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POSSIBILITIES OF USING HYDROGEN AS MOTOR VEHICLE FUEL

ABSTRACT

Hydrogen is the fuel of the future, since it is the element of water (H_2O) which surrounds us and the resources of which are unlimited. First water is divided into hydrogen and oxygen. The paper presents the laboratory and industrial methods of obtaining hydrogen, types of fuel cells for various purposes, hydrogen-propelled motor vehicles, as well as advantages and drawbacks of hydrogen used as fuel under the conditions that have to be met in order to use it as propulsion energy for motor vehicles.

KEY WORDS

hydrogen, fuel cells, fuel converters, Otto-engine, propulsion energy

1. INTRODUCTION

Hydrogen (H_2) is the fuel of the future, which surrounds us just like water (H_2O). But in order to turn water into useful energy, it must first be divided into hydrogen and oxygen by means of electrolysis, by conducting electricity into the water. Hydrogen and oxygen float separately on the surface as gases. This is where hydrogen is «captured» and cooled at -250°C so as to be stored in liquefied state. Basically, this energy carrier is available without limits, but extreme amount of electricity is necessary for its production and storage. Therefore, the hydrogen production has sense only when the electricity is obtained from clean plants (solar, water and wind). [1]

2. PRODUCTION OF HYDROGEN

In *laboratory* hydrogen is usually obtained in Kipp apparatus by means of the reaction of zinc and diluted chloride or sulphate acid:

$$\overset{0}{Zn}(s)+2\overset{+1}{H^+} \longrightarrow Zn^{2+}+\overset{0}{H_2}(g)$$

Thus, the reaction is based on the oxidation activity of hydrogen which reduces the oxidation level +1 to elementary state. This causes adequate oxidation of zinc. In fact, the redox-system:

$$2H^+ +2e^- \longleftrightarrow Zn_2(g)$$

whose redox-potential is 0.0 V, with activity H^+-ion = 1, can oxidise any other system with a negative redox potential. Since redox potential of the system

$$Zn^{2+}+2e^- \longleftrightarrow Zn(s)$$

amounts to –0.76 V, the given reaction occurs relatively easy.

The second laboratory method used to obtain hydrogen is the action of water on solid hydrides, and usually on the calcium hydride:

$$2\overset{+1}{H_2}O+Ca\overset{-1}{H_2}(s)\longrightarrow 2\overset{0}{H_2}(g)+Ca^{2+}+2OH^-$$

This is in fact the redox-process in which the hydrogen atom from the water molecule oxidises negative hydride-ion from Ca-hydride:

$$H^+ + H^- \longrightarrow H_2(g)$$

As **third** laboratory method for obtaining hydrogen the reaction of some metals (those that have a negative redox-potential) with bases can be used, if such metals make hydroxo-complexes. Such metals are e. g. aluminium and zinc:

$$2Al(s)+6H_2O+2OH^- \longrightarrow 2Al(OH)_4^- +3H_2(g)$$

$$Zn(s)+2H_2O+OH^- \longrightarrow Zn(OH)_3^- +H_2(g)$$

Finally, for obtaining hydrogen in the laboratory also water electrolysis may be used. Since water is a poor electricity conductor, it occurs in practise as electrolyte of the alkali hydroxide solution. During the electrolyte process hydrogen is reduced on the cathode, and oxygen oxidizes on the anode. Electrochemical reactions on electrodes are the following:

Cathode:	$4H_2O+4e^- \longrightarrow 2H_2(g)+4OH^-$
Anode:	$4OH^- \longrightarrow O_2(g)+2H_2O+4e^-$
Ukr. reaction:	$2H_2O \longrightarrow 2H_2(g)+O_2(g)$

For *industrial* obtaining of hydrogen there are several methods:

The first and the most important method for industrial production of hydrogen is *cracking* (pyrolysis) of *hydrocarbon*:

$$C_2H_6(g) \longrightarrow C_2H_4(g) + H_2(g)$$

Methane from natural sources can also be thermally divided into carbon and hydrogen, but reaction with vapour at temperature of 1100°C is used more frequently:

$$CH_4 + 2O_2(g) \longleftrightarrow CO_2(g) + 3H_2(g)$$

$$\Delta_r H = 212.4 \text{ kJ mol}^{-1}.$$

The reaction is endothermic, and the necessary energy is most easily compensated by the combustion of part of methane with oxygen:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

$$\Delta_r H = -801.6 \text{ kJ mol}^{-1}.$$

The combustion of one mole of methane releases enough energy for the reaction of almost four moles of methane with water.

The second important method of industrial obtaining of hydrogen is the *reduction of water vapour with carbon,* i. e. oxidations of carbon with hydrogen from the water vapour:

$$C(s) + O_2(g) \longrightarrow CO(g) + H_2(g)$$

$$\Delta_r H = -131.25 \text{ kJ mol}^{-1}.$$

This is also endothermic reaction and for compensation of energy it is usually combined with hydrogen combustion:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

$$\Delta_r H = 41.4 \text{ kJ mol}^{-1}. \text{ [2]}$$

The third, and for us the most important method is the *electrolysis*. The principle of electrolysis is the transfer of ion by means of electricity. Water creates free ions only to a small extent, and their pH shifts in classical methods of electrolysis by adding electrolyte in alkali or acid medium. Along direct current the reaction occurs on the electrodes, with hydrogen being extracted on the cathode. Electrolytically permeable membrane prevents mixing of hydrogen and oxygen gases. By improvement of this separator the level of action in alkali electrolytes up to 85% can be achieved. The main drawback of this technology is expensive electricity. There is a project of the European Community and the district of Quebec from Canada, based on the electrolysis of 100 MW, propelled by inexpensive electricity from the hydropower plant, and the produced hydrogen is transported by ship to Hamburg. Such hydrogen would be used for the propulsion of jet engines, buses, as well as internal combustion engines. Countries that do not have cheap electricity have developed another procedure and that is in Germany the high-temperature electrolysis of vapour called "Hot Elly". This procedure operates at the temperature of 1000°C and uses the yttrium-stabilized zircon as electrolyte. [3]

3. TYPES OF FUEL CELLS

Several types of fuel cells for various purposes have been developed up to now. Since technically the electrolyte determines the key characteristics, the fuel cells are divided according to the type of electrolyte.

Fuel cells with proton-exchange membrane or PEM are considered the most acceptable for the propulsion of automobiles and light cargo vehicles since the working temperature is relatively low (allows fast moving), uses air and realizes excellent performances (power density regarding mass and volume) in operating with hydrogen. One PEM fuel cell with the currency density of 1 A/cm^2, of 0.7V voltage and area of 500 cm^2 realizes power of 50-65kW or 150-200 cells of power cells 350W (greater number of cells is necessary in order to maintain the necessary level of cell power within a small space). The potential problem lies in the contamination of hydrogen by gases such as carbon monoxide (CO) and dioxide (CO_2). Should small quantities of carbon monoxide come into fuel, the performances of PEM fuel cells are significantly reduced. However, hydrogen can be easily produced and stored with the necessary cleanliness so that contamination by carbon monoxide does not present a problem. For the application in vehicles, the cells have to be very compact, of up to 50 litres volume, i. e. 250-350 cm^3 per cell. In case of cells of 500 cm^2 area, this means a thickness of 0.5-0.7 cm. Such small space has to accommodate: the membrane, anode and cathode, inputs for the distribution of gas to every electrode and provision of space for conductors resistant to gases between adjacent cells.

Fuel cells as membrane-electrode assembly or MEA provided the solution for the drawbacks of PEM. MEA consists of anode, PEM electrolyte and cathode, in which each layer is as thin as possible, without mechanical losses in the assembly i. e. electrochemical losses between electrodes. Anode and cathode are usually made of carbon in the porous form and coated by platinum or its alloys as the process catalysts.

Alkali fuel cells (AFC) are characterized by great density of power, but they do not withstand even the minimal concentrations of carbon dioxide (otherwise the main element in the treated fuel). Carbon dioxide would react with alkali electrolyte and the electrodes and electrolyte would be saturated by solidified carbon, generated by this reaction. For the application in vehicles it would be impractical to remove carbon oxide from the treated fuel.

Phosphor acid fuel cells (PAFC) are currently used as stationary energy sources. They use ambient air and the processed fuel, but they have low power density, and therefore have large mass and volume, which means high production costs. Another drawback is high operating temperature, i. e. the cells start to produce electricity only above 100°C. This is a big drawback regarding the requirement for quick starting of the vehicle. At operating temperature PAFC must always have a voltage below 0.8 V per cell in order to protect the vital cell parts against corrosion. The advantage of this type of cell is the acceptance of up to one percent of carbon monoxide in fuel, thus simplifying the fuel treatment process. PAFC could be used in heavy cargo road and railway vehicles, if somewhat higher costs of this technology were acceptable.

Methanol is the only applicable carbon-based fuel that features significant electrochemical reaction on the fuel cell electrodes at temperatures acceptable for the vehicles. Using this advantage, the direct methanol-air fuel cell (DMFC) may be almost equal to hydrogen-air fuel cell, using easily storable and relatively inexpensive fuel. DMFC consists of similar components as PEM hydrogen-air fuel cell: the catalysts are platinum and its alloys, porous electrodes for air and methanol (in gaseous state), with proton exchange membrane. This fuel cell features two key drawbacks: poor characteristics (electricity power is much lower than the level necessary for in-vehicle application) and too fast dispersion of methanol through the membrane towards air electrodes where it oxidizes easily in the electrochemical reaction of "short circuit". This problem reduces the fuel utilisation level by 30 percent or more, and methanol reduces the potential of the air cathode, i. e. the voltage of the entire cell and additionally reduces the overall utility. During the recent years great improvement of methanol-anode activity has been made. Table 1 shows the overview of fuel cells with the basic characteristics. [4]

4. FUEL CONVERTERS

Neither hydrogen nor oxygen is suitable for use in vehicles due to the technical restrictions caused by their storage in on-vehicle tanks and high costs related to these restrictions. Like internal combustion engines, the fuel cells use ambient air as source of oxygen, and they have to be able to operate with easily available hydrocarbon fuels, such as petrol and other oil products that are easily stored in vehicles. Alcohol methanol is also being seriously considered as possible fuel cell vehicle fuel. In order to be able to apply alcohols and hydrocarbons in fuel cells, they must first be converted into hydrogen-rich gas in chemical-catalytic reactors. These "fuel converters" additionally increase mass, volume and fuel cell production costs, and reduce the level of operation of the entire fuel cell system.

The hydrogen requirement in fuel cells depends on the electrical load, and therefore the in-vehicle fuel converters have to be capable of fast starting (changes in the driving regime) and to be efficient with a wide range of conversion degrees. The fuel conversion must be complete in the entire area of load, the carbon monoxide level in the treated fuel must be very low due to the anode protection, and the emission of harmful components equals zero or is around zero. Also, fuel converters must have compact and low prices.

The best-known two principles of fuel conversion are:

a) **Water vapour supported conversion:**

$$2H_3COH + H_2O(vapour) + heat \longrightarrow$$
$$\longrightarrow 5H_2 + CO + CO_2 \text{ (for methanol)}$$

$$H_3C(CH_2)_6 + H_2O(vapour) + heat \longrightarrow$$
$$\longrightarrow 21H_2 + 4CO + 4CO_2 \text{ (for petrol)}$$

Table 1 - Overview of fuel cells

Types of fuel cells	Types of electrolyte	Operating temperature (°C)	Density of electricity	Fuel converter requirement	Compatibility with CO_2	Development stadium	Possibilities	
							High utility	Low price
PEMFC	Proton Exchange membrane	70-80	high	yes	yes	Early prototype	good	good
AFC	Aqueous Alkaline	80-100	high	yes	no	Application in space	good	good
PAFC	Phosphoric Acid	200-220	medium	yes	yes	Early commercial application	good	correct
MCFC	Molten Carbonate	600-650	medium	yes	yes	Field trials	good	correct
SOFC	Solid-Oxide	800-1000	high	yes	yes	Laboratory trials	good	correct
DMFC	Proton Exchange Membrane	70-80	medium	no	yes	Research	low	no

Source: Literature ad [4]

b) **Partial oxidation:**

$$2H_3COH + O_2(air) \longrightarrow$$
$$\longrightarrow 3H_2 + CO + CO_2 + H_2O + heat \text{ (for methanol)}$$
$$H_3C(CH_2)_6CH_3 + 71/2\,O_2(air) \longrightarrow$$
$$\longrightarrow 6H_2 + 4CO + 4CO_2 + 3H_2O + heat \text{ (for petrol)}$$

The third known principle is the "**auto-thermal conversion**". This is a combination of conversion by means of water vapour and partial oxidation. Table 2 shows the quantity of hydrogen obtained by fuel conversions by means of water vapour and partial oxidation. [4]

Table 2 - Quantity of hydrogen obtained by fuel conversion

Approx. value, kg hydrogen / kg fuel		
Fuel	Water vapour	Partial oxidation
Methanol (CH3OH)	0.189	0.126
Ethanol (C2H5OH)	0.263	0.219
LNG (CH4)	0.503	0.377
LPG (C3H8/C4H10)	0.456	0.316
Petrol (C8H15.4)	0.430	0.284
Diesel (C14H25.5)	0.424	0.279

Source: as in Table 1

5. USING HYDROGEN AS FUEL IN VARIOUS VEHICLES

5.1. Using hydrogen as fuel in fuel cell vehicles

5.1.1. Opel Zafira hydrogen

The manufacturers of automobiles **Opel** and **Mazda** have promoted their so-called mid-solutions in which hydrogen is stored into special metal-hybrid tanks. Hydrogen energy source consists of 300 fuel cells, separated by platinum coated foil. The installed propulsion power is 50kW (68KS), out of which 33kW (45KS) can be used for propulsion. This is sufficient for the maximum speed of 110km/h and autonomy of movement up to 250 kilometres.

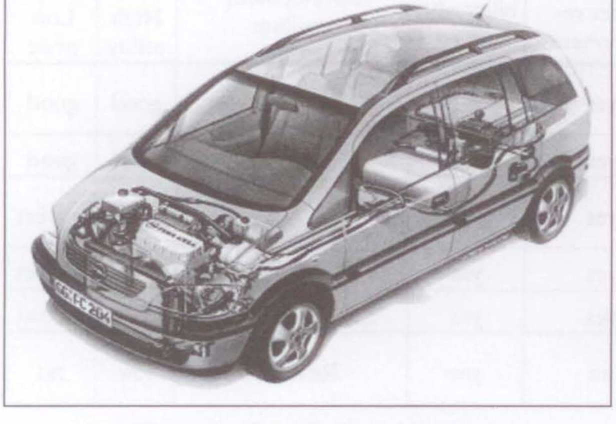

Figure 1 - Opel Zafira hydrogen

Initially the **automobile Opel Zafira HydroGen I** had propulsion of 50kW (68KS), and now it has been upgraded to 55kW (75KS). The marketing promotion will present **Opel Zafira** with five seats, propelled by three-phase electrical motor of 55kW power. [5]

5.1.2. DaimlerBenz Nebus [5]

For the moment, pure hydrogen fuel cells are most successfully used in urban buses (NEBUS) and vehicles of big transport companies where in centralized warehouses the storage of hydrogen and filling of vehicle tanks is most easily organized.

NEBUS is propelled by 150 fuel cells and has power of 250kW with a range of 250 kilometres. This concept could bring revolution into modern urban transport, since it fully satisfies the transport needs without any emission of harmful gases. [6]

Figure 2 - Nebus - Daimler Benz fuel cell bus

5.1.3. DaimlerBenz Sprinter

DaimlerChrysler delivered to the Hermes Versand company service the first fuel cell propelled **Sprinter**. DC is one of the leading world companies in the development of fuel cell technology. In the last ten years 16 prototypes of various vehicles have been developed in which the possibilities for the application of this technology were studied. This special sprinter has front wheel propulsion and uses hydrogen as propulsion

Figure 3 - Sprinter – fuel cell truck

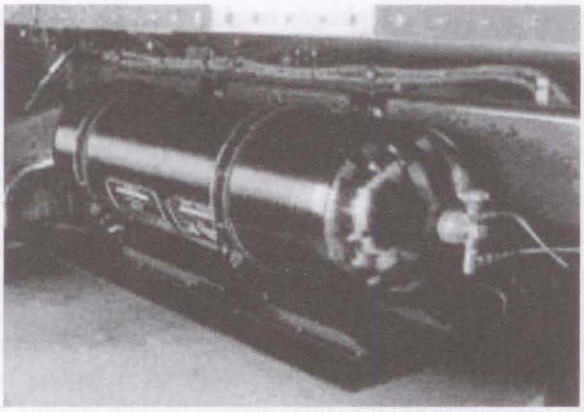

Figure 4 - Fuel cells in trucks

fuel. It belongs to the group of "zero-emission vehicles", i. e. vehicles that produce no harmful exhausts. Electrical motor of 55kW power allows vehicle speeds of up to 120 kilometres per hour.

Freightliner, liquefied hydrogen is located in special tank of 200 litre-volume

5.1.4. Freightliner

Electrical installations in the cabin consume a great amount of energy which requires engine running even when the truck is not moving. Freightliner offered a solution which eliminates this need.

After the solutions which use fuel cells to propel passenger cars (the mentioned Mercedes A class, i. e. NECAR, as the fuel cell propelled design is called, or Opel's Zafira Hydrogen) and coaches (Mercedes-Benz and MAN) the fuel cell truck appeared which uses fuel cells for the propulsion of electrical installations in the cabin, which significantly reduces fuel consumption and noise.

5.2. Using hydrogen as fuel in Otto-engines

BMW sees the alternative to petrol and diesel fuel in hydrogen, but they have chosen another method of converting energy and rely on the Otto-engine. In other words, the engine operates in the same way as the petrol engine; the air and fuel mixture is ignited by the electric spark, but instead of petrol, hydrogen is consumed. In BMW, they believe that only in this way the driver can be provided full joy of driving, for which the German manufacturer is well known, and at the same time keeping the "green" satisfied and the natural balance undisturbed. The proof lies in as many as nine records, set by the H2R study, presented for the first time to the public at the auto-show in Paris in 2004.

The prototype H2R has profited from the results of the serial development of the future BMW hydrogen engine for the first in the world premium limousine with bivalent propulsion: already during the manufacture of actual seven, BMW will launch one such model on the market, which will use hydrogen as well as petrol. The 6.0 litre V12 engine, known from model 760i has been chosen as propulsion aggregate. However, due to the different type of propulsion fuel this engine had to be completely redesigned. The double system vanos has been retained as well as completely variable control by suction valves (valvetronic), but due to high hydrogen combustion temperatures and the need for additional fresh air cooling of the combustion chamber, the times of opening and closing of valves are completely changed. Another important difference is in the method of fuel mixture generation: while in petrol version the fuel is injected directly into the cylinders, hydrogen is mixed with air already in the engine suction pipe.

Hydrogen propulsion allows significant saving in fuel. Only under full load, and in order to achieve maximum power, the engine runs on the mixture of the stoichiometric ratio (lambda = 1). However, at partial loads it duly turns to the lean mixture with high air share (lambda > 2), thus eliminating the suction losses. It should be noted that in the lean mixture area the hydrogen combustion does not generate harmful nitrogen oxides (NOx), so that the engine does not pollute the atmosphere.

Unlike fuel-cell prototypes, in which hydrogen is stored in tanks under very high pressure (250 to 500 bars), in its study, the BMW uses vacuum insulated double-wall crio-tank, which stores at a very low temperature somewhat more than 11 kg of liquefied hydrogen. Hydrogen is in the tank which is right behind the driver's back, under the pressure of only 4.5 bars. In order to avoid excessive pressure due to heating or some other unforeseen situation, there are automatic safety valves, which release it without any danger into the atmosphere the moment the pressure rises above five bars. The function of the fuel pump is taken over by the heat exchanger, after reducing the fuel pressure by means of the throttle valve to 3 bar, the heat brought by the cooling liquid into the exchanger allows evaporation of hydrogen, which is in turn conducted away by nozzles.

However, the engine power is much lower than in case of petrol. Thus 6.0-litre V12 engine develops "only" 285 (200 kw) instead of 445 KS (310kw). This is caused by the fact that hydrogen as gas occupies a much greater volume than the dispersed droplets of petrol and thus "steals" space from the air, including oxygen, necessary for the combustion of a greater volume of fuel. However, the aerodynamic experts have invested efforts and managed to reduce the air resistance coefficient to as little as 0.21, which with small area of the front projection (1.85 m^2) enabled H2R to reach the dizzy maximum velocity of 302.4 km/h. The

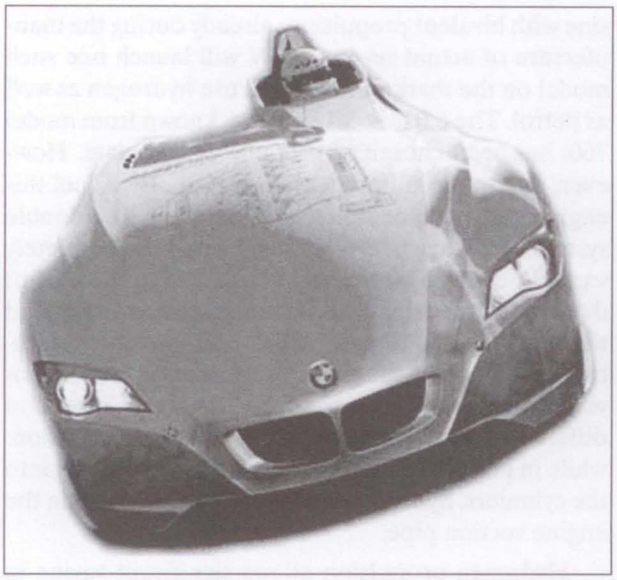

Figure 5 - BMW H2R – motor vehicle with hydrogen propelled Otto-engine

vehicle, weighing with full tank and the driver 1560 kg, accelerates from spot to 100 km/h in only six seconds, proving that hydrogen engine is capable also of explosive starts. [7]

6. ADVANTAGES AND DRAWBACKS OF HYDROGEN AS FUEL

Certain **advantages** of hydrogen technology include:

- hydrogen is one of the oldest industrial gases and its handling is safe;
- storing of smaller or greater quantities of hydrogen was tested without losses in quantity;
- due to some properties similar to natural gas during service undisturbed conversion is possible first through a mixture to subsequent full substitution, using the existing infrastructure;
- hydrogen is a multiple energy carrier that can be used for the production of electricity, heat, as well as propelling fuel;
- hydrogen is a neutral element, which means friendly to the environment, and in the ideal case only water and nitrogen oxides are generated.

Two major **drawbacks** in the technology of hydrogen are:

- storage, and
- for the production of hydrogen 90% of energy is consumed (for water electrolysis).

However, the usage of hydrogen as propelling energy must also satisfy:

- new infrastructures with special robotic filling stations,
- since liquefied hydrogen needs to be maintained at a temperature of –253°C (critical pressure 12.98 bar), special technique is necessary for the filling of an automobile tank,
- the driver should get used to driving without a regular gear-shift, since the lever serves only to adapt the driving to the road driving conditions.

By converting hydrogen at low temperatures into liquefied hydrogen, much higher tank storage density is achieved. The liquefied hydrogen evaporation level amounts per tank volume between 0.1 and 1% daily. The free storage losses allow absorption in metals. In the metal hybrid tank, high density of tank volume is achieved. Methyl-cyclohexane and ammonia are offered as chemical tank.

Since the entire technology requires greater attention and precision not matched by today's filling stations, one should wait for the expansion of new infrastructure with special robotic filling stations (the first have been installed at the Munich airport). Since liquefied hydrogen needs to be maintained at a temperature of –253°C, special technique is required for filling of automobile tank, so that at present hydrogen propulsion is mainly used for buses operating in public urban passenger transport.

6. CONCLUSION

Hydrogen fuel cells and fuel cell propelled vehicles face a great future as alternative to conventional motor vehicles. Fuel cells have many advantages: they allow zero emission of harmful substances, they realize high efficiency and good performances, they are quiet, and have a long lifecycle and low costs. Hydrogen as fuel can be produced from various renewable and non-renewable sources: oil, coal, natural gas, biomass and water. Hydrogen fuel cells combine advantages of electrical propulsion and conventional motor propulsion.

Finally, in a certain way, the dream about automobile hydrogen propulsion has come true. Hydrogen is interesting because of exemplary clean combustion and high energy value. The fuel cell uses hydrogen which in synthesis with oxygen releases electrical energy. The emission of harmful gases is reduced to a negligible minimum. Automobiles are almost noiseless. Regarding power, acceleration and final speed they do not differ significantly from the standard passenger cars, and with full tank they travel equal distances.

Hydrogen is fuel considered by the BMW Company as alternative to petrol and diesel fuel, but they selected another method of energy conversion. They rely, namely, on Otto-engines, rather than fuel cells. This engine operates in the same manner as a petrol engine, the air-fuel mixture being ignited by electric spark, but instead of petrol it consumes hydrogen.

In the automotive industry only, every major company has plans for the production of serial automobiles using alternative fuels. Let us mention just a few of the leading automotive industry firms which are investing billions of euros for this type of energy, such as: DaimlerBenz, Ballard, Opel, Toyota, Mazda, Nissan, BMW, Ford. In truck and bus industry, the focus is on: DaimlerBenz, DC, MAN, etc.

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SAŽETAK

MOGUĆNOSTI PRIMJENE VODIKA ZA POGON MOTORNIH VOZILA

Vodik je gorivo budućnosti, jer je sastavni dio vode (H_2O), koja nas okružuje i njihovi resursi su neograničeni. Voda se prvo mora rascijepiti na vodik i kisik. U članku je prikazano: laboratorijsko i industrijsko dobivanje vodika, vrste gorivih ćelija za različite namjene, motorna vozila na pogon vodikom, te prednosti i nedostaci vodika kao goriva uz uvjete koje mora zadovoljiti da bi se koristio kao pogonska energija motornih vozila.

KLJUČNE RIJEČI

vodik, gorivi članci, pretvarači goriva, Otto-motor, pogonska energija

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