http://bhuan02.tripod.com/photoelectrolysis.htm>
- Kříž, V. and Brožová, Z.: 2007, Hydrogen – the product of coal thermal conversion, Proc. of the 11th Conference on Environment and Mineral Processing, Part I, Ostrava, May 31–June 2, 7–10.
- Kříž, V., Káš, V. and Brožová, Z.: 2008, Continuous pyrolysis of carbonaceous materials with model gasification of the solid product, Proc. of the 12th Conference on Environment and Mineral Processing, Part I, VŠB-TU Ostrava, June 5–7, 7–10.
- Kříž, V., Brožová, Z., Příbyl, O. and Sýkorová, I.: 2008, [Possibility of obtaining hydrogen from coal/waste-tire mixture](#), *Fuel Processing Technology*, 89, 1069–1075.
- Kříž, V. and Brožová, Z.: 2007, Co-pyrolysis of coal/waste polymers mixtures, *Acta Geodyn. Geomater.*, No. 2 (146), 39–42.
- Kříž, V.: 2007, Dynamic model of coal/organic wastes pyrolysis, *Acta Research Reports*, No. 16, 39–60.
- Matsui, Y., Kawakami, S., Takashima, K., Katsura, S. and Mizuno, A.: 2005, Liquid-phase fuel re-forming at room temperature using nonthermal plasma, *Energy and Fuels*, 19, 1561–1565.
- Ni, M., Leung, D.Y.C., Leung, M.K.H. and Sumathy, K.: 2006, An overview of hydrogen production from biomass, *Fuel Processing Technology*, 87, 461–472.
- Palmová, I. and Schöngut, J.: 2004, Outlook of production and utilization of hydrogen, *Chemické listy*, 8, 205–210.
- Paulmier, T. and Fulcheri, L.: 2005, [Use of non-thermal plasma for hydrocarbon reforming](#), *Chemical Engineering Journal*, 106, 59–71.
- Song, H., Zhang, L., Watson, R.B., Braden, D. and Ozkan, U.S.: 2007, [Investigation of bio-ethanol steam reforming over cobalt-based catalysts](#), *Catalysis Today* (129), 346–354.
- Straka, P. and Kříž, V.: 2008, Hydrogen production by two-stage co-pyrolysis of bituminous coal-polymers mixtures, *Acta Geodyn. Geomater.*, 5 (149), 77–82.
- Straka, P., Náhunková, J. and Brožová, Z.: 2004, Kinetics of copyrolysis of coal with polyamide 6, *Journal of Analytical and Applied Pyrolysis*, 71, Issue 1, March, 213–221.
- Straka, P. and Náhunková, J.: 2004, Thermal reactions of polyethylene with coal (TG/DSC approach), *Journal of Thermal Analysis and Calorimetry*, 76, 49–53.
- Turner, J., Sverdrup, G., Mann, M.K., Maness, P.C., Kroposki, B., Ghirardi, M., Hans, R.J. and Blake, D.: 2009, Renewable hydrogen production, *International Journal of Energy Research*, 32, 379–407.
- Turner, J.A., Deutsch, T., Head, J. and Vallett, P.: 2007, Photoelectrochemical water systems for H₂

- production, DOE Hydrogen Program Annual Merit Review, U.S. Department of Energy, Washington, DC.
http://www.hydrogen.energy.gov/pdfs/review07/pd_10_turner.pdf, 1–20.
- T-Raissi, A.: 2003, Analysis of solar thermochemical water-splitting cycles for hydrogen production; Hydrogen, Fuel Cells, and Infrastructure Technologies, FY 2003 Progress Report, Florida Solar Energy Center (FSEC).
- Wang, Y., Chin, Y.H., Rozmiarek, R.T., Johnson, B.R., Gao, Y., Watson, J., Tonkových, A.Y.L. and Vander, Wiel D.P.: 2004, [Highly active and stable Rh/MgO-Al₂O₃ catalysts for methane steam reforming](#), *Catalysis Today*, 98, 575–581.
- Žmuda, W.A. and Minkina, M.: 1999, A method for the utilization of organic waste materials, Proc. of the 10th Int. Conf. on Coal Science. Shanxi, Taiyuan, P. R. China, II, 1219–1222.