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Hydrogen technologies: principles and prospects

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Abstract. The urgency of the paper is based on the growing interest in hydrogen stemming from the high energy capacity of that element. This makes hydrogen a promising vector for the future development of energetics. The paper examines the main chemical properties of hydrogen and the methods and technologies for hydrogen production from renewable energy sources as well as from the fossil fuels. The data on the volume and prospects of hydrogen production and usage are summarized.

Keywords: hydrogen, energy storage, energy source, energy density, hydrogen production techniques, hydrogen production from renewable sources, hydrogen production from fossil fuels, hydrogen production in the world, use of hydrogen.

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Introduction

With increase in population, the energy demand has increased significantly as well. Industrialization and urbanization pushed the energy demand on the rise. Presently, most of worldwide energy consumption is covered by non-renewable fossil fuels such as coal, natural gas and oil. The development of alternative energetics from renewable and sustainable sources is challenging.

Hydrogen is widely recognized as an energy storage medium. Growing interest in hydrogen is explained by its energy capacity that allows to conclude that hydrogen is the promising energy vector for the future. The interest is partially related to the ability of hydrogen to be a feedstock for many industries from transport to the power-utility sectors as well as household applications. Hydrogen has great chemical activity as well as easiness of creating new substance by reactions. It can be found in combination with other elements such as oxygen in the form of water and carbon in the hydrocarbons as well as in majority of organic composites. Being an abundant element on the planet, nonetheless it has to be produced. Presently, there are various techniques for hydrogen production, such as steam reforming and water electrolysis. These two processes have reached nowadays commercial maturity level when at the same time many others are still under research and development. Several energy sources exist to supplement hydrogen production as conventional course, which are hydrocarbons for steam petrification as well as nuclear and renewable energy sources. Producing hydrogen from renewable energy sources will not improve its sustainability neither insure its market penetration. Future hydrogen production will succeed implementing consumers' acceptance, distribution infrastructure as well as economic competitiveness.

Actual energy resources such as hydrocarbons are limited and there is a risk of their rapid depletion in the near future. Energy consumption optimization and its intensification are not solving the problem of energy sources. It provides only the so-called delaying effect. The problem of a future energy source arises from using hydrocarbons in present days with greenhouse gases produced by transportation. International agreements in regulation of greenhouse gas capture indeed reduced negative environmental impacts but still have not eliminated them. The bigger advantage of hydrogen is zero greenhouse gas emission, but only if it is produced from renewable energy sources. Only water vapor is generated from combustion of hydrogen, thus it is considered as the cleanest energy source. Considering hydrogen production drawbacks and its sustainability it remains an attractive energy vector. It offers the same environmental friendliness as renewable energy.

Chemical properties of hydrogen

Hydrogen is a chemical element denoted by the symbol H and has atomic number of 1. With standard atomic weight of 1.008, hydrogen is the lightest element in the periodic table. Its monatomic form (H) is the most abundant chemical substance in the Universe, constituting roughly 75% of all baryonic mass. Non-remnant stars are mainly composed of hydrogen in the plasma state. The most common isotope of hydrogen, termed protium (name rarely used, symbol ^1H), has one proton and no neutrons [1]. At standard temperature and pressure, hydrogen is a colorless, odorless, tasteless, non-toxic, nonmetallic, highly combustible diatomic gas with the molecular formula H_2. Since hydrogen readily forms covalent compounds with most nonmetallic elements, it plays a particularly important role in acid–base reactions because most acid-base reactions involve the exchange of protons between soluble molecules. In ionic compounds, hydrogen can take the form of a negative charge (i.e., anion) when it is known as a hydride, or as a positively charged (i.e., cation) species denoted by the symbol H^+. Hydrogen gas (dihydrogen or molecular hydrogen, also called diprotium when consisting specifically of a pair of protium atoms) is highly flammable and will burn in air at a very wide range of concentrations between 4% and 75% by volume. The enthalpy of combustion is −286 kJ/mol:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) + 572\ \text{kJ}\ \ (286\ \text{kJ/mol}) \qquad (1)$$

Hydrogen has three naturally occurring isotopes (Fig. 1) denoted ^{1}H, ^{2}H and ^{3}H. Other, highly unstable nuclei (^{4}H to ^{7}H) have been synthesized in the laboratory, but not observed in nature. Hydrogen gas forms explosive mixtures not only with air but also with chlorine at volume concentrations 5–95%. The explosive reactions may be triggered by spark, heat, or sunlight. The hydrogen autoignition temperature – the temperature of spontaneous ignition in air, is 500 °C (932 °F) [2].

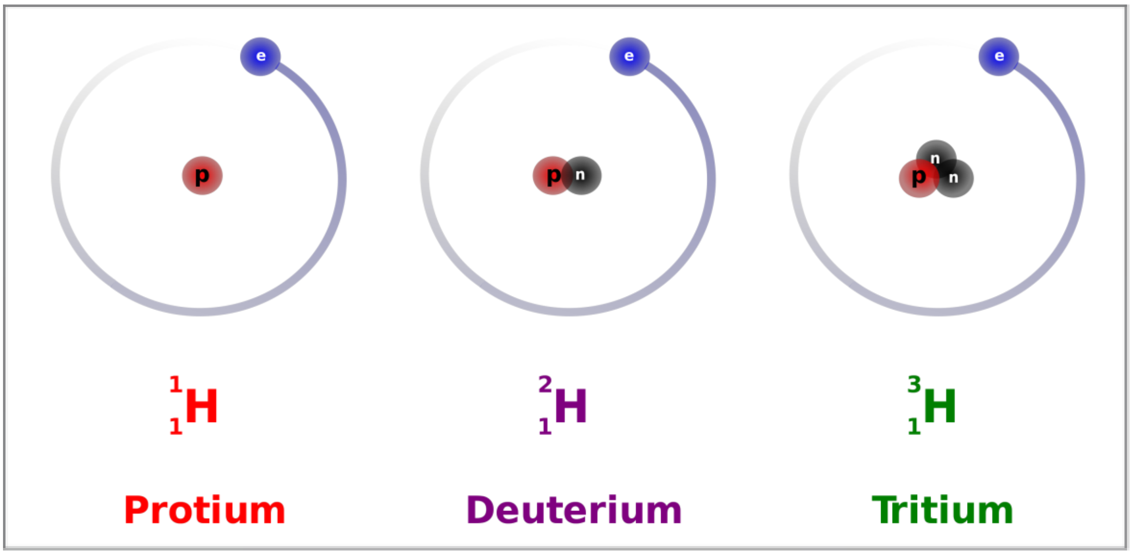


Fig. 1. Naturally occurring hydrogen isotopes [1]

Hydrogen can exist in different forms such as:

- *Gaseous;*
- *Liquid;*
- *Slush* which is a combination of liquid hydrogen and solid hydrogen at the triple point with a lower temperature and a higher density than liquid hydrogen. It is formed by bringing liquid hydrogen down to nearly the melting point (14.01 K or −259.14 °C) that increases density by 16–20% as compared to liquid hydrogen. It is proposed as a rocket fuel in place of liquid hydrogen in order to improve tankage and thus reduce the dry weight of the vehicle [3];
- *Solid* – is the solid state of the element hydrogen, achieved by decreasing the temperature below hydrogen's melting point of 14.01 K (−259.14 °C; −434.45 °F);
- *Metallic* – is a phase of hydrogen in which it behaves like an electrical conductor.

Energy density of hydrogen gas

Energy density is the amount of energy stored in a given system or region of space per unit volume. Colloquially it may also be used for energy per unit mass, though the accurate term for this is specific energy. In energy storage applications the energy density relates the mass of an energy store to the volume of the storage facility, e.g. the fuel tank. The higher the energy density of the fuel, the more energy may be stored or transported for the same amount of volume.

Energy density of hydrogen is extremely high. It varies between 120 MJ/Kg (Lower Heating Value, LHV) and 142 MJ/Kg (Higher Heating Value, HHV). It imposes additional challenges for storage capabilities and transportation. Considering natural gas energy density in liquid form at 250 bar, it is almost twice lower than the hydrogen energy density (Fig. 2).

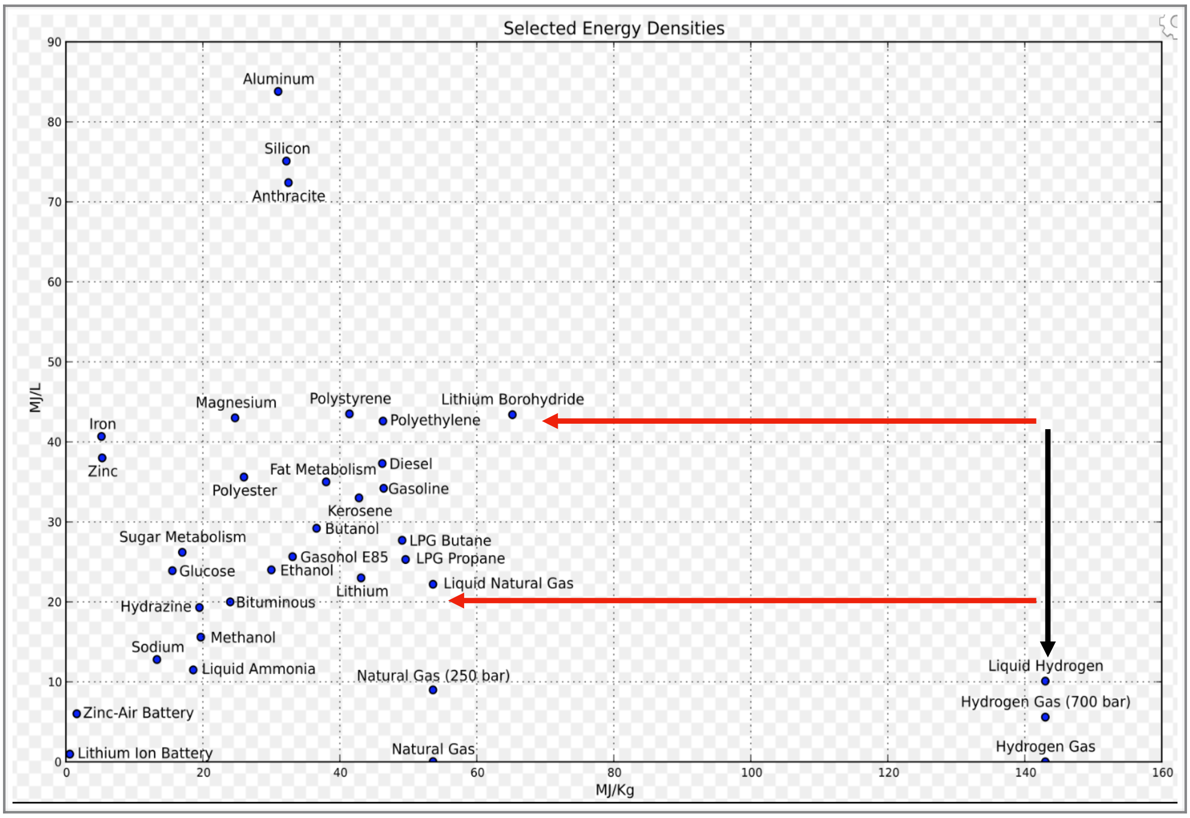


Fig. 2. Energy density chart for selected materials (in MJ/Kg) [4]

Hydrogen production techniques

There are several techniques available for hydrogen production. It can be produced from both renewable sources and fossil fuels. Hydrogen production from fossil fuels can be performed throughout steam reforming, partial oxidation, auto thermal oxidation and gasification. Hydrogen production from renewable sources can be performed through biomass/biofuels technologies and water splitting (electrolysis) by solar energy or wind energy.

Hydrogen production from hydrocarbons (primarily from natural gas) can be differentiated into three chemical reactions: Steam CH_4 reforming (SMR), Partial oxidation (POX), Autothermal reforming (ATR). During all these processes, other chemical reactants also involved. In SMR, steam reacts with hydrocarbons by endothermic reaction, whereas in POX oxygen is another reactant, which results in exothermic reaction. When two reactions are combined, it is called ATR [5].

SMR hydrogen production method gives high efficiency of approximately 74% with estimated cost of $1.8 per kg [6]. The process starts from removal of impurities, catalytic reforming for synthetic gas generation, water gas shift and methanation or gas purification. In order to obtain hydrogen, the process goes under the high temperature of 700–800 °C, and pressure of 3–25 bars, with steam to carbon ratio of 3.5. The process proceeds with catalyst, which can be made of precious metals such as platinum and rhodium, but mostly non-precious metals such as nickel are used. Their catalyst effectiveness, which includes heat and mass transfer, can be as minimal as 5%. However, due to the metal price difference, non-precious metals are widely used for that process. Attempts to use non-metallic catalysts have not had commercial success because of low activity. The main reactions for SMR are:

Reformer: $C_nH_m + nH_2O \leftrightarrow nCO + (n+m/2)H_2 \quad (-\Delta H^{\circ}298 = -1109 \text{ kJ/mol for } nC_7H_{16})$ (2)

Water gas shift reactor: $CO + H_2O \leftrightarrow CO_2 + H_2 \quad (-\Delta H^{\circ}298 = 41 \text{ kJ/mol})$ (3)

Methanator: $CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (-\Delta H^{\circ}298 = -206 \text{ kJ/mol})$ (4)

In the Fig. 3 it is shown that in order to obtain a good utilization of the feed for hydrogen production, it is necessary to operate the steam reformer with an outlet temperature around 800 to 950 °C. Heat has to be supplied to the process to achieve this outlet temperature. Several reforming technologies are available for getting the heat into the process.

These technologies can be differentiated by the means of heat transfer, which ranked in increasing intensity are based on convective heat transfer, radiant heat transfer and internal combustion. Most industrial hydrogen plants are based on radiant heat transfer in tubular steam reformers as described in the following.

The activity of catalysts depends on the nickel surface area. It can be shown by computer simulations that the catalyst is not the limiting factor for the operation of a tubular reformer. An increase of the heat flux and the load at given exit temperature by a factor of two results in an increase in methane leakage by only 10% [8].

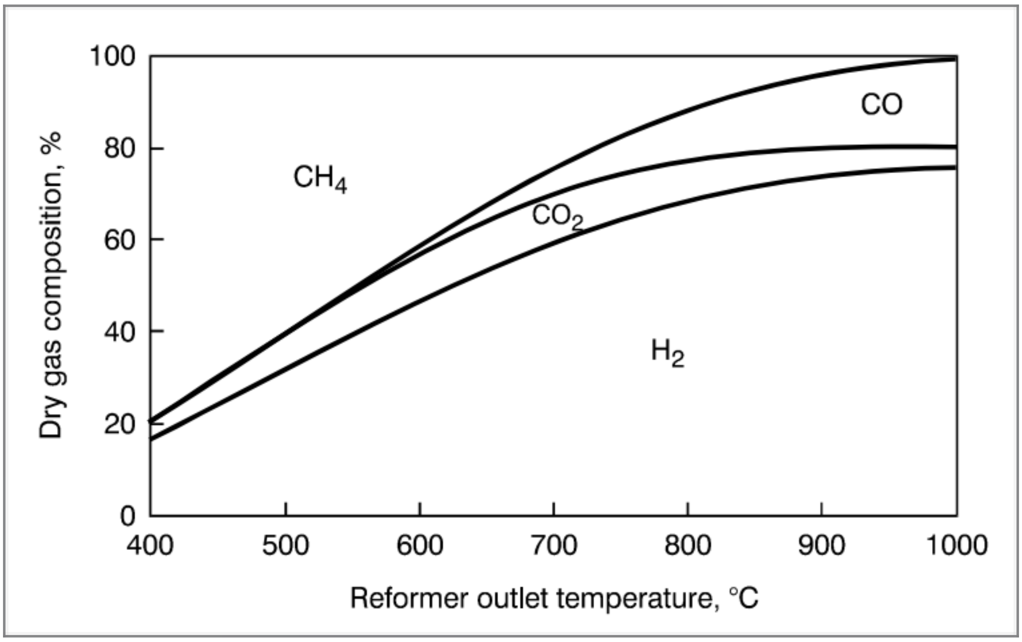


Fig. 3. Equilibrium composition out of a steam reformer at 26 bar with a feed steam to methane ratio of 2.5 [7]

For normal steam reforming catalysts, the utilization of the activity (as expressed through the effectiveness factor) is smaller than 10% because of transport restrictions. The low effectiveness factor means that for a given catalyst type, the activity is roughly proportional to the external surface area. The shape of the pellet should be optimized in order to achieve activity with minimum increase in pressure drop. The pressure drop depends strongly on the void fraction of the packed bed and decreases with increasing particle size. Hence, the optimum is a catalyst filling of pellets with large external diameter and with high void fraction as achieved with rings or cylinders with several holes (Fig. 4). Other solutions may be based on the use of catalysts based on ceramic foam, monoliths and even catalyzed hardware.

Fig. 4. Steam reforming catalysts [7]

Steam reforming of liquid hydrocarbons is also used for hydrogen generation for fuel cells, with diesel and jet fuel considered as «logistic fuels». The formation of carbon may lead to break-down of the catalyst and the build-up of carbon deposits and disintegrated catalyst pellets may cause partial or total blockage of the reforming tubes resulting in development of hot spots or hot tubes. The uneven flow distribution will cause a self-accelerating situation with further overheating of the hot tubes. Therefore, carbon formation cannot be tolerated in tubular reformers. The important problem is whether or not carbon is formed and not the rate at which it is formed.

Higher hydrocarbons show a higher tendency for carbon formation on nickel than methane does (Fig. 5). Therefore, special catalysts either containing alkali or rare earths or based on an active magnesia support are required. With low catalyst activity, the thermal cracking route (pyrolysis) may also take over in the reformer tube. This is the situation in case of severe sulphur poisoning or in attempts to use non-metal catalysts with low activity. The risk for carbon formation depends on type of hydrocarbon with the contents of aromatics being critical. Ethylene formed by pyrolysis results in rapid carbon formation on nickel [8].

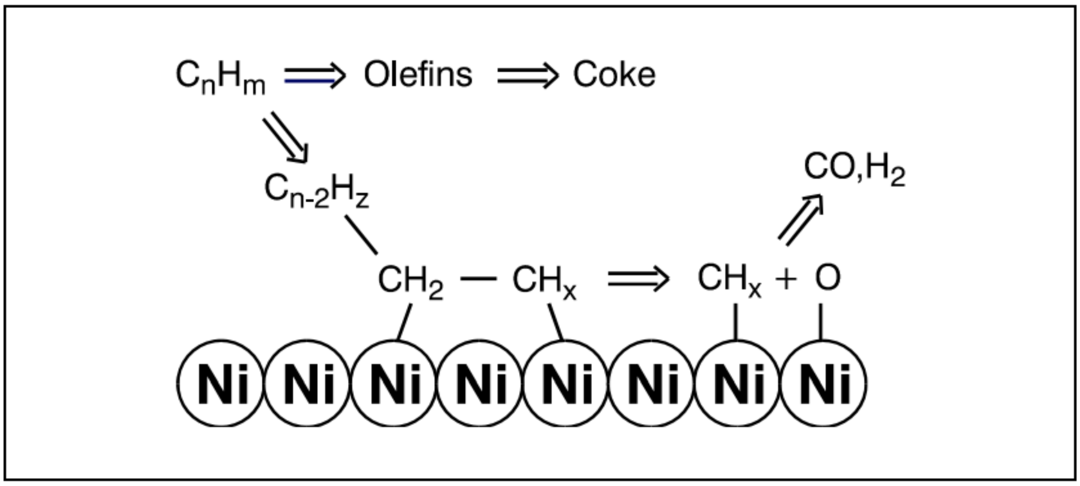


Fig. 5. Steam reforming mechanism of higher hydrocarbons [7]

It can be processed directly in the tubular reformer when using special catalysts as practiced in many industrial units, but the control of the preheat temperature and heat flux profile may be critical. These constraints are removed when using a pre-reformer as illustrated in Fig. 6. The pre-reforming catalyst is typically a highly active nickel catalyst. This catalyst also works as an effective sulphur guard for the tubular reformer and downstream catalysts, by removing any traces of sulphur still left after the desulphurization section.

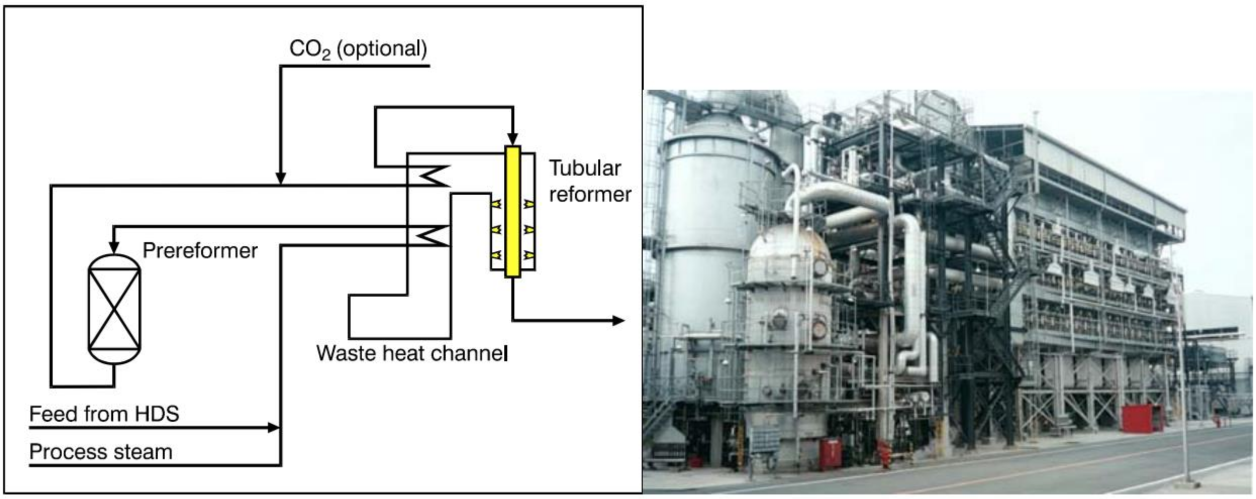


Fig. 6. Installation of a pre-reformer. Pre-reformer shown in front of a tubular reformer in a 70,000 Nm^3/h hydrogen plant at SK Corporation, Korea [7]

In industry, the reforming reactions are typically carried out in a heated furnace. In Fig. 7 an example is shown. Such reformers are built today for capacities up to 300,000 Nm^3 H_2 (equivalent)/h. The furnace consists of a box-type radiant section including the burners and a convection section to recover the waste heat of the flue gases leaving the radiant section.

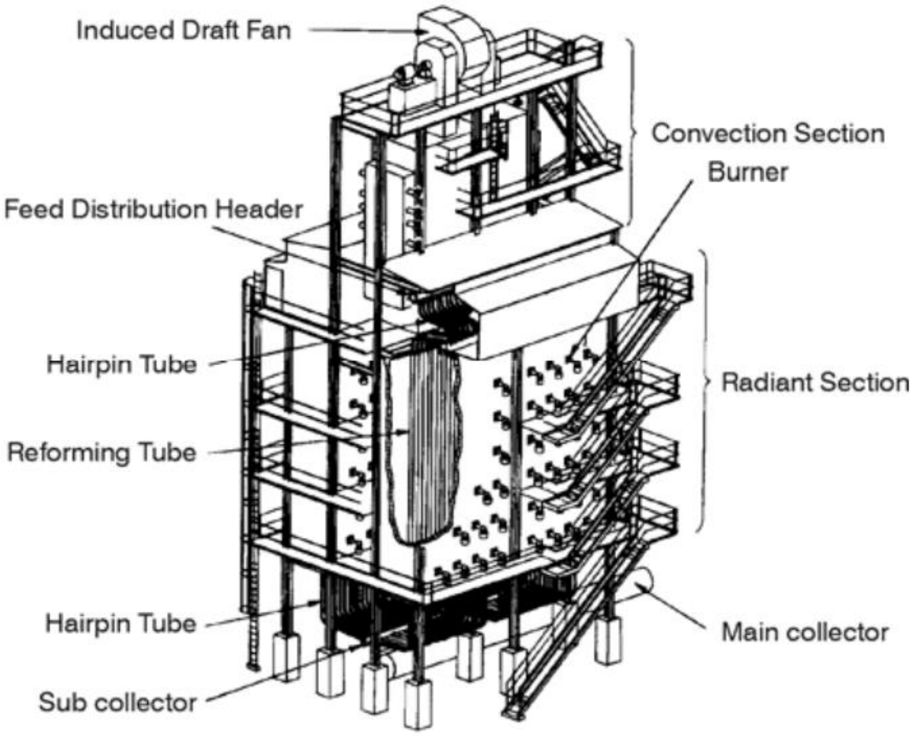


Fig. 7. Topsoe reformer with burners placed on side walls [7]

In this lay-out, the convection section for recovery of waste heat is placed on top of the furnace. The convection section can also be placed at the side of the furnace. In the radiant section, a nickel catalyst is loaded in a number of high alloy reforming tubes placed in a row along the furnace. The outer diameter of the tubes ranges typically from 100 to 150 mm and the length is from 10 to 13 m. Typical inlet temperatures to the catalyst bed are 450–650 °C, and product gas leaves the reformer at 800–950 °C depending on the application. Tubular reformers are designed with a variety of tube and burner arrangements. These include side-fired furnaces, top-fired furnaces and terrace wall furnaces.

Recent years have shown progress in steam reforming technology resulting in less costly plants not the least because of better materials for reformer tubes, better control of carbon limits, better catalysts, and process concepts with high feedstock flexibility. This has been supplemented by better understanding of the reaction mechanism and the mechanisms for carbon formation and sulphur poisoning, as well as the reasons for tube failure.

Modern hydrogen plants will almost invariably be designed using a low steam to carbon ratio. A high steam to carbon ratio (4–5 mol H_2O/C-atom) would result in higher conversion of the hydrocarbons, but a low steam to carbon ratio (typically 2.5 or lower) reduces the mass flow through the plant and thus the size of equipment. The lowest investment is therefore generally obtained for plants designed for low steam to carbon ratio. Also, a low steam to carbon ratio results in a more energy efficient plant and thus in lower operating costs. In principle, a low steam to carbon ratio increases the methane leakage from the reformer, but this can be compensated for by increasing the reformer outlet temperature to typically 920 °C.

Operation at a low steam to carbon ratio requires the use of non-iron containing carbon monoxide conversion catalyst, i.e. a copper-based medium temperature shift (MTS) catalyst. The conventional iron catalyst for high temperature shift (HTS) will be active for the Fischer–Tropsch synthesis below a certain steam to carbon ratio, when there is potential for formation of iron carbide. Pressure Swing Adsorption (PSA) for final hydrogen purification is normally used today. This layout gives a high purity hydrogen product (99.9% or higher) and a more efficient operation than traditional lay-outs with CO_2-absorption.

A typical process lay-out of a feedstock flexible hydrogen plant operating at 25 bar on refinery gas and natural gas is shown in Fig. 8. Refinery gas, containing large amounts of hydrogen, is sent to a PSA unit where pure hydrogen is extracted. The off-gas from the PSA, containing non-converted methane, is compressed and used as feed in the hydrogen plant. In this way, low grade refinery gas is used as feed to a hydrogen plant and thereby substituting more expensive natural gas [8]. PSA off-gas is mixed with natural gas or vaporized naphtha, and the gas mixture is preheated, desulphurized (over CoMo-catalyst and ZnO), mixed with process steam and further heated before entering the adiabatic prereformer. Typical inlet temperatures are in the range 450–550 °C, depending on feedstock and steam to carbon ratio.

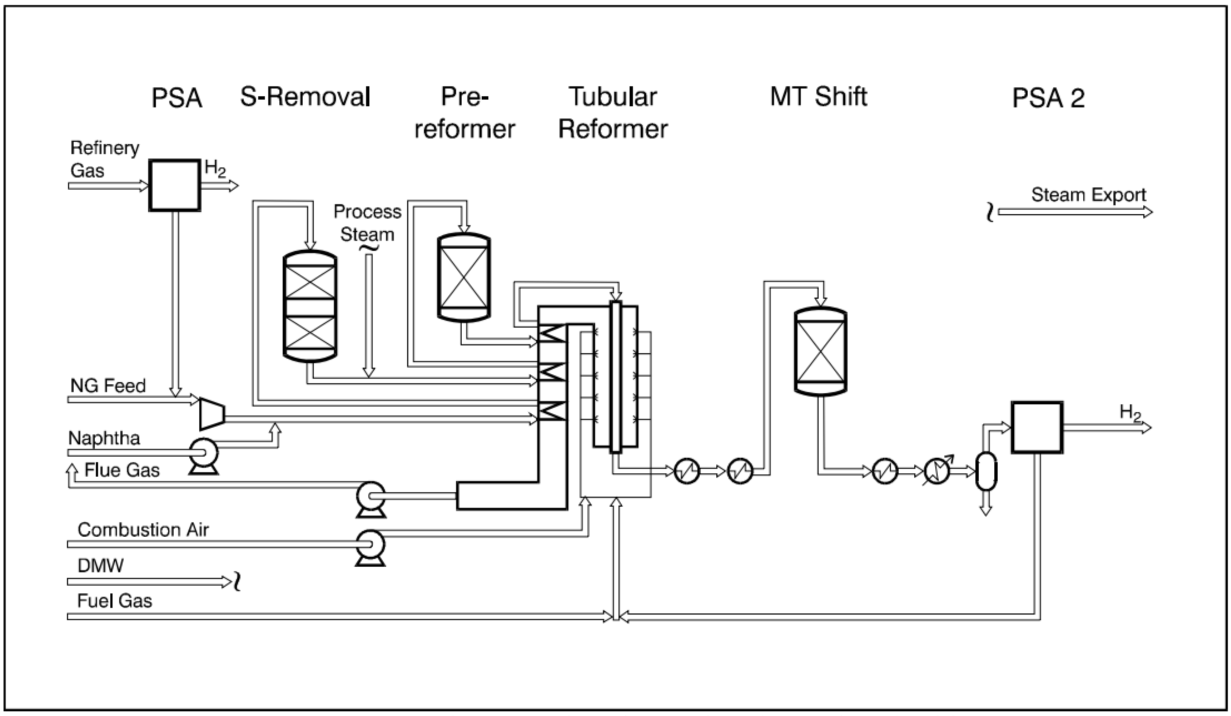


Fig. 8. Process lay-out of a typical multi feedstock H_2-plant [7]

The prereformed gas is then heated to 650 °C before entering the tubular reformer where final conversion of methane into hydrogen, carbon monoxide and carbon dioxide takes place at 850–950 °C depending on lay-out. The reformed gas is cooled by producing steam before entering the shift converter, typically containing a medium temperature shift (MTS) (210–330 °C). Over the copper-based shift catalyst, more hydrogen is produced by converting carbon monoxide and steam to carbon dioxide and hydrogen (reaction (3)). The shifted gas is cooled to ambient temperature before entering the second PSA-unit. The off-gas from this PSA unit is used as fuel in the tubular reformer supplemented with fuel gas.

In the Partial Oxidation process (POX), the generation of H_2 goes through the steam conversion, oxygen and hydrocarbons. It is both non-catalyst and catalyst process. Non-catalyst way of producing hydrogen is sulfur residue tolerant comparing with SMR method. Temperature range is between 1150–1315 °C. The feedstock may vary from methane, heavy oil and coal. Catalytic process has temperature range ~950 °C from methane to naphtha.

Partial Oxidation: $C_nH_m + n/2O_2 \leftrightarrow nCO + (m/2)H_2$ (5)

For very large grass root hydrogen plants (in excess of about 200.000 Nm^3 H_2/h), the different economy of scale of tubular reformers and oxygen plants may favour the use of oxygen for partial oxidation of the hydrocarbon feed as practiced in the autothermal reforming process.

Autothermal reforming or ATR is the combination of SMR and POX. In the autothermal reforming process, the feedstock is reacted with a mixture of oxygen and steam by the use of a burner and a fixed nickel catalyst bed for the equilibration (reactions (2) and (3)) of the gas (Fig. 9). This results in a lower oxygen consumption, $O_2/CH_4 = 0.5–0.6$ than used in noncatalytic routes. With addition of steam, it is possible to adjust the H_2/CO ratio. This cannot be achieved by non-catalytic routes, because the addition of steam results in a reduction of temperature and soot formation. On the other hand, the non-catalytic routes are the only technologies available for gasification of resid and at the non-destillate fuels. Two-step reforming features a combination of tubular reforming (primary reformer) and oxygenfired secondary reforming. In this concept the tubular reformer is operating at less severe operation, i.e. lower outlet temperatures. The comparison showed that the net energy consumption (feed + fuel – steam) was quite similar for the three technologies. The process scheme with the fired tubular reformer gives the highest export of steam. When comparing the oxygen-fired reforming technologies with the fired tubular reforming on investment cost, it shows that about 15–25% of the investment is reduced mainly by savings in the reformer section. However, the cost of oxygen supply must be added to the oxygenfired processes. Even for large scale plants (220,000 Nm^3 H_2/h) the oxygen price necessary for making the ATR technology attractive is about 5–10 $/ton, which is well below the current large-scale production cost of oxygen [9].

Coal hydrogen production methods are fixed bed, fluidized bed or entrained flow. For the industrial scale, high temperature entrained flow method is used to maximize the conversion of carbon to gas. The reaction is:

$$C(S)+H_2O+heat \rightarrow CO+H_2 \quad (6)$$

Hydrogen production happens along with coal gasification, with H_2 and CO produced, where H_2 is extracted and CO undergoes WGS reaction to produce more H_2. The process is endothermic, it requires heat and is energy-intensive.

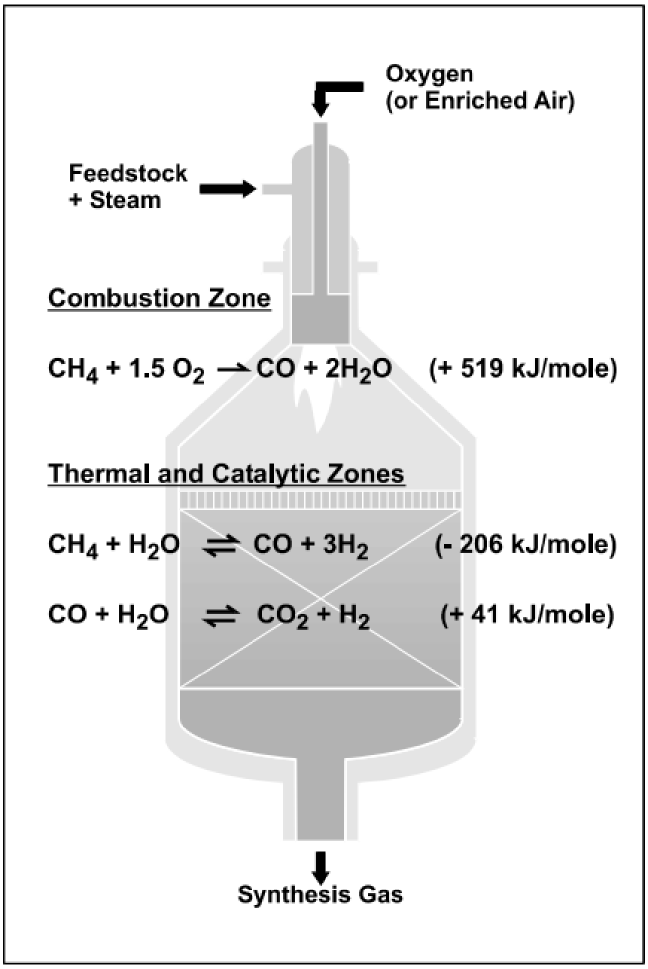


Fig. 9. Autothermal Reforming Process [7]

The current percentage of H_2 production from coal and SMR is presented in Fig. 10.

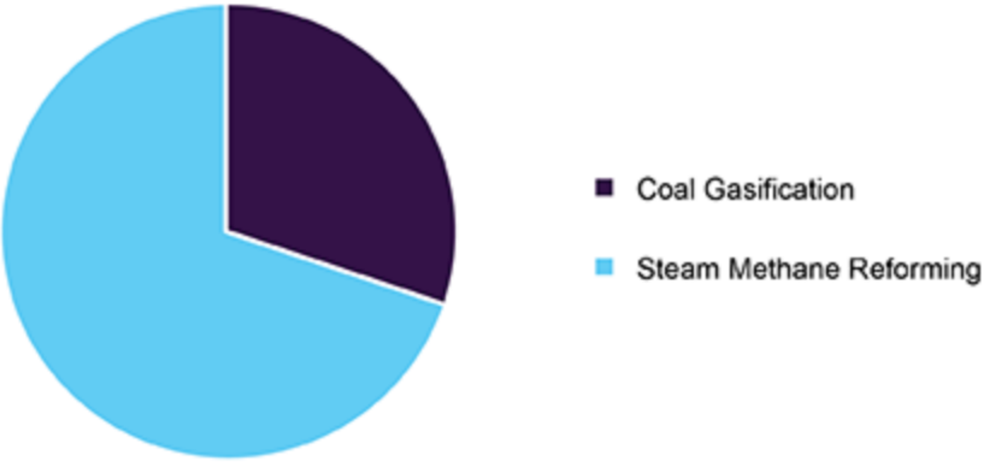


Fig. 10. Global hydrogen market share for 2016, by application [10]

Biomass process is another hydrogen production method. It is considered one of the most sustainable methods of hydrogen production from biomass resources. Variety of resources can be used to be converted to energy such as crops, waste and residue; forests waste and residue; as well as industrial and community waste. The method of energy (hydrogen) production mainly classifies into two categories: thermochemical and biological.

Thermochemical process has four types including pyrolysis, combustion, liquefaction and gasification. It is a process where hydrogen and hydrogen rich gases are obtained from conversion of biomass.

Combustion process involves the direct burning of biomass raw materials in the air in order to obtain heat from biomass chemical energy, as well as mechanics power or electricity by using equipment such as stoves, furnaces, boilers or steam turbines.

Pyrolysis process happens in the range of biomass heating temperature from 650 K to 800 K at 0.1–0.5 MPa and in reduced atmosphere (no air supply). Liquid oils are easily obtained. It is crucial to consider very important factors such as feedstock type, type of catalysis and temperature and the time of biomass residence to pyrolysis. This process is categorized into two categories: slow pyrolysis technique and speedy (flash) pyrolysis technique. In the fast pyrolysis biomass is heated rapidly to higher temperature in the absence of air producing vapor which is later condensed into a dark drown mobile bio-liquid [11].

The following phases are obtained during pyrolysis:

- Gaseous products including hydrogen, methane, CO_2, CO;
- Liquid products including tar and oil;
- Solid products – mainly consisting of char, pure carbon and some other inert materials.

The generation of hydrogen during speed pyrolysis can be presented as:

$$\text{Biomass} + \text{heat} \rightarrow H_2 + CO + CH_4 + \text{other products} \tag{7}$$

Methane and other hydrocarbon vapors can be processed later in STR for more hydrogen production. The reactions are presented below:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{8}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{9}$$

The produced oils can be further separated based on their solubility in which the soluble fraction is processed for H_2 production to increase the amount of hydrogen. Control parameters such as temperature and type of catalysis are vital in the pyrolysis process in order to produce hydrogen.

Pyrolysis process can be summarized into three main categories. The first is catalytic pyrolysis through the analysis of catalyst weight/biomass with continuous supply of biomass [12]. The second is catalytic steam reforming of pyrolysis liquids (bio-oil) through the pyrolytic reaction and optimization of the gas contents of N_2 and O_2 of the pyrolytic bio-oil. The third category includes some recent studies of in-line steam reforming of volatiles from biomass fest pyrolysis, by the effect of reforming parameters such as temperature, space time and steam/biomass ratios. This resolves bio-oil reforming problems related to bio-oil handling.

Gasification process occurs at higher temperatures (above 100 K) for which biomasses can be converted into a gas. The product of this process is charcoal after partial oxidation. Hydrogen is produced from reduction of charcoal (Fig. 11). The reaction of the process is:

$$\text{Biomass} + \text{heat} + \text{steam} \rightarrow H_2 + CO + CO_2 + CH_4 + \text{light and heavy hydrocarbons} + \text{char} \qquad (10)$$

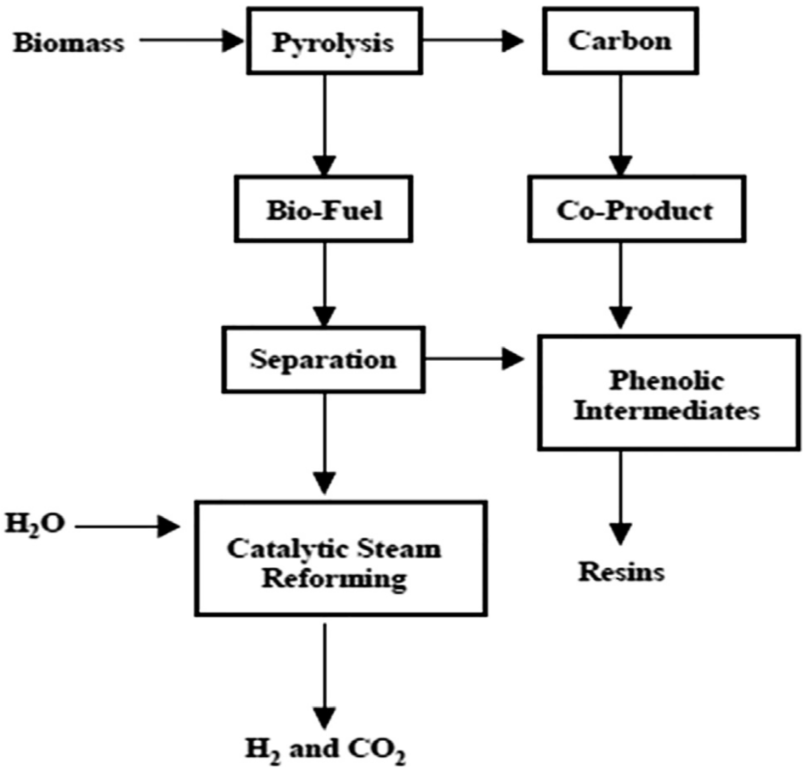


Fig. 11. The conversion of biomass to hydrogen by pyrolysis with co-products strategy [5]

Oxygen is needed for this process. The main goal is to obtain gaseous products whereas pyrolysis aims to obtain bio-oils and charcoal. The products can undergo steam reformation for hydrogen generation. This process can later be improved by WGS reaction. There are three main types of reactors: fixed bed, fluidized bed and indirect gasifiers used for gasifications. The type of biomass affects the hydrogen percentage during the production. Temperature ranges/rates, catalysis type are also essential parameters which affect hydrogen percentage. The main limitation is low thermal efficiency due to the moisture content in the biomass. It can be stated that this process can only be used for biomass with low moisture content (less than 35%) [13].

Biological process recently gained a lot of attention as it operates mostly at the ambient temperature and pressure thus less energy is required. Different waste materials and feedstock may be used for this process. It can be categorized into different types: direct biophotolysis, indirect biophotolysis, biological WGS reaction, photo-fermentation and other [14].

This process is mainly well controlled through hydrogen producing enzymes, such as hydrogenase and nitrogenase. Nitrogenase are MoFe and Fe proteins. With the possibility of nitrogenase to use magnesium adenosine triphosphate, hydrogen can be produced by the following reaction:

$$2e^- + 2H + 4ATP \rightarrow H_2 + 4ADP + 4Pi \qquad (11)$$

The bigger part of photosynthetic microorganisms contains hydrogenases which can further be categorized as uptake hydrogenase and reversible hydrogenase. It can act as catalysts for hydrogen consumption as follows:

$$H_2 \rightarrow 2e^- + 2H^+ \qquad (12)$$

The reversible hydrogenase have both the ability to produce hydrogen and consume it:

$$H_2 \leftrightarrow 2e^- + 2H^+ \qquad (13)$$

Direct photo-biolysis is a biological process shown in Fig. 12 and 13. In these pictures the solar energy absorption is shown into chemical energy by micro algae photosynthetic systems in order to produce hydrogen:

$$\text{Solar Energy} + 2H_2O \rightarrow 2H_2 + O_2 \qquad (14)$$

The process constitutes of two parts: photosystem 1 (PSI) producing reductant for CO_2 emission and photosystem 2 (PSII) splitting water and evolving oxygen. CO_2 reduction in PSI can yield hydrogen, which can be produced in the existence of hydrogenase from two photons of water. In microalgaes, water splitting occurs and hydrogen is produced. When oxygen content is beyond 0.1% the ability to produce hydrogen is reduced. Thus, oxygen content must be preserved [12]. Table 1 presents comparison of hydrogen production between wild-type microorganisms and their mutants [5].

Table 1

Comparison of hydrogen production between wild-type microorganisms and their mutants [5]

Microorganism	Comparison between wild-type microorganisms and mutants in its hydrogen production
Azotobactervinelandii	H_2 oxidation/H_2 evolution Wild type: O_2 inactivation of the wild-type enzyme causes approximately equal decreases in both evolution and oxidation activities and more efficient at catalyzing H_2 oxidation than mutants. Mutants have approximately equal H_2 oxidation and evolution activities
Rhodobactercapsulatus	Hydrogen from malate Wild type: show highly hydrogenase activity especially with consideration of carbon and nitrogen sources. Mutants exhibit almost no hydrogenase activity (hydrogenase deficient).
Anabaena	Mutants show higher tolerance to O_2 compare to wild type Anabaena
Rhodobactersphaeroides	Mutants produce 1.5 times higher H_2 than wild-type Mutants produce 50% more H_2 than wild types

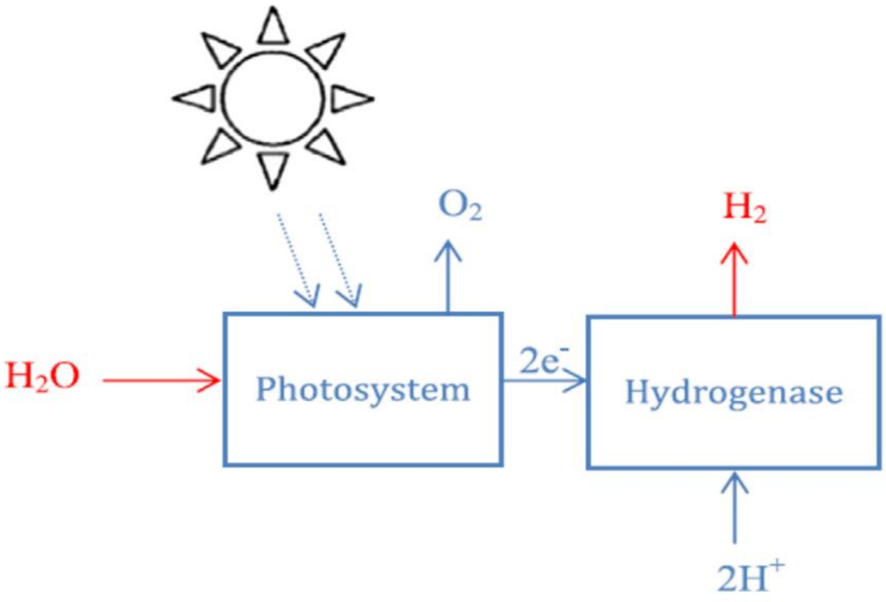


Fig. 12. Direct bio-photolysis flow diagram [15]

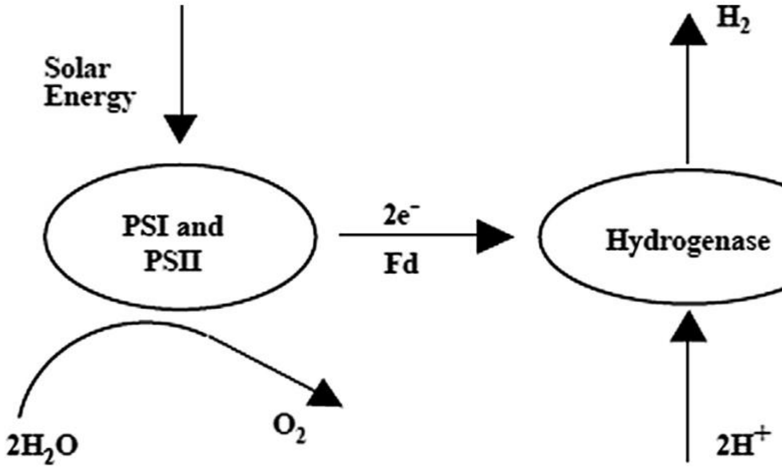


Fig. 13. Direct bio-photolysis [16]

Indirect photo-biolysis involves four main steps as illustrated on the Fig.14 and 15.

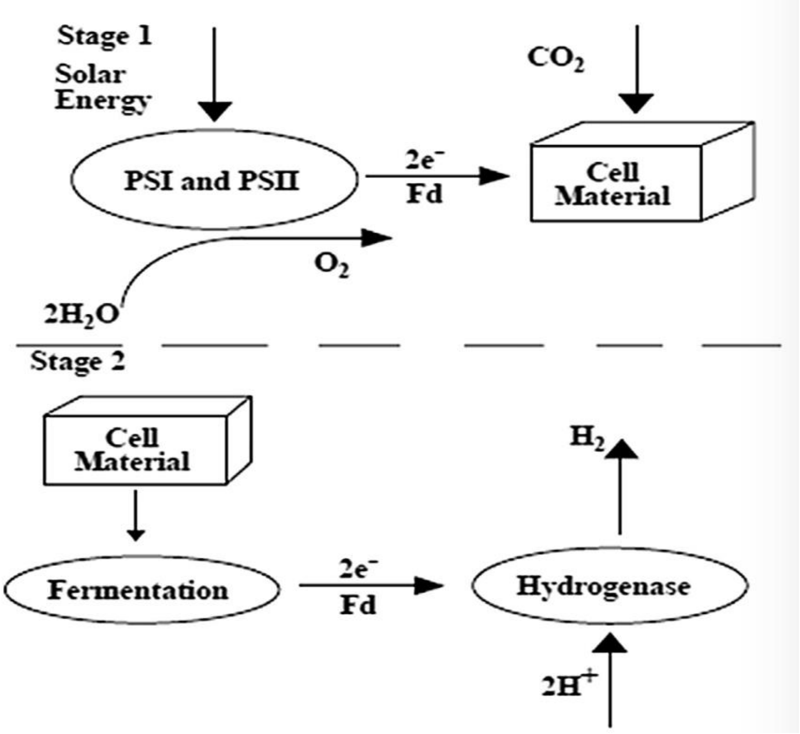


Fig. 14. Indirect bio-photolysis [16]

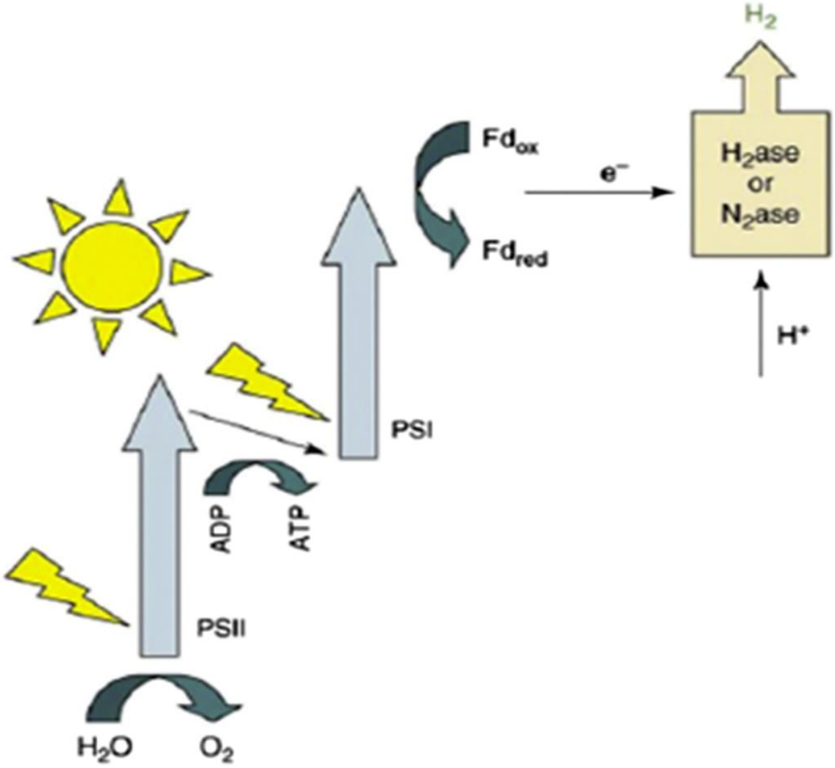


Fig. 15. Bio-photolysis of green algae or cyanobacteria [17]

Photosynthesis technique consists in biomass production, biomass concentration, aerobic dark fermentation and yields 4 mol hydrogen/mol biomass and conversion of 2 mol of acetates into hydrogen. The reaction can be presented as follows:

$$12H_2O+ 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2 \text{ light energy} \qquad (15)$$

$$C_6H_{12}O_6 + 12H_2O \rightarrow 12H_2 + 6CO_2 \qquad (16)$$

Hydrogen is produced by preserving the pH value between 6.8 and 8.3. The production is doubled with increasing temperature from 30 °C to 40 °C. One of the main challenges is that this process requires significant surface area.

Biological WGS process can be presented by formula (3)/(9). It utilizes carbon monoxide as a sole carbon source of some photoheterotrophic bacteria such as Rhodospirillumrubrum, which can survive in the dark where coupling oxidation of CO to the reduction of H+ to H_2. Organisms such as gram-negative bacteria and gram-positive bacteria are grown making process favorable for H_2 production. The main reason to make it was to identify whether there is suitable organism with high CO consumption and in order to calculate the rate of producing H_2. There were several tests using the new chemoheterotrophic bacterium Citrobaster [15]. The biological WGS is cheaper due to the elimination of reformer and associated equipment.

Photo fermentation hydrogen production goes through the use of solar energy and organic acids or biomass and with the action of nitrogenase. Hydrogen is produced by photosynthetic bacteria in a process known as photo-fermentation (see Fig. 12).

Light harvesting bacteria pigments such as chlorophylls scavenge light energy, transferred to membrane reaction centers, likewise photolytic plants. The water splits into protons, electrons and oxygen depending on sunlight conversion [16]. One of the major drawbacks for that technology is high-energy demand and low efficiency of solar energy conversion which requires detailed anaerobic photobioreactors covering large areas. In the long run, this method is not competitive for hydrogen production.

Dark fermentation primarily focuses on fermentation by anaerobic bacteria as well as some micro algae, on the carbohydrate-rich substances under anoxic condition (no oxygen) to obtain hydrogen at 30 °C to 80 °C in the dark.

The main process is presented in Fig. 16. The process differs from the bio photolysis process in which only hydrogen is produced. In the dark fermentation other gases in combination with H_2 and CO are also produced such as CH_4 and H_2S which depends on the reaction process and the substrate used. The reactions are:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \quad (17)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_2CH_2CH_2OOH + 2H_2 + 2CO_2 \quad (18)$$

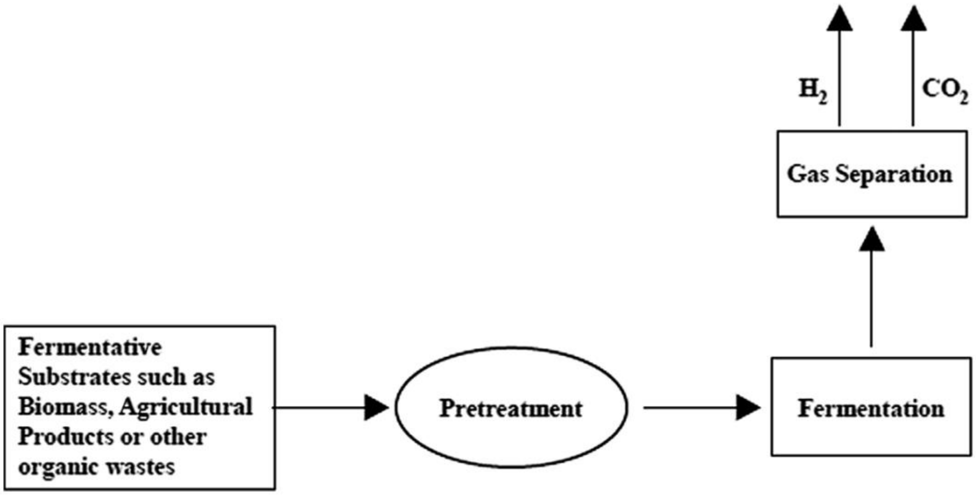


Fig. 16. Dark fermentation pathways [16]

The important aspect for this process is that partial pressure of H_2 should be maintained to prevent the formation of reduced substrate as lactate and ethanol, so the pH value is to be maintained between 5 and 6. This method has several advantages over the others such as simplicity, lower net energy input and use of lower-value waste, and continuity of hydrogen production without light existence.

Solar Energy. In general, methods of hydrogen production utilizing solar energy are classified into four main types, namely: photovoltaic, solar thermal energy, photo-electrolysis and bio-photolysis. The latter two have yet been described.

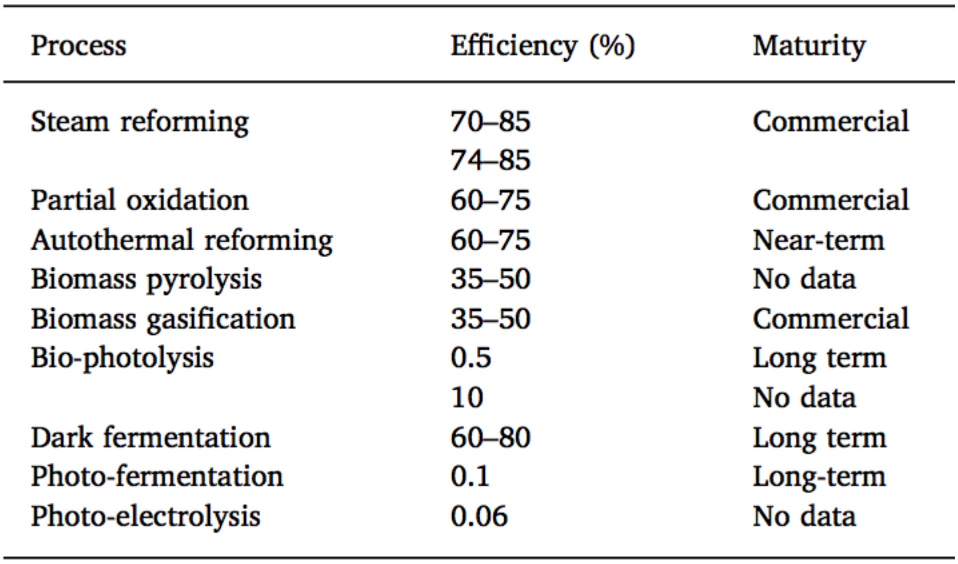
The history of hydrogen production by photovoltaic method (PV) starts from 1970, when first PV cells were introduced for electrolysis of water. With current photo-converter efficiency of 20% and electrolyzer efficiency of about 80%, the efficiency of solar energy conversion is 16% [18, 19].

This technology needs more investigation and improvements towards energy efficiency, safety, durability and reliability. For hydrogen production using PV cells, similar procedure is used except that the solar energy is harvested and concentrated in order to obtain high temperature heat source for endothermic reaction of water decomposition.

Table 2 presents a comparison of different hydrogen production methods.

Table 2

Selected hydrogen production processes with efficiency and advancement of the technology [5]



Process	Efficiency (%)	Maturity
Steam reforming	70–85	Commercial
	74–85	
Partial oxidation	60–75	Commercial
Autothermal reforming	60–75	Near-term
Biomass pyrolysis	35–50	No data
Biomass gasification	35–50	Commercial
Bio-photolysis	0.5	Long term
	10	No data
Dark fermentation	60–80	Long term
Photo-fermentation	0.1	Long-term
Photo-electrolysis	0.06	No data

In photo-electrolysis, water directly decomposes into H_2 and O_2 by using sunlight. The mechanism of hydrogen production is:

- Photon with sufficient energy will generate an electron-hole pair;
- Electricity is generated from the electrons flow in a chemical reaction from anode to cathode;
- Water is decomposed into H+ ions and O_2;
- H+ ions are reduced at cathode to H_2;
- Product gases are separated, processed and stored.

The process occurs as follows:

$$\text{Anode:} \quad 2p^+ + H_2O \rightarrow 0.5O_2 + 2H^+ \tag{19}$$

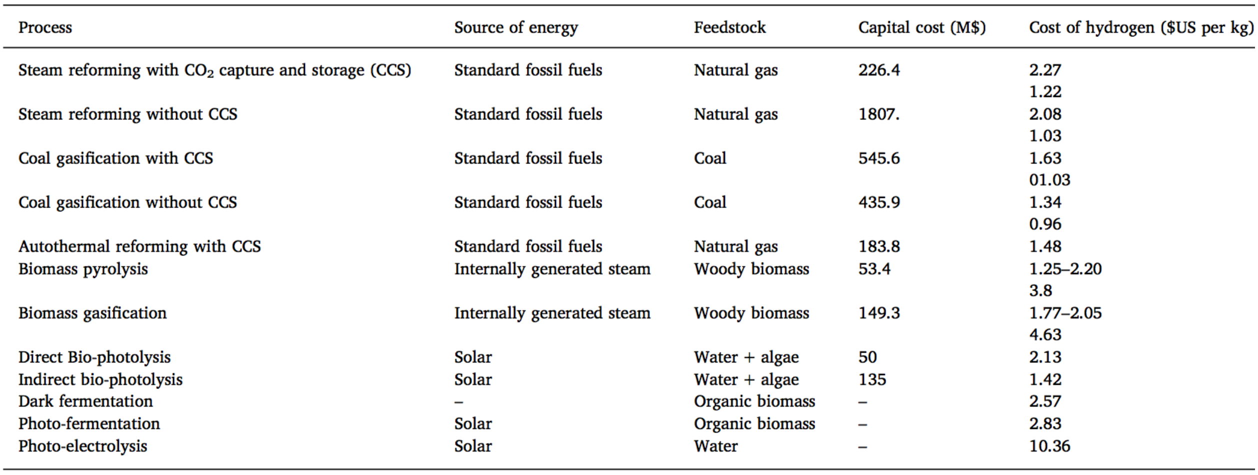
$$\text{Cathode:} \quad 2e^- + 2H^+ \rightarrow H_2 \tag{20}$$

The efficiency is mainly dependent on the properties of photoelectron materials. Characteristics of an efficient photoelectrode include stability, inexpensive materials, low conduction band. Also, it should provide most absorption capability during photon generation in the solar spectrum.

The capital cost comparison of hydrogen generation methods is presented in Table 3.

Table 3

Selected hydrogen production processes feedstock and it's capital cost with the cost of hydrogen [5]



Process	Source of energy	Feedstock	Capital cost (M$)	Cost of hydrogen ($US per kg)
Steam reforming with CO_2 capture and storage (CCS)	Standard fossil fuels	Natural gas	226.4	2.27 1.22
Steam reforming without CCS	Standard fossil fuels	Natural gas	1807.	2.08 1.03
Coal gasification with CCS	Standard fossil fuels	Coal	545.6	1.63 01.03
Coal gasification without CCS	Standard fossil fuels	Coal	435.9	1.34 0.96
Autothermal reforming with CCS	Standard fossil fuels	Natural gas	183.8	1.48
Biomass pyrolysis	Internally generated steam	Woody biomass	53.4	1.25–2.20 3.8
Biomass gasification	Internally generated steam	Woody biomass	149.3	1.77–2.05 4.63
Direct Bio-photolysis	Solar	Water + algae	50	2.13
Indirect bio-photolysis	Solar	Water + algae	135	1.42
Dark fermentation	–	Organic biomass	–	2.57
Photo-fermentation	Solar	Organic biomass	–	2.83
Photo-electrolysis	Solar	Water	–	10.36

Nowadays, water electrolysis method is one of the simplest methods of hydrogen production. One of the main advantages of this method is the possibility to produce hydrogen from renewable energy sources such as wind or solar power. Water electrolysis is small scale process and it is suitable for mobile hydrogen units. It can be more sustainable if electrical course is delivered from renewable energy sources. Hydrogen is also a perfect energy storage material in case of abundance of reliable energy. In remote areas with no renewable energy resources for generating electricity one can take advantage of water electrolysis to produce hydrogen in order to meet energy needs such as transportation with fuel cells. Produced hydrogen from renewable energy has the advantage of mobility, which is essential for supplying energy in areas away from the main electricity grid.

Small scale hydrogen production units by water electrolysis can be used to produce pure hydrogen and oxygen for various purposes including life-supporting systems and may avoid the need for large numbers of cryogenic, liquid hydrogen tanks or a huge hydrogen pipeline system. For developed infrastructure of hydrogen, mobile units by water electrolysis can co-operate with existing electric power grid as the backbone, contributing to the load leveling by changing operational current density in accordance with the change in electricity demand. This process has advantages of availability and flexibility, and high purity. Electrolysis process for hydrogen production needs improvements in energy efficiency, safety, durability, operability and portability and reduction in installation and operational costs [19].

Presently, reliable technologies are integrating in water electrolysis hydrogen production, such as methods for distributed hydrogen production, storage and use, particularly in remote communities. There exist several new concepts for hydrogen production such as photovoltaic electrolysis and steam electrolysis.

Fig. 17 represents the simplest water electrolysis unit.

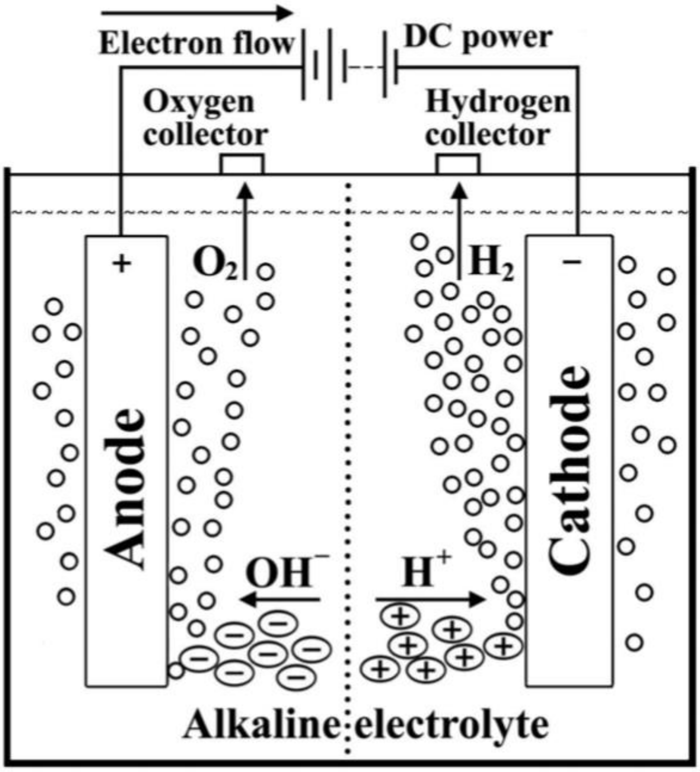


Fig. 17. Basic scheme of a water electrolysis system [19]

The unit consists of an anode and a cathode connected through an external power supply and immersed in a conducting electrolyte. A direct current (DC) is supplied to the unit. The flow of electron goes from the negative terminal of the DC power source to the cathode. On the cathode electrons are consumed by hydrogen ions (protons) to form atoms. A diaphragm is used to separate the two compartments. In order to collect produced oxygen and hydrogen gases, special collectors are installed.

For water electrolysis, several types of liquids can be used – acid, alkali or neutral aqueous electrolyte. The chemical reaction of water electrolysis in an acid is:

Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ ($E_0 = 0.00$ V vs. SHE, standard hydrogen electrode) (21)

Anode: $H_2O(l) \rightarrow 1/2\ O_2(g) + 2H^+(aq) + 2e^-$ ($E_0 = 1.23$V vs. SHE) (22)

The sum of the equations (21) and (22) will give the overall reaction of water electrolysis:

Overall: $H_2O \rightarrow H_2 + 1/2\ O_2$ ($E_0 = -1.23$ V vs. SHE) (23)

In case of alkali water electrolysis, a strong base is used as the electrolyte where hydroxide anions head towards anode surface and lose their electrons. The reactions for alkali water electrolysis are given by equations (24) and (25), with the sum of them giving the same overall reaction (25).

Cathode: $2\ H_2O + 2e^- \rightarrow H_2 + 2OH^-$ ($E_0 = -0.83$ V vs. SHE) (24)

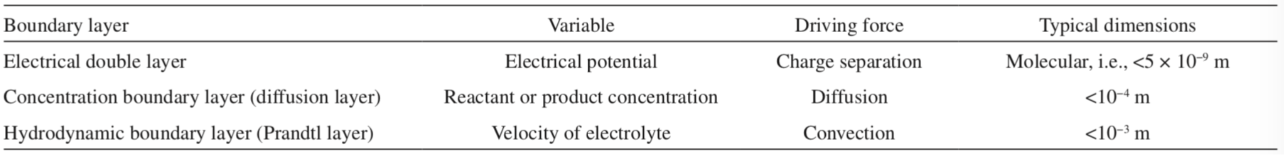
Anode: $2\ OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^-$ ($E_0 = 0.40$ V vs. SHE) (25)

The overall reaction has the same value (−1.23V) for the theoretical cell voltage [19]. For this process there are several barriers which have to be overcome such as boundary layers at electrode surface, electrode phase, electrolyte phase, separator, and electrical resistance of the whole circuit.

The electrolytic reaction is heterogeneous takes place at the boundary between the electrode phase (solid metal) and electrolyte phase (aqueous solution). Different boundary layers near the electrode surface lead to different consequences. The nature of such phenomena is different and requires attention during production (Table 4).

Table 4

Table of boundary layers at the electrode surface [19]



Boundary layer	Variable	Driving force	Typical dimensions
Electrical double layer	Electrical potential	Charge separation	Molecular, i.e., $<5 \times 10^{-9}$ m
Concentration boundary layer (diffusion layer)	Reactant or product concentration	Diffusion	$<10^{-4}$ m
Hydrodynamic boundary layer (Prandtl layer)	Velocity of electrolyte	Convection	$<10^{-3}$ m

It can be seen from Table 4 that hydrodynamic and concentration boundary layers lead to mass transfer of reactants and products within the solution [19]. The electrical double layer is sized over molecular dimensions at the electrode/electrolyte interface. It arises from the charge separation between an electrode and the surroundings electrolyte. The simplified model of the problem of double layer (negatively changed electrode) bound is presented below in Fig. 18. This layer prevents having a surplus of electrons.

Fig. 18a shows the compact layer consisting of cations, which are attracted electrostatically to the surface of the electrode, and absorbed solvent molecules. Out of the compact layer one can see a diffuse layer where ions retain a structure that is stronger than in the bulk electrolyte. In Fig. 18b, the potential field is presented. The potential decays linearly over the compact layer and then exponentially over the diffuse layer. The electrolysis system operates in two capacitances, one for the compact and another for the diffuse system.

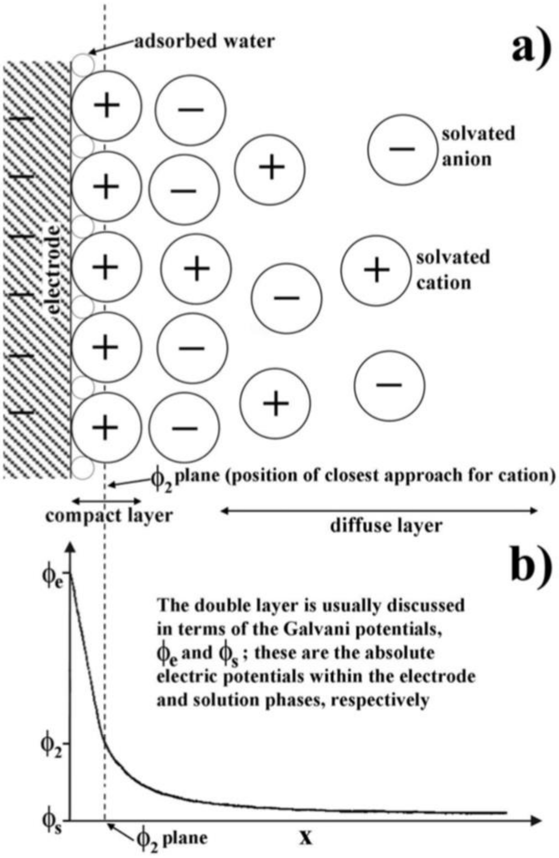


Fig. 18. Double layer near a negatively charged electrode surface:
a) Simplified schematic of the layer structure; b) Potential vs. distance profile [19]

This double layer has several important consequences. First is the difference in potentials between electrode and solution phase. It provides the main driving force for the process transferring the reaction across the interface. The second consequence is that this driving force may be affected by absorption of species such as reactants, products, solvent, ion, and contaminants in the solvent at the electrode surface. The third consequence is that local differences in potentials between the electrode and the solution may change the cringing force for reaction and its rate, and so the electrical current. The fourth consequence is that potential difference across the interface is localized over molecular distances, causing the potential gradient to be extremely large [19]. The fifth consequence is that the double-layer capacitance measurements can provide useful information for adsorption on electrodes. This process tends to create several problems with electrodes when it changes the current. The problem is in kinetic studies, at high surface area electrodes, when the process of changing the current is rapid. In this case, it tends to deteriorate. It is crucial for big scale industrial reactors; power supplies should be designed and controlled to handle such start-up, shut-downs, and other conditions where the electrode potential changes abruptly.

The water electrolysis is an emission free and environmentally friendly technology. The modern big-scale hydrogen production by water electrolysis units tends to have low efficiency in comparison with small-scale units. Big-scale units have efficiency of almost 60–75% (early units). However, small-scale units have 80–85% (best practice units).

As it was mentioned above, water electrolysis prices are associated with a lot of technical challenges and issues for sustainable hydrogen production with higher efficiency. The future trends show that higher efficiency can be reached through process optimization and using renewable energy sources for electricity. Renewable energy sources spring additional issues into the water electrolysis process such as intermittence and frequency balance for stable supply. It requires additional and special equipment for water electrolysis process for hydrogen production.

Hydrogen production in the world

Presently there are several countries which focus on hydrogen production. These countries can be classified into regions, such as Asia, Europe, and the rest of the world.

In Asia there are a lot of countries where hydrogen production is developed nowadays, namely Japan, China, Indonesia, Malaysia, Philippines, Saudi Arabia, Singapore, Taiwan, Thailand, Vietnam, India, South Korea, etc. The companies which operate in the Asia region are Air Liquid, Air Products, Deokyang, Iwatani, Linde, Messer, Praxair, Shanghai HuaLin Industrial Gases, Taiyo Nippon Sanso. All these companies produce hydrogen in gaseous form. There are not that many companies which produce liquid hydrogen. Liquid hydrogen production companies are located in Japan (Iwatani, Kawasaki) and in Russia, Magadan region. For liquid hydrogen, the main source is SMR, whereas for location in Russia it is electrolysis due to the availability of nuclear power station in that city (the Bilibino nuclear power station). For the rest of the companies listed above, the main sources for gaseous hydrogen production are SMR and by-production with the syngas.

In Europe there are a lot of countries where hydrogen production is developed presently, namely France, Netherlands, Germany, Belgium, Italy, Portugal, Spain, Switzerland, Czech Republic, Slovakia, UK, Austria, Finland, Sweden, Hungary, Ireland, Serbia, Norway, Poland, Iceland, Denmark. There are a lot of companies which operate in Europe, including

Scandinavian Peninsula. The main sources of hydrogen production are SMR and by-production, and only one country (Greece) utilizes electrolysis process.

The rest of the world. The rest of the countries which produce hydrogen (not mentioning USA) are Argentina, Brazil, Madagascar, Trinidad and Tobago, Venezuela, Australia, Chile, Peru. The main sources of hydrogen production are SMR and byproduction, and there are no electrolysis production sites. It may be stated that SMR is used due to the big natural gas resources in the countries such as Argentina, Chile, Australia, and Venezuela. Liquid hydrogen is produced by only one country, Guiana, as a rocket fuel.

There are not that many open sources of information regarding the companies' incentives and infrastructure developments towards hydrogen production. But some information about several hydrogen producing countries is available. The general information of those countries is presented below.

Norway does not have numerical goals, but there have been set ambitious goals for reducing vehicular emissions in the Oslo region (50% below 1990 levels by 2030 despite projected population increase of 40%) [20]. To reach these goals, they have adopted strong incentives aimed at stimulating the demand for zero emission vehicles (ZEV), whether battery electric (BEV) or fuel-cell electric (FCEV). They have also announced ambitious plans for supporting the required infrastructure.

Norway has several incentives to stimulate sales of zero emission vehicles (BEVs and FCEVs), including:

- Exemptions on sales and value added taxes;
- 90% discount on annual road taxes;
- Exemptions on highway and ferry tolls and municipal parking fees;
- Access to public transport lanes;
- Access to thousands of public charging stations for BEVs.

Hydrogen is currently produced as an industrial byproduct and from electrolysis. Despite its abundant supplies of natural gas, Norway does not foresee using the natural gas as a feedstock for H_2 production. Future H_2 production for the transport sector is expected to come from electrolysis powered by renewable resources, mainly hydro and wind. Approximately 96% of electricity produced in Norway comes from renewable resources. Norway and Sweden recently established the Green Certificate Market, which aims to increase the role of renewables in both countries [20]. There are six operational hydrogen-refueling stations in Norway. Development of the refueling structure was initiated in 2004 with the HyNor project. The Ministry of Transport and Communications support the infrastructure development and recognize the need for further investment to support early adopters and to enable the H_2 economy.

France does not have numerical goals for FCEVs. The French Environment and Energy Management Agency (Agence de l'Environnement et de la Maîtrise de l'Énergie) has developed a hydrogen roadmap that specifies needs for projects demonstration of low carbon vehicles, either electric or fuel cell. In addition, France launched the H_2 Mobility project in 2013. Objectives include development of a common roadmap for H_2 deployment in France and to support its implementation, including deployment of local fleets [20]. France has not yet defined policy mechanisms for incentivizing the sales of FCEVs. Incentives will be addressed by the H_2 Mobility France project. Hydrogen is currently produced for industrial needs from natural gas (40%) and byproduct production (60%) [21]. Future H_2 production for the transport sector is expected to come primarily from electrolysis, using low-CO_2 intensive electricity. The current infrastructure is limited to a handful of private locations. The infrastructure necessary to support future transport-sector growth will be defined by the H_2 Mobility France project [20].

Spain has not adopted numerical goals for the introduction of FCEVs but has adopted a number of incentives aimed at promoting the introduction of zero emission vehicles, whether BEV or FCEV [20]. As for 2014, the main incentive was a subsidy of 7,500–21,000 € for the purchase of ZEV vehicles. Proposed additional incentives include parking discounts and exclusive access to city centers. Spain views H_2 production from wind as a possible solution to current problems associated with the intermittency of renewable energy. While the focus will likely remain on utilizing wind resources, other potential pathways may include using imported natural gas, coal, and biomass, depending on the economics. There are four operational hydrogen-refueling stations in Spain; three are designated for FC buses. Longer-term goals are based on the recent EU directive suggesting that countries develop networks of stations approximately 300 km apart.

Italy has an overall goal of 10% renewable fuels in the transportation sector by 2020. This goal includes the possibility of H_2 produced from renewable resources [20]. FCEVs are eligible for subsidies available for vehicles emitting less than 50 gCO_2/km. In order to meet renewable fuels goal, Italy expects that H_2 production will come from renewable resources. There is currently one operating H_2 fueling station in Milan, producing H_2 from solar [20].

Japan has set a goal of two million FCEVs and 1,000 fueling stations by 2025. The Fuel Cell Commercialization Conference of Japan is tasked with solving the challenges associated with the rollout and making the FCEV and fueling station business viable by 2025 [20]. The government will announce policy mechanisms for encouraging the purchase of FCEVs soon. Subsidies for construction of refueling stations were announced in 2013 and cover up to 50% of the construction cost of new stations. While current H_2 production comes from fossil fuels and as a byproduct of industrial processes, in the longer term, Japan expects H_2 will come from reformation of either oil or natural gas with CCS (Carbon Capture and Sequestration), as well as renewable resources. They have not ruled out the possibility of imports from other countries in the longer term. As of 2012, there were 17 refueling stations in operation in Japan, and they expected to have 100 stations by 2015 and 1,000 by 2025 [20].

Germany has established ambitious goals for the adoption of electric vehicles, whether BEV, PHEV (plug-in hybrid vehicles), or FCEV. These goals are part of a master plan for sharply curtailing CO_2 emissions (40% below 1990 levels by 2020 and 80% by 2050). Specific targets for the transport sector include one million electric vehicles by 2020 and six million by 2030. The H_2 Moblility Industry Initiative, which includes Air Liquide, Daimler, OMV, Shell and Total have agreed on a plan for the construction of a hydrogen refueling network that will have 400 stations by 2023, pending FCEV market availability. The National Innovation Program for Hydrogen and Fuel Cells (NIP II) established numerical goals for 2025 including: 500 filling stations, 500,000 FCEVs, 2,000 FC buses, 1500 MW of electrolysis capacity, 500,000 micro CHG PC units, and integration of hydrogen production into renewable energy systems as a way to increase flexibility and storage. Achieving these goals was expected to cost €3.9 billion between 2014 and 2023, with approximately 60% paid for by industry [20]. Germany expects to use sales targets coupled with a wide range of incentives and subsidies to achieve the FCEV goals. The 2009 EU Directive limiting CO_2 emissions of new vehicles will drive Germany policy on transport options. The National Innovation Program for Hydrogen and Fuel Cells envisions hydrogen produced from renewable resources. The plan does not specify the percentage that should come from renewables. Germany will not allow the option of using coal gasification with CCS technologies. As of 2014, there were 15 operational hydrogen refueling stations in Germany [20]. Plans call for a public hydrogen infrastructure that includes 200 stations by 2023. Ideally, the refueling stations will be located within 90 km of each other.

United States does not have numerical goals for the adoption of FCEVs. In 2013, the federal government launched a public-private partnership (H_2 USA), which is similar in spirit and principle to other public-private partnerships worldwide (UK Mobility, German Mobility, HySut, etc). The U.S. Department of Energy Fuel Cell Technology Office (FCTO) funds hydrogen-related research and development focused on addressing the barriers to getting significant quantities of hydrogen technologies, focusing on fuel cells, into the energy and transportation infrastructure (stationary power and on- and off-road vehicles). The many elements of the FCTO program can be found in the Multi-Year Program Plan (MYPP). Although the USA does not have a stated goal for the adoption of fuel cell vehicles, several states have set goals for FCEVs, including California, South Carolina, Connecticut, 47 Maryland, Massachusetts, New York, Oregon, Rhode Island, and Vermont. The California Air Resources Board (CARB) has adopted a program for the introduction of zero-emission vehicles (ZEVs) in the state. Vehicle manufacturers are required to show increasing sales of ZEVs (including PHEV, BEV and FCEV) over time. California’s goal is for 1.5 million ZEVs by 2025. The U.S. has adopted new corporate average fleet efficiency (CAFE) standards that will incentivize companies to adopt new technologies. Some states, including California, have policies in place to support the future role of H_2 in a wide range of vehicles. Eight state governors have signed an agreement to develop zero-emission vehicle mandates similar to California. As in California, this will create policy mechanisms (mandates) to improve market entry of ZEVs. Note, California recognizes a FCEV as a ZEV. Also, the H_2 USA is focusing on advancing the development of the hydrogen infrastructure by coordinating research efforts and identifying cost-effective solutions to deploy infrastructure. Incentive funding is widely acknowledged as necessary to make the business case for investing in the early commercial stations. CARB’s Clean Fuel Outlet regulation triggers the construction of up to 500 stations once over 20,000 FCEVs are deployed statewide or 10,000 in a designated air basin (California Fuel Cell Partnership, 2013).

In the U.S., hydrogen will come from many sources, dependent primarily on costs. The most likely sources are natural gas, biomass and wind electrolysis. In some states, such as California, a percentage of the hydrogen must come from renewable resources, where the percentage and definition of «renewable» are currently being established. Of the hydrogen stations currently operating in California, one is fueled entirely from a renewable source – digester gas from a Southern California wastewater treatment facility. Another, the AC Transit station in Oakland, is partially filled by PV electrolysis [20]. For the future stations, state law requires that 1/3 of the hydrogen be produced from renewable energy. New stations being proposed may also use California electricity, which must be at least 33% renewable by 2020, according to the Renewable Portfolio Standard.

Whereas 100% renewable hydrogen is the ultimate goal, establishing an adequate and reliable infrastructure has higher priority in the near term. Approximately 14 publicly available H_2 refueling stations are operational in the USA at present. H_2 USA is focusing on options for advancing a cost-effective infrastructure.

The use of produced hydrogen

The main use of hydrogen today is as a key means for energy storage, which nowadays, with aggressive wind and solar energy developments, make the questions of energy storage more intense. Hydrogen since the space exploration times have been used as the main rocket fuel for shuttles. Liquefied form has been used in shuttle tanks for lunching the shuttles in space. Due to its energy density, it is the only source for such purpose. Nowadays, the future of hydrogen is the use in automotive transport. Most of the automotive companies produce vehicles with fuel cells for hydrogen use. Recent hydrogen development in automotive industry showed that you can go a long way using only small amount of hydrogen. Fuel cells are 2–3 times more efficient than combustion engines, and making hydrogen is an energy efficient chemical process. You can drive as far as you drive today on about 1/3 as much fuel.

Fuel cells create electricity from reactants stored externally. A proton exchange membrane (PEM) fuel cell uses hydrogen and oxygen as the reactants. In its simplest form, a PEM fuel cell is two electrodes – the anode and the cathode – separated by a catalyst-coated membrane. Hydrogen from the vehicle’s storage tank enters one side of the fuel cell stack and air on the other side. The hydrogen is naturally attracted to the oxygen in the air. As the hydrogen molecule moves through the stack to get to the oxygen, the catalyst forces the hydrogen to separate into electron and proton. The proton moves through the membrane and the electron moves to the anode. The electricity flows into a power module, which distributes electricity to the electric motor that turns the wheels of the car. The power module also distributes electricity to the air conditioning, sound system and other on-board devices. At the cathode, the electron recombines with the proton, and the hydrogen joins with the oxygen to create the vehicle’s only tailpipe emission – water. Fuel cells produce electricity as long as fuel is supplied.

The simplified picture of the process with PEM is presented in Fig. 19.

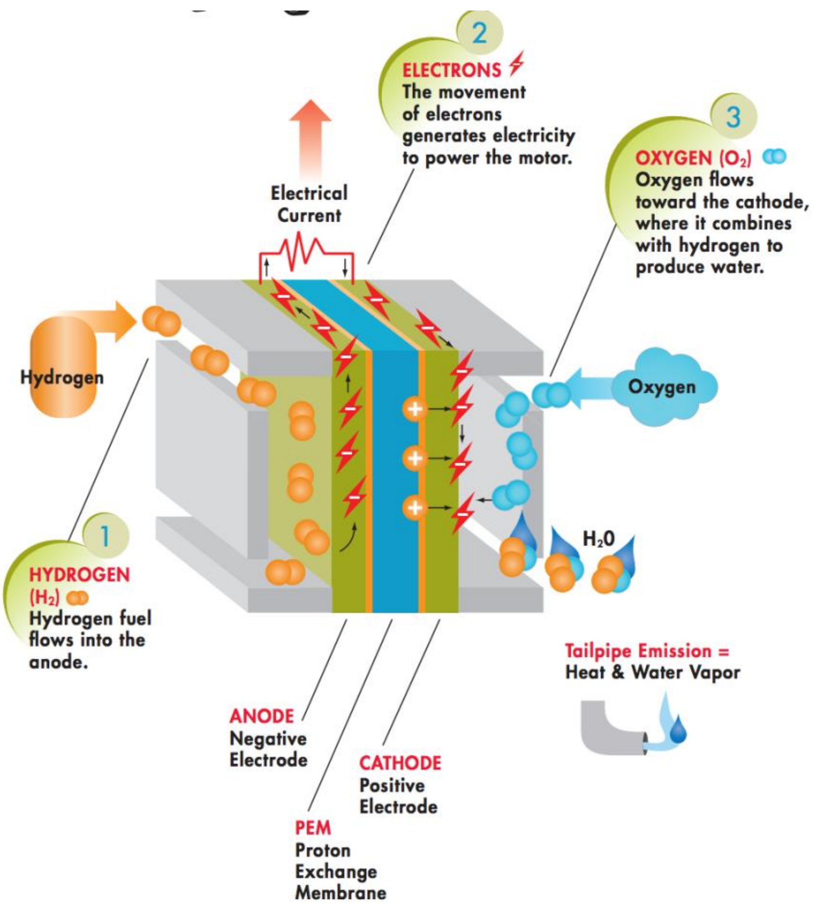


Fig. 19. Fuel cell process with PEM [22]

Conclusion

In this paper, hydrogen production methods available worldwide have been reviewed in order to make the first step to implement the system approach to hydrogen usage as an energy storage medium.

The overall effectiveness of the system is the sum of many parameters such as materials, type of solvents, renewable energy use, power consumption, as well as geographical conditions. The modern hydrogen production with renewable energy supply brings up the effectiveness of the process, thus making hydrogen an attractive option for energy storage.

One of the crucial problems for the industry is the appropriate choice of the hydrogen storage systems which are an essential part of any hydrogen production project. In addition to integrated storage of production units and mobile solutions for transport applications, underground storage of H_2, including combined storage with methane, is a relevant field of current research.

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Водородные технологии: основы и перспективы

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Аннотация. Актуальность тематики статьи продиктована растущим интересом к водороду, который объясняется высокой энергетической емкостью данного элемента. Это делает водородное направление перспективным вектором развития будущей энергетики. В статье рассмотрены основные химические свойства водорода, методы и технологии его производства как из возобновляемых источников, так и из ископаемого топлива. Обобщены сведения об объемах и перспективах производства и использования водорода в разных странах мира.

Ключевые слова: водород, накопление энергии, источник энергии, плотность энергии, методы производства водорода, производство водорода из возобновляемых источников, производство водорода из ископаемого топлива, производство водорода в мире, использование водорода.

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